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The Fate and Transport of Microplastics within Estuaries

by

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Abstract

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Doctor of Philosophy

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Microplastics are an emerging and environmentally problematic suite of contaminants. Their fate, transport and impacts are poorly understood. The so-called "missing plastic problem", in which global surface ocean plastic aligns with only a single year's estimate of inputs, may be partially solved by considering if microplastics are retained within estuaries, by way of an "estuarine filter", similar to that which exists for suspended sediment and other contaminants. To investigate the fate of microplastics in estuaries, a series of field and laboratory studies were conducted, using Southampton Water, U.K., as a study site. These investigated environmental controls on microplastic abundance in estuarine waters; the intertidal trapping of microplastics in a salt marsh system; and the settling and resuspension of microplastics. The sea surface microlayer (SML) was sampled, to better understand this key interface between atmosphere and oceans, and the role it plays in the estuarine filter. Environmental controls were considered during a four-month water sampling campaign, which determined that within Southampton Water, the partially-mixed nature of the estuary meant that there were limited controls exerted by environmental variables such as weather conditions and river flow. The strong tidal currents in Southampton Water meant that abundances were highly variable with time and space. Intertidal trapping was investigated using high-resolution salt marsh creek sampling, which found a significant decrease in microplastic abundance when comparing abundances in flood tide samples to ebb tide samples, during both neaps and springs. Laboratory settling column and flume studies were utilised to investigate settling and resuspension. Limited settling was seen after an extended period, but flocculation of microfibres was not observed. During resuspension experiments, microplastic fibres were suspended at velocities similar to those that moved fine unconsolidated cohesive sediments. Nurdles were suspended at velocities that eroded sand of a smaller grain size than the nurdles themselves, but were also were observed to be buried by moving sediment.

The findings within this thesis support the hypothesis of an estuarine filter for microplastics, indicating that salt marshes and other low-energy intertidal areas are significant sinks. Both burial and resuspension might occur depending on the tidal cycle, so that whether an estuary acts as a filter depends on the balance of these processes, driven by tidal asymmetry. However, results also suggest that the hydrodynamic regime of estuaries is a key control of microplastic abundance and distribution. Southampton Water's partially-mixed, ebb-dominant system likely transports microplastics out of the estuary. There are significant global implications from this research, including to microplastic budgets and estimates of global ocean inputs, and to the potential risks posed to estuaries and intertidal wetlands.

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List of Accompanying Materials

FTIR spectra are available for Chapter 3 at: https://doi.org/10.5258/SOTON/D1892

ADV, OBS and SSC data are available for Chapter 5 at: https://doi.org/10.5258/SOTON/D1893

Two additional papers to which I contributed are also included as accompanying material.

To Anderson *et al.* (2018), I contributed to the editing of the manuscript.

To Birkenhead *et al.* (2020), I contributed to the manuscript draft and editing.

Anderson, Z.T., Cundy, A.B., Croudace, I.W., Warwick, P.E., Celis-Hernandez, O., Stead, J.L., 2018. A rapid method for assessing the accumulation of microplastics in the sea surface microlayer (SML) of estuarine systems. Sci Rep 8, 9428. https://doi.org/10.1038/s41598-018-27612-w

Birkenhead, J., Radford, F., Stead, J.L., Cundy, A.B., Hudson, M.D., 2020. Validation of a method to quantify microfibres present in aquatic surface microlayers. Sci Rep 10, 17892. https://doi.org/10.1038/s41598-020-74635-3

Research Thesis: Declaration of Authorship

Print name: Jessica Laura Stead

Title of thesis: The Fate and Transport of Microplastics in Estuaries

I declare that this thesis and the work presented in it are my own and has been generated by me as the result of my own original research.

I confirm that:

1. This work was done wholly or mainly while in candidature for a research degree at this University;
2. Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;
   Data from Chapter 3 was used in: Allen, E., 2020. MSci Thesis. University of Southampton. Microplastics abundance in an estuarine setting: sources & environmental factors.
   & Brooks, O.T., 2020. MSc Thesis. University of Southampton. Ecotoxicological risk assessment of microplastics in marine bivalves using a novel environmental technique.
   Data from Chapter 4 was used in: Webster, O., 2019. MSci Thesis. University of Southampton. Behaviour of microplastics in the upper coastal intertidal zone.
   Data from Chapter 5 was used in: Wain, R.L., 2020. Geology Independent Research Project. University of Southampton. The remobilisation of microplastics from estuarine sedimentary sinks.
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7. Parts of this work have been published as:-

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Definitions and Abbreviations

ABP.....Association of British Ports

ADCP .....Acoustic Doppler Current Profiler

ADV .....Acoustic Doppler Velocimeter

ATR-FTIR.....Attenuated Total Reflection – Fourier Transform Infrared Spectroscopy

CMF .....Core Mini Flume

CSO.....Combined Sewer Overflow

EPS.....Extracellular Polymeric Substances

FTIR .....Fourier Transform Infrared Spectroscopy

GC-MS .....Gas Chromatography – Mass Spectroscopy

HDPE .....High Density Polyethylene

LMPs.....Large Microplastics

OBS.....Optical Backscatter Point Sensor

OEP.....Oil Extraction Protocol

PCBs.....Polychlorinated Biphenyls

PET .....Polyethylene Terephthalate

POPs .....Persistent Organic Pollutants

PP .....Polypropylene

PVA.....Poly Vinyl Alcohol

SML.....Surface Microlayer, or Sea Surface Microlayer

SMPs.....Small Microplastics

SSC.....Suspended Sediment Concentration

SSSI .....Site of Special Scientific Interest

SWAC.....Southampton Water Activities Centre

WWTW .....Waste Water Treatment Works

Chapter 1 Introduction and Background

Plastics are a wide-ranging group of synthetic or semi-synthetic organic materials. They have become an integral part of everyday modern life since their invention at the start of the 20th Century. Plastics are utilised in clothing, to preserve food, in our homes, workplaces and vehicles, and have a great number of benefits. They are durable, resistant to breakdown, light, non-toxic and relatively low cost. Life cycle assessments have shown that plastic packaging has fewer environmental impacts than single-use glass or metal, due to the smaller amount of mass needed for performance, this lower mass causing fewer emissions in transport and less energy and material in production (Miller, 2020). The use of plastic in healthcare and public health settings has enabled greater access to clean drinking water, and medical devices such as aseptic medical packaging are reliant on plastic (Andrady and Neal, 2009). However, our reliance on plastic has come at a cost. Plastic does not break down quickly, and the single-use, throw-away nature of many plastic items has filled landfills and littered the environment. Approximately 79% of plastic ever produced until 2015 is estimated to have accumulated in landfills and the natural environment (Geyer *et al*., 2017), which equates to around 6,300 Mt. This huge quantity of plastic is a significant environmental hazard, and its effects, scale and fate are yet to be entirely understood. In particular, the smaller size fractions of this plastic waste, known as 'microplastics' are of growing concern both scientifically and to the general public, as they are available for a much wider range of organisms to ingest. The majority of this plastic in the environment is produced and sourced on land, approximately 80% (Horton *et al*., 2017), although the majority of research on both larger plastic debris – often termed 'macroplastics' and microplastics has occurred in the marine environment. Estuaries act as the interface between the terrestrial and marine environments, and are a major transfer pathway of plastics from land to sea (Alligant *et al*., 2018).

1.1 Microplastics: Definition and Context

The scientific field of plastic pollution research has been growing rapidly in recent years, and in particular, the field of science concerned with the research into small pieces of plastic, termed 'microplastics' is the focus of increasing research, funding and public interest. However, there is still a lack of a common, consistently-used definition of microplastics that is inclusive of all the criteria that could be used to define them (Frias and Nash, 2019). This has led to a wide range of studies with little inter-comparability, and a limited ability to integrate literature datasets to assess global microplastic contamination (Hartmann *et al*., 2019).

The term ‘microplastic’ describes a small particle (or fibre) of plastic, but this is not explicit in its definition. There are several criteria that need to be considered when determining a viable definition of microplastic, which will then be used throughout this project. These are the definition of a plastic, its size and its source.

Even when considering the various criteria that together define ‘microplastics’, there is limited consensus around some of the definitions of the criteria. An example is ‘plastic’, as, with the exception of the ‘commodity polymers’, such as polyethylene and polypropylene, there is no agreement on which materials are included as ‘plastics’ (Hartmann *et al*., 2019). Plastics are synthetic and semi-synthetic[1] polymers, mostly derived from oil or gas (Cole *et al*., 2011) but increasingly also formed from biological materials such as vegetable oil or corn starch, so called ‘bio-plastics’. Given that bio-plastics degrade (or persist in the environment) similarly to conventional petroleum-based plastics, they should also be considered as plastic for the purpose of assessing plastic debris in the environment (Verschoor, 2015). Historically natural polymers such as rubber and shellac, now also should be considered within this; for example, due to presence of chemical additives to these compounds, producing (effectively) modified or new materials. This includes other microdebris such as tyre wear particles and brake wear, which also fit the definition of microplastics (Knight *et al*., 2020).

In addition to synthetic polymers, plastics typically contain other chemicals, added to improve characteristics of the plastic for use, such as safety, performance or durability. While these additives do not and should not be considered when defining a microplastic, their use may turn a non-plastic into a particle that could be considered one. For example, cellulose processed to form nitrocellulose or rayon should be considered as a source of microplastic due to its modifications from its natural origin.

As there are a wide variety of polymers and associated chemicals that make up the range of materials that comprise plastic debris and microplastics, one proposal is to consider microplastics as a suite of contaminants, rather than as a single type of material (Rochman *et al*., 2019). In a similar way to pesticides, microplastics comprise a diverse range of chemical compounds, and arguably should be considered as such.

Size is the criterion most often used to classify microplastics, and other plastic debris (Hartmann *et al*., 2019). However, a range of size categories are reported in the literature, some of which overlap (Figure 1-1). This is the most common discrepancy between studies, and most often leads to the incomparability of data. While initially, the term ‘microplastic’ referred to small plastic

[1] Mixture of synthetic and mineral oils.

items without defining a set size range (Thompson *et al.*, 2004), a set size range for microplastic will allow for comparability of data, as well as less overlap between size categories of plastic debris, including nanoplastics.

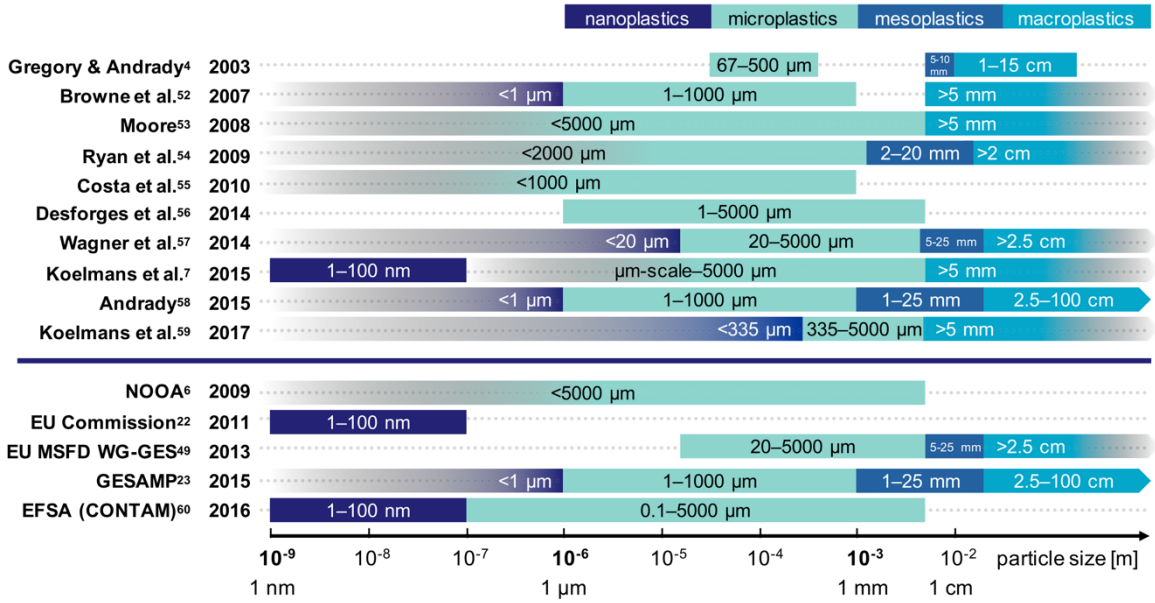

Figure 1-1 A non-exhaustive range of plastic debris size classifications (from Hartmann *et al.*, 2019)

(Subscripts indicate citations in the original paper, Hartmann *et al.* (2019))

Within the literature, there are several proposed definitions of microplastic size, most of which only include an upper size limit. With advances in analysis methods, the lowest detectable size of small plastic debris is decreasing. Failing to define a lower size limit for microplastics will lead to overlap with nanomaterials including nanoplastics. The lower limit given often relates to the detection limits of techniques such as Fourier-Transform Infrared Spectroscopy (FTIR) e.g., the European Marine Strategy Framework Directive Working Group on Environmental Status set a lower limit at 20 µm (Verschoor, 2015). However, definitions should not be based on the restrictions of analytical techniques due to the rapid developments being made in this field. This use of operational definitions has led to a wide variety of lower limits, such as the use of 333 µm, which is a commonly used trawl mesh size (e.g., as used by Rowley *et al.* (2020); down to 20 µm or smaller, as defined by the smallest detectable particle by Raman spectroscopy (Araujo *et al.*, 2018). This is a difference of orders of magnitude in the smallest microplastics; and given that some studies report an exponential increase of microplastics (in terms of particles numbers) with decreasing size of particles (e.g., Song *et al.* (2014), could lead to significant effects on reported microplastic abundances. Some methods, such as Pyrolysis GC-MS (as used by Gomiero *et al.*,

2021; Kirstein *et al*., 2021) may enable the quantification of masses of smaller still particles, but will not enable the counting of particle numbers.

Several definitions are proposed for the upper limit of a 'nanoplastic', which should therefore be considered as potential lower limits for microplastics. These are: 20 µm (Henke, 2013), 25 µm (Galgani *et al*., 2013), 100 nm and 1000 nm (Gigault *et al*., 2018). Here, it is proposed to use 1000 nm (1 µm) as the upper definition of nanoplastic, with this also forming the lower definition of microplastic. This follows several recent papers (Frias and Nash, 2019; Gigault *et al*., 2018), and whilst it means that inherently, some microplastic particles may remain unidentified in field samples in this study due to limitations of analysis, it will align the research to recent studies.

The upper size limit for microplastics is the most common definition given in the literature. Whilst a variety of upper size limits are given, ranging from 100 µm to 5 mm, there is still no consensus on which should be used to define microplastics. A value of 100 µm, while intuitive for the International Union of Applied and Pure Chemistry (Vert *et al*., 2012), should be disregarded as it does not include a range of particle sizes that are currently included in the vast majority of microplastics studies. Most literature tends to utilise either 1 mm or 5 mm as the upper size limit; while 1 mm is considered a more 'logical' split, due to the use of the phrase 'micro', 5 mm is the more commonly used definition and will therefore form the upper bound of the definition used here. This should allow for greater comparability to existing data. The International Organization for Standardization (ISO) standard for microplastic definition (ISO/TR 91260:2020) divides at 1 mm (1000 µm) into microplastics and large microplastics, and so where this division and measurement of (suspected) microplastics is possible, it should be carried out. This would enable a wider range of comparisons to be made to previous studies using either common definition (1 or 5 mm). This is done in some studies that refer to the size fractions as small microplastics (SMPs) and large microplastics (LMPs) (Alves and Figueiredo, 2019; Ghayebzadeh *et al*., 2021).

Degradability, referring to the susceptibility to breakdown of a substance, may also be used to define plastics. Plastics are considered persistent materials, resistant to degradation (Verschoor, 2015). While some newly developed 'bioplastics' degrade quickly under the correct conditions (five tested polymers or polymer blends tested by Narancic *et al.* (2018) degraded in home composting conditions in less than a year), most plastics remain in the environment for years and decades at a minimum. Therefore, whilst some polymers are degradable to the point of not being considered an environmental hazard, most have long half-lives and should be considered as potential polymers to be included in definitions of plastic debris and microplastics. Here, degradability refers to the breakdown of a particle into harmless substances, in this case, the final products would be H_2O and CO_2 (Andrady, 2017). For plastics, this process takes a long time, and

the true mineralisation of plastics will likely take many decades. In the meantime, plastic debris is known to pose a risk through ingestion (Gall and Thompson, 2015) and while the field of ecotoxicology in reference to plastic debris is growing rapidly, there is some evidence of the harmful effects of microplastics (Duis and Coors, 2016). While plastics are broken down – into smaller and smaller pieces, micro and then nanoplastics, this takes a long period of time (years, decades). As a result of their slow degradation and rapid increase in abundance, the integration of plastic into the rock record has been suggested as a geological marker for the so-called Anthropocene (De-la-Torre *et al*., 2021). Plastics are degraded and broken down through a number of processes. These include UV weathering, physical and mechanical weathering, reaction with water (hydrolysis), and loss of additives within plastics, as described by Andrady (2011). Due to the slow rate of breakdown of particles within water; it is proposed that the majority of breakdown of larger particles occurs due to UV radiation and mechanical breakdown on beaches and land (Andrady, 2017).

Degradability of plastics, and their breakdown into smaller particles – but not into their constituent parts (CO_2 and H_2O (Andrady, 2017)) - is one of the generating processes of microplastics. Whilst some microplastics are intentionally manufactured to be of a small size – for example, microbeads used in cosmetics or blasting media, or nurdles used as raw materials for plastics manufacturing – others are formed due to the breakdown of larger plastic debris. Primary microplastics are those intentionally manufactured to be of a small size. Secondary microplastics are microplastics which have become microplastics-sized as a result of degradation and fragmentation of larger plastic debris.

Further categorisation of microplastics is possible due to the numerous morphologies observed. Microplastics are commonly categorised by their shape, which may also give indications as to their origins. For example, pellets, or nurdles, are often pre-production raw materials for plastics moulding; and fibres often result from clothing wear and laundering. Other morphologies of microplastics include: fragments, spheres, films and foams (Rochman *et al*., 2019). Fragments are particles which generally form as a result of the breakdown of larger debris and litter; spheres includes microbeads which are found in some cosmetic products; films may originate from plastic bags or plastic sheeting used in construction and agriculture; and foams could originate from food containers and packaging (Helm, 2017), although these sources are non-exhaustive. It is difficult to determine a precise origin of microplastic particles due to their small size, though macroplastic is often easier to identify.

These elements all combine to produce a working definition of microplastics, used in this thesis, which is “microplastics are synthetic and semi-synthetic polymer materials, and consist of solid

particles smaller than 5 mm and larger than 1 µm, which are very slow to degrade". Additionally to this, whether microplastics are from a primary or secondary origin may be included in any definition or description.

1.2 Microplastics Research, and Current Limitations / Knowledge Gaps

Microplastics are an emerging suite of contaminants, which vary widely in their properties. As discussed above, their definition is not universally agreed upon, and the rapidly expanding field of research into microplastics has led to a variety of limitations and research gaps. Microplastics have been detected globally, from the deepest point of the oceans (Peng *et al*., 2018) to the poles (Bergmann *et al*., 2017; Lusher *et al*., 2015; Munari *et al*., 2017; Reed *et al*., 2018) in both urbanised and remote and unpopulated regions (Allen *et al*., 2019), including in the atmosphere (Zhang *et al*., 2020), and in a variety of biota, from crustaceans (Abbasi *et al*., 2018) to large marine mammals (Nelms *et al*., 2019, 2018). Microplastics are considered ubiquitous in the marine environment (Cole *et al*., 2011) and given that they have been observed in even remote locations on land (Allen *et al*., 2019; Gateuille *et al*., 2020), they could also be considered ubiquitous in terrestrial environments including freshwater.

The effects of microplastics on the environment, biota and human health remain unclear. Many studies have pointed to a negative impact on health of individual organisms ranging from algae to fish, although the applicability of laboratory exposure studies using unrealistic microplastic at unrealistic concentrations has been discussed (Phuong *et al*., 2016). Besseling *et al.* (2014) found that algal growth was significantly reduced by microplastic exposure. A review of studies by Wang *et al.* (2019) found microplastic exposure could be linked to reduced feeding of aquatic species such as copepods and molluscs and additional associated effects as a result including reduced fertility, reduced body weight and reduced mobility. However, studies have also found no effect (Wang *et al*., 2019), and given microplastics are a wide-ranging and complex suite of contaminants, the applicability of exposure studies, which by necessity use a small range of microplastic types (shape, polymer, size) are perhaps limited. Alongside studies to determine the hazard posed by microplastics, studies are still needed to determine the exposure to microplastics, in order to fully understand the risk posed by microplastics.

Alongside the lack of a universal definition of microplastics, there is a lack of a standard sampling method to enumerate microplastics in the environment (Underwood *et al*., 2017). As such, an accurate global picture of microplastic abundance cannot be produced. Even when multiple studies are carried out in the same location, it can be difficult to compare them given that different sampling methods, sample processing methods, enumeration and identification

methods, and units are used in studies. For example, Fok and Cheung (2015) and Lo *et al.* (2018) both sampled at Lai Chi Chong in Hong Kong within their studies (both studies, while also sampling several other locations around Hong Kong, did not otherwise overlap in their sampling locations). They did not sample at the sample location within the beach (high strandline; 1.0 and 1.5 m above chart datum and at the back of the shore); they did not use the same sample depth (4 cm; 2-3 cm); they use different density separation media (in situ seawater; $ZnCl_2$); had a different methodological lower size limit (0.315 mm; 250 µm); only one study utilised digestion to reduce the organic content (Lo *et al*., 2018) and they used different identification techniques (visual only; visual supported by a sub-sample analysed by ATR-FTIR); and reported in different units for which a conversion is complex at best (items/m^2; items/kg). Therefore, it is difficult to draw definite conclusions about the paths of microplastics through the environment, and their ultimate fate, as well as the risk they may pose.

1.3 (Micro) Plastics in Estuaries

An estimated 80% of annual plastic input to the world's ocean is derived from terrestrial sources (Horton *et al*., 2017). One transport pathway for this plastic to reach coastal seas and oceans is through rivers, and modelling studies suggest that an approximate 1.15-2.417 million tonnes of plastic debris is transported by rivers into coastal seas (Lebreton *et al*., 2017). With estuaries being the dominant connection between rivers and coastal seas, and as a result of the large amounts of plastic being transported by rivers, estuaries are a likely primary zone of transfer of (micro)plastics between continental and marine water (Alligant *et al*., 2018; Dris *et al*., 2020). In addition to this, estuaries are influenced by marine inputs due to tidal inflow, and therefore plastic may flow into estuaries from coastal seas (Holmes *et al*., 2014). However, fluxes of microplastics in estuaries are rarely quantified, and so the input of plastic into estuaries worldwide and the apportionment of sources is unknown. Microplastics are also deposited directly into estuaries through, for example, waste water and runoff, or through maritime activities occurring in estuaries, including fisheries and recreation. Whilst unquantified in terms of their contribution to microplastic abundance in estuaries, these direct inputs are likely also to be significant sources.

Estuaries are known as sinks for sediment, and other pollutants, via the so-called 'estuarine filter' (Holmes *et al*., 2014; Vermeiren *et al*., 2016). These pollutants, including heavy metals and organic micropollutants, are known to be deposited and 'trapped' in estuaries (Cundy *et al*., 1997), thereby reducing the amount entering coastal seas. However, the increased retention in estuaries increases the risk of harm they pose to estuarine environments and biota, including coastal wetland environments (Cundy and Croudace, 2017) such as salt marshes, mudflats and

mangroves. Via these environments, there may be potential routes into the human food chain, although the evidence to date of any harm to humans posed by this are limited to radioactive contaminations entering the human food chain via cattle grazing on tide-washed pastures (Sanchez *et al*., 1998). The estuarine filter, in essence, can be described as being the result of enhanced deposition and lowered resuspension in estuaries, but this is influenced by a number of processes occurring in estuaries. The potential retention of microplastics in estuaries, and the balance between plastic debris retained and plastic debris released is important knowledge for the understanding of the fate of plastic litter on a global scale (Dris *et al*., 2020).

The addition of salt water to riverine freshwater causes flocculation, a process by which repulsive surface charges on clay particles are overcome by charged ions present in seawater (or in the case of estuaries, brackish water formed as riverine freshwater mixes with incoming seawater), enabling particles to aggregate. These larger aggregates of clay are termed 'flocs' and have a faster sinking velocity than individual clay particles. This process enhances deposition of cohesive sediment in estuaries, and potentially also the deposition of microplastics (Paduani, 2020). Microplastics gain a net negative charge as a result of degradation and interaction with seawater (Vermeiren *et al*., 2016), which is comparable to cohesive sediments. Aggregation of small particles may also occur through biologically mediated processes, such as that caused by extrapolymeric substances (EPS), sticky substances excreted by biota such as phytoplankton, or through "faecal packaging" (incorporation into faecal material (Cole *et al*., 2016)). Several authors have proposed that biologically-mediated aggregation (and the enhanced sinking velocities that result from this aggregation into larger particles) is of more relevance than so-called 'salt flocculation' for cohesive sediments (Eisma, 1986; Geyer *et al*., 2004). Biofouling of microplastics, as well as leading to aggregation, may also increase particle density and settling rates (Kooi *et al*., 2017).

Habitats within estuaries may also enhance deposition. Wetland environments such as saltmarshes and mangroves, as well as seagrass meadows, slow flows via their presence, with the reduced turbulence allowing for more sediment deposition (Mudd *et al*., 2010). Thus, sediment deposition (and potentially microplastics deposition) is enhanced in vegetated areas, both intertidal and subtidal. Alongside deposition as the result of slowed flows, deposition is directly influenced by plants, which may capture sediment and suspended solid particles on their stems and leaves (Mudd *et al*., 2010). Particles may also interact directly with cohesive sediments on mudflats and exposed intertidal sediment surfaces, via EPS (e.g., biofilms), which is known to decrease erodibility of cohesive sediments (Tolhurst *et al*., 2008), and could increase retention of microplastics within estuarine sediments.

Tides also influence deposition and resuspension. Deposition is enhanced by slowed currents and turbulence on slack tides, and rising tides allow the flooding of the intertidal, including intertidal wetlands. Additionally, estuarine morphology may provide an element of protection from wave energy, preventing some resuspension of deposited material. Together with flocculation, aggregation and enhanced deposition in wetlands, estuaries show large amounts of deposition of suspended sediment, along with associated contaminants. The efficiency of this filter is determined by how much suspended material is deposited within the estuary and is retained for a period of time (i.e., not resuspended and transported out of the estuary).

As estuaries are highly efficient filters for suspended material and dissolved material, it is also proposed that they are a filter for microplastics. High concentrations of microplastics have been found in estuarine sediments (e.g., Fok and Cheung (2015)). In addition, correlations have been found between microplastics and the metal pollution index (∑ As-Cd-Cr-Cu-Hg-Ni-Pb-Zn) in Venice lagoon (Vianello *et al*., 2013). Dissolved heavy metals are known to be trapped in estuaries (Cundy *et al*., 1997), and a correlation between these and microplastics further supports the hypothesis of an estuarine filter for microplastics. When considering plastics observed in the global surface oceans, and comparing to the annual estimates of plastic into the ocean, there is a significant mismatch. Annual inputs to the oceans have been estimated by Jambeck *et al.* (2015) to be between 4.8 – 12.7 million metric tons in 2010, but various estimates of accumulated floating plastic debris are considerably smaller than this. van Sebille *et al.* (2015) estimated that the accumulated microplastic in the surface ocean is 93 – 236 thousand metric tons and Cozar *et al.* (2014) estimate that the plastic load in the surface waters of the open ocean is in the order of 10 – 40 thousand tons. The accumulated plastic in the surface ocean is orders of magnitude smaller than estimated annual inputs, the so called “missing plastic problem” (Cozar *et al*., 2014). An estuarine filter retaining plastic debris within estuaries has the potential to reduce the “missing plastic” gap, as plastics are trapped in estuaries before they can be transported to the oceans.

While estuaries show high abundances of microplastics in various compartments, they are relatively understudied in comparison to other environments such as ocean beaches or ocean surface waters (Akdogan and Guven, 2019). Estuarine studies have been carried out in most continents, and a wide range of concentrations of microplastics have been found using a variety of techniques, which complicates inter-study comparison. Estuarine waters are usually sampled using net tows, typically at the surface, with observed concentrations ranging between 1.21 particles/m^3 (Tampa Bay, FL, USA (McEachern *et al*., 2019)) to 641,292 particles/m^3 (Long Beach, CA, USA (Wiggin and Holland, 2019)). Subsurface waters are less frequently sampled, but one study in the Jiaojiang, Oujiang and Minjiang estuaries (China) found a range between 100 to 4,100 particles/m^3 (Zhao *et al*., 2015). Sediments reported are typically estuarine beach sediments,

which range in observed abundances between 2.92 particles/kg dry weight (Po River Delta, Italy (Piehl *et al*., 2019)) to 422 particles/kg dw (Ebro River Delta, Spain (Simon-Sánchez *et al*., 2019)), which cannot be compared to other studies which utilise particles/m^2 as a unit of measurement. These range between 3 particles/m^2 (Guanabara Bay, Brazil (de Carvalho and Baptista Neto, 2016)) and 5,595 particles/m^2 (Pearl River Estuary, Hong Kong (Fok and Cheung, 2015)). It is difficult to compare these without full knowledge of the sampling depth and sediment density, even assuming similar recovery and identification rates of microplastics from these sediment samples.

Estuaries are productive habitats, and studies on the microplastic intake by estuarine species have also been conducted. For the most part, these are on aquatic species, bivalves and fish, although crabs, prawns, macroinvertebrates and birds have also been studied. Microplastic particles were found in the digestive tract of anywhere between 7.9% (Goiana Estuary, Brazil (Dantas *et al*., 2012)) and 100% (Río de la Plata, Argentina (Pazos *et al*., 2017)) of fish sampled. A maximum concentration of 16.5 particles/individual oyster were found in Florida (USA) by Waite, Donnely and Walters (2018), and microplastics were found in 74% of bird faeces sampled in the Tejo Estuary, Portugal (Lourenço *et al*., 2017). A variety of estuaries globally have been sampled to determine their microplastic abundance, but few conclusions can be drawn from these studies about what the observed abundances mean in terms of the risk posed to estuaries, and how microplastics are transported through these environments. One important conclusion is that sediments in estuaries tend to have higher abundances of microplastics than the water column, supporting the proposal of estuarine sediments as a sink for microplastics (Vermeiren *et al*., 2016).

While, as described above, a range of microplastic abundances have been found in a variety of estuarine environments worldwide, this is a small fraction of the total studies investigating the environment for microplastic abundances. The majority of microplastic research is focused on marine environments and therefore, terrestrial and edge zone environments are frequently neglected. Estuarine sub-environments such as salt marshes and mudflats are potentially more favourable for deposition over high-energy environments such as sandy beaches, yet the majority of studies investigate the latter (Lo *et al*., 2018). A variety of sometimes contrasting conclusions have been drawn about microplastic behaviour in estuaries based on these studies, which given that estuaries are highly variable and ever-changing environments, is somewhat to be expected.

1.4 Key Knowledge Gaps

There is significant potential for the estuarine filter to trap microplastics, however, there is limited information on whether this is consistently the case. While estuaries have been studied for microplastics abundance, there are recognised issues with a lack of standardised methods (Underwood *et al*., 2017), and it is therefore difficult to draw conclusions in terms of preferential accumulation in estuarine environments. The majority of studies focus on the presence or absence of microplastics, rather than on their transport, cycling and trapping processes (Akdogan and Guven, 2019). Thus, there is limited knowledge of how the behaviour of microplastics is influenced by the hydrodynamics of these environments (Ivar do Sul *et al*., 2014) from either field or laboratory observations, though it is proposed that, as with any other suspended material in an estuary, microplastic distribution is controlled by estuarine hydrodynamics (Frère *et al*., 2017; Luo *et al*., 2019).

Estuarine hydrodynamics are complex and how they influence the distribution and fate of microplastics is uncertain from the limited data available. While the hypothesis of an estuarine filter for microplastics is based on the presence of one for suspended sediment, there is very little laboratory data on parameters such as the sinking or biofouling rates of microplastics to be able to predict the behaviour of microplastics. If microplastics behave in a drastically different way to sediment, then estuaries may not trap a significant proportion of microplastics being transported by rivers. This may also depend on the type of estuary; for example, a fully mixed estuary with a high flushing rate may not retain many microplastics due to its hydrodynamics. Studies suggest that the behaviour of microplastics in suspension, particularly non-spherical microplastics such as fibres, differs greatly from that of the spherical sediments that are modelled in equations such as Stoke's Law (Bagaev *et al*., 2017). In addition to hydrodynamics, other mechanisms are involved in the estuarine filter, including chemical and biological mechanisms, and how these influence plastic distributions in estuaries is not understood (Vermeiren *et al*., 2016). The estuarine filter, and how microplastics behave in estuaries will also be dependent on the properties of the plastics, with different shapes and polymer types interacting differently with the environment (Vermeiren *et al*., 2016).

Little is known about how the processes described above that form the 'estuarine filter', including flocculation, vegetative trapping, settling, biofouling and resuspension, act on microplastics, and this has led to a limited ability to accurately estimate retention of microplastics in estuarine environments and how this impacts upon inputs to coastal seas and the global ocean. Modelling studies are limited, although one investigating the Adour Estuary (France) has been carried out (Defontaine *et al*., 2020). Microplastic characteristics (density, settling velocity and buoyancy)

were found to be significant factors determining whether particles were retained within the estuary or flushed out to sea. While neutrally buoyant microplastics were more affected by tidal flushing, heavier microplastics tended to remain in the estuary in the modelled tidal cycles. The hydrodynamics of the estuary (salt-wedge) also interacted with the microplastics, with the strong density stratification typical of a salt-wedge estuary acting to dampen turbulent mixing and reduce resuspension and transport of microplastics within the estuary (Defontaine *et al*., 2020).

The implications of such an estuarine filter for microplastics is significant, in terms of evaluating the risk to estuarine biota, predicting the quantities of plastic that are believed to be entering the global ocean, and more generally for managing the marine plastics problem. Additionally, the retention of microplastics in salt marshes or estuarine sediments could pose a future risk as a legacy contaminant, particularly under predictions of future sea level rise even if there is a reduction in the supply of plastic through e.g., legislation. Estuaries which also host large ports are often dredged to maintain navigation, which would also pose a risk in terms of a legacy contaminant being moved back into the water column or being available for further transport. An estuarine filter would be one hypothesised sink of microplastic that could start to explain the 'missing debris' in the surface global oceans, although it is likely not the only location where plastic debris is under-estimated (e.g., recent work on the ocean interior suggests a large quantity of microplastics that have previously been underreported (Pabortsava and Lampitt, 2020). Quantifying the effect of the estuarine filter could also improve the accuracy of estimates of annual inputs of plastic to the oceans and better inform future policy decisions on how we minimise inputs.

It is proposed that the estuarine filter, as well as the influences of rivers, tides and waves, combine to affect microplastic abundance in estuaries and coastal seas. Figure 1-2 shows a proposed summary of the processes likely to affect microplastic distribution in estuaries. Very few, if any, of these processes are quantified for even a single system. Additionally, plastic has a high capacity for exchange between the compartments shown in this figure (Paduani, 2020), but this exchange is poorly understood.

It is known that microplastics originate from a wide variety of sources. Primary (intentionally manufactured to be < 5 mm in size) or secondary (originating from the fragmentation of larger plastic debris) microplastics may be formed within the estuary itself, perhaps through breakdown of larger debris, pollution from industries (such as plastic manufacturing factories, or laundrettes directly discharging into the estuary), fishing gear, outflows from waste water treatment works (WWTWs) or combined storm overflows (CSOs). Rivers are a key input to estuaries, and carry microplastics transported from further upstream, which may enter the river through WWTW and

CSO outflows, or through surface run off. Flood events are known to increase the transport of microplastics in rivers (Hurley *et al*., 2018), and will therefore likely generate high-input events into estuaries. Additional inputs to estuaries also occur as deposition from the atmosphere (e.g., Liu *et al.* (2019)), though this sampling occurred in coastal seas, atmospheric deposition is also likely to occur in estuaries), and with tidal inflow into estuaries from coastal seas. These inputs are poorly quantified, though limited research is now occurring. There is certainly not sufficient data yet to determine which sources are most important, and where perhaps prevention and mitigation methods should be focused.

Fragmentation of debris to smaller debris will change the size profile of plastic debris within estuaries. Processes that have been well-described for sediments will influence the deposition, resuspension or continued transport of microplastics; and this may vary depending on the properties of the microplastics in question, given that microplastics are a diverse suite of contaminants. Microplastics may thus remain deposited in estuarine sediments, or flow out to coastal environments. They may also be ingested by biota, an area of increasing concern.

1.5 Conclusions

Microplastics are a new, broad suite of emerging contaminants that are increasingly recognised as an environmental concern. Research is occurring rapidly, and understanding of the sources, fate and impacts, while increasingly rapidly, remains limited, and there are significant knowledge gaps. High concentrations of microplastics are observed to occur in estuaries, but the transport (and trapping) pathways of these are poorly quantified.

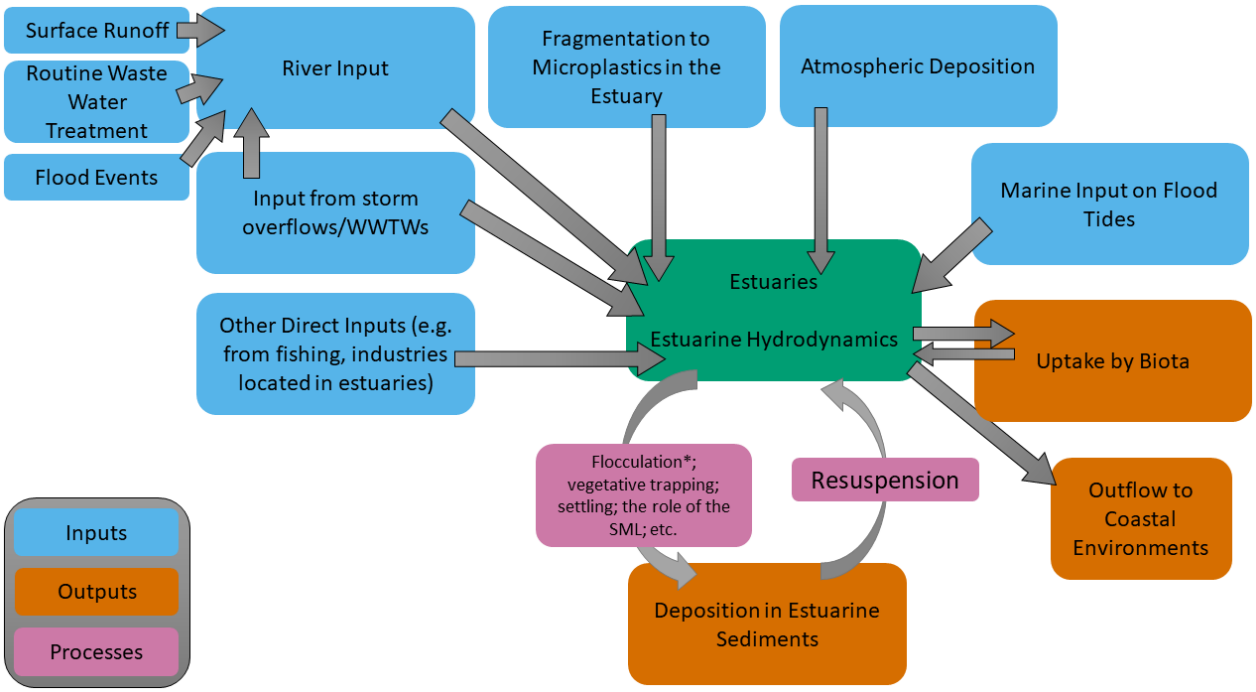

Figure 1-2 A summary of the processes controlling microplastic abundance in estuaries.

Blue boxes represent inputs of microplastics; orange boxes outflows or potential sink locations from the water column; and pink boxes represent processes involved in moving microplastics from the estuarine water column to sink locations.

1.6 Aims and Objectives of Thesis

The aim of this thesis is to identify processes which affect microplastic transport and fate in estuaries, focusing on Southampton Water, but also considering how these processes may impact on microplastic fate globally. The hydrodynamics of estuaries are complex and are known to influence the transport of sediments and pollutants, and understanding how microplastics are affected by this will enable improved modelling of inputs to oceans and risk assessments in estuaries.

Southampton Water is a representative temperate estuary and was selected as a suitable study location. It has a well-defined hydrodynamic regime; and despite the uniqueness of its tidal cycle (2.3), is a typical European industrialised temperate estuary, with port activity, a large population centre and tidal domination over river inputs. As such, it is a suitable estuarine case study to examine the fate and transport of microplastics within estuaries, with pre-existing literature and information on microplastics within the estuary, which is a relatively unique situation within the UK. Processes identified in Southampton Water will be considered in terms of their importance for the fate of microplastics on a global scale.

The objectives of this study are as follows:

1. Identify the processes involved in transport and fate of suspended material in estuaries, and how these might influence microplastics transport and fate (Chapter 1).
2. Identify how these processes might act in Southampton Water, and identify suitable studies to investigate them.
3. Investigate how microplastic abundance varies within Southampton Water, and how abundance relates to a number of environmental variables that have been previously identified as influencing microplastic abundance (Chapter 3)
4. Investigate the effect of intertidal wetlands on microplastics trapping, using high resolution salt marsh creek sampling in Hythe, Southampton Water (Chapter 4)
5. Investigate the flocculation and aggregation of microplastics, using settling column experiments (Chapter 5).
6. Investigate the resuspension of microplastics, in a series of flume experiments with varied sediment beds and microplastic types (Chapter 5).
7. Evaluate how the field and laboratory studies contained within the thesis contribute to understanding the transport and fate of microplastics within Southampton Water (Chapter 6).
8. Evaluate how the field and laboratory studies contained within the thesis contribute to understanding the transport and fate of microplastics within estuaries on a global scale (Chapter 6).

Chapter 2 Southampton Water

2.1 Introduction

This chapter provides an overview of the characteristics of Southampton Water, the location of much of the fieldwork carried out during the course of this study. It provides relevant information about the estuary, its surrounding population and activities, as well as on the hydrodynamics, and sediment transport and behaviour, within Southampton Water. This information will aid interpretation and discussion of later results within the thesis

2.2 Southampton Water

Southampton Water is a macrotidal estuary, located on the southern coast of England (Figure 2-1). It flows into the Solent, the strait which divides the Isle of Wight from mainland England, at Calshot. Three main rivers flow into Southampton Water, the Rivers Itchen, Hamble and Test, draining a catchment of approximately 1500 km² (Townend, 2008). Southampton Water, due in part to its hydrodynamics (2.3), is the location of one of the busiest deep water ports in the UK (ABP Southampton, 2014). Welcoming 2 million cruise ship passengers annually across four cruise terminals, the port also hosts several container terminals, and handles 900,000 vehicles for export/import per year. With an export value of £40 billion/year, it is the UK's top export port (ABP Southampton, 2014). In order to maintain access to the port, dredging is carried out to retain the deep water channel, including capital dredging. Maintenance dredging occurs on an annual basis, carried out by both ABP, who have a legal requirement to maintain port access, and by users of the port, including the Ministry of Defence, Exxon Mobil, and other private berth owners. ABP typically undertakes its maintenance dredging period during the autumn period. Of relevance to the current study, dredging focused on the Port's berths, the Container Terminal, the Western and Eastern Docks and into the lower River Itchen during the autumn of 2019 (ABP, pers comms). The port owns reclaimed land across from its existing location, known as Dibden Bay, a notified Site of Special Scientific Interest (SSSI), for possible future expansion onto the western shore.

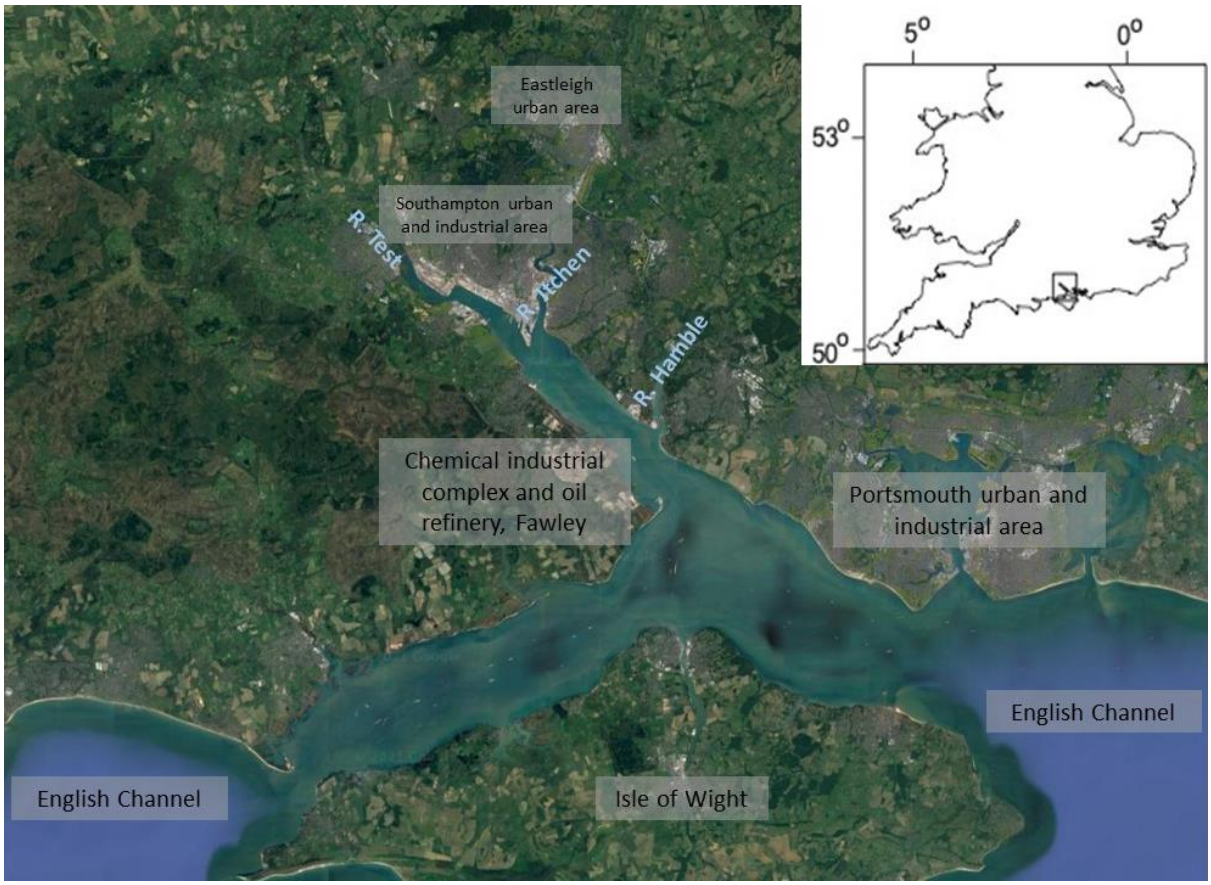

Figure 2-1 Location of Southampton Water within the UK (inset) and potential microplastic sources around Southampton Water and the surrounding region

(Imagery: Google)

On the western shore of Southampton Water, the area around the village of Fawley has been host to a petrochemicals refinery since 1925 (Figure 2-1). Owned by Exxon Mobil, the site processes 270,000 barrels of crude oil per day, with an associated 2,000 ship movements per year (Exxon Mobile, 2019). The site was historically noted for significant hydrocarbon and heavy metal pollution to Southampton Water, but pollution from the refinery has since been reduced significantly (Croudace and Cundy, 1995).

Southampton Water is also host to other industries. Alongside the refinery at Fawley, there are chemical companies, usually linked to the petrochemical industry. Additionally, other smaller industries are located within the Southampton city area and around the Itchen, including boat building, cable manufacturing, electrical engineering, and aggregate supply. Businesses including vehicle repair, supermarkets, laundrettes and other small industries associated with urban areas are also located in Southampton and particularly, along the shore of the Itchen. Whilst fishing boats moor in the marinas located in Southampton Water, they do not usually catch inside Southampton Water (Hampshire County Council, 2021). However, some degree of commercial fishing (including for oysters) did take place within Southampton Water and its tributaries; the

Solent including Southampton Water was previously host to the largest oyster fishery in Europe (Carrington, 2017).

The city of Southampton is the largest settlement located on Southampton Water, with a population of 253,651 (2011 census) and several smaller towns and villages are located on its shores. In addition to the deep water port, there are several smaller marinas and boatyards within Southampton Water, including ones located on the Rivers Itchen, Hamble and Test. There are eleven marinas recorded by the Port authorities as being located on Southampton Water's main channel or a tributary (ABP Southampton, 2014) mostly used for recreational mooring or houseboats, rather than for industrial uses. Southampton Water is also used for recreational fishing, with the River Itchen additionally noted for its fly fishing.

The Solent and Southampton Water have been designated under the Natura 2000 network of protected areas, with areas within this region designated as Special Protection Areas and Special Areas of Conservations. In addition, several habitats within Southampton Water have been notified as Sites of Special Scientific Interest. The SPAs and SACs underpin the importance of Southampton Water as a site of national and international importance for birds in particular, but also other wildlife and plants. During the summer, the Solent is an important breeding site for gulls and four tern species (Treby, 2017), and overwintering birds include the UK conservation Red listed black-tailed godwit and ringed plover (RSPB, 2008). The marshes at Hythe and Calshot are the location of the first discovery of *Spartina* hybrids in the 1860s, retaining a great diversity of genetic material for *Spartina* to this day. Dibden Bay is of national importance for its invertebrate populations.

2.3 Southampton Water Hydrodynamics

In addition to the presence of the dredged deep water channel, the hydrodynamics of Southampton Water contribute to its usage as a port. The bathymetry of Southampton Water and the surrounding Solent region are shown in Figure 2-2, which also shows how Southampton Water is connected to the wider Solent.

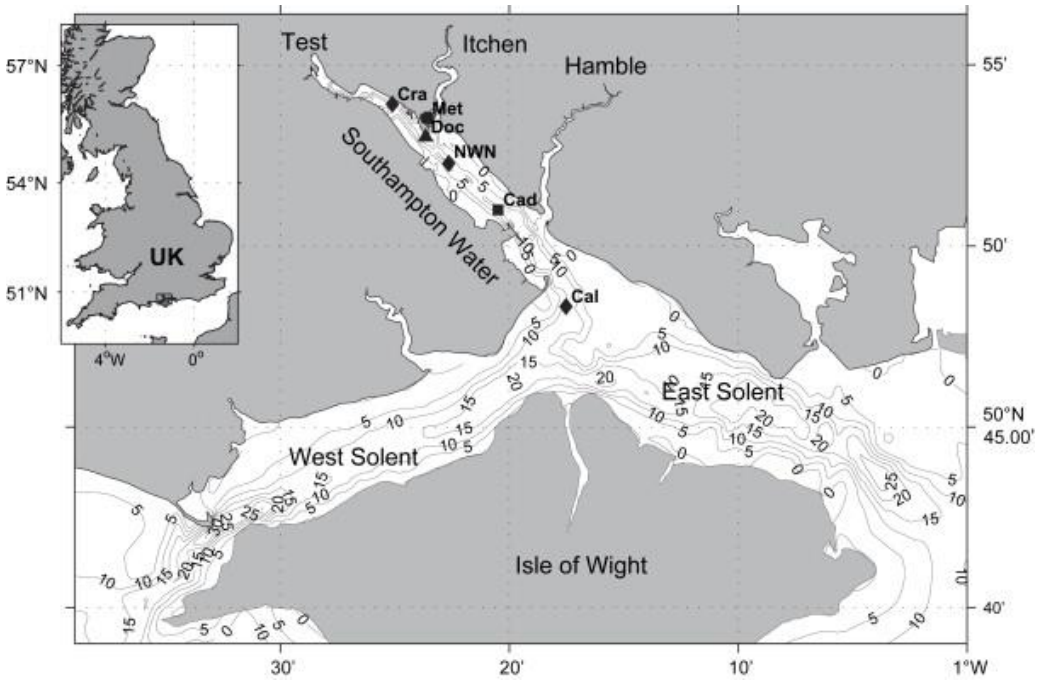

Figure 2-2 Bathymetry of Southampton Water and wider Solent region (from Levasseur *et al.*, 2007)

Black squares/triangles/diamonds/circles indicate locations used in Levasseur *et al*. (2007), and do not relate to this work.

Southampton Water, and the Solent, have unique tidal characteristics, as described by Price and Townend (2000). This is usually referred to as a double high tide, and features a young flood stand, with an extended high water period, which shows little change in water level. It is more prominent on the spring tide, and can clearly be seen in a tidal height curve (Figure 2-3). This extended high tide period offers a longer period for ship movements, but also a longer period of slack water in which sediment deposition and accumulation could occur.

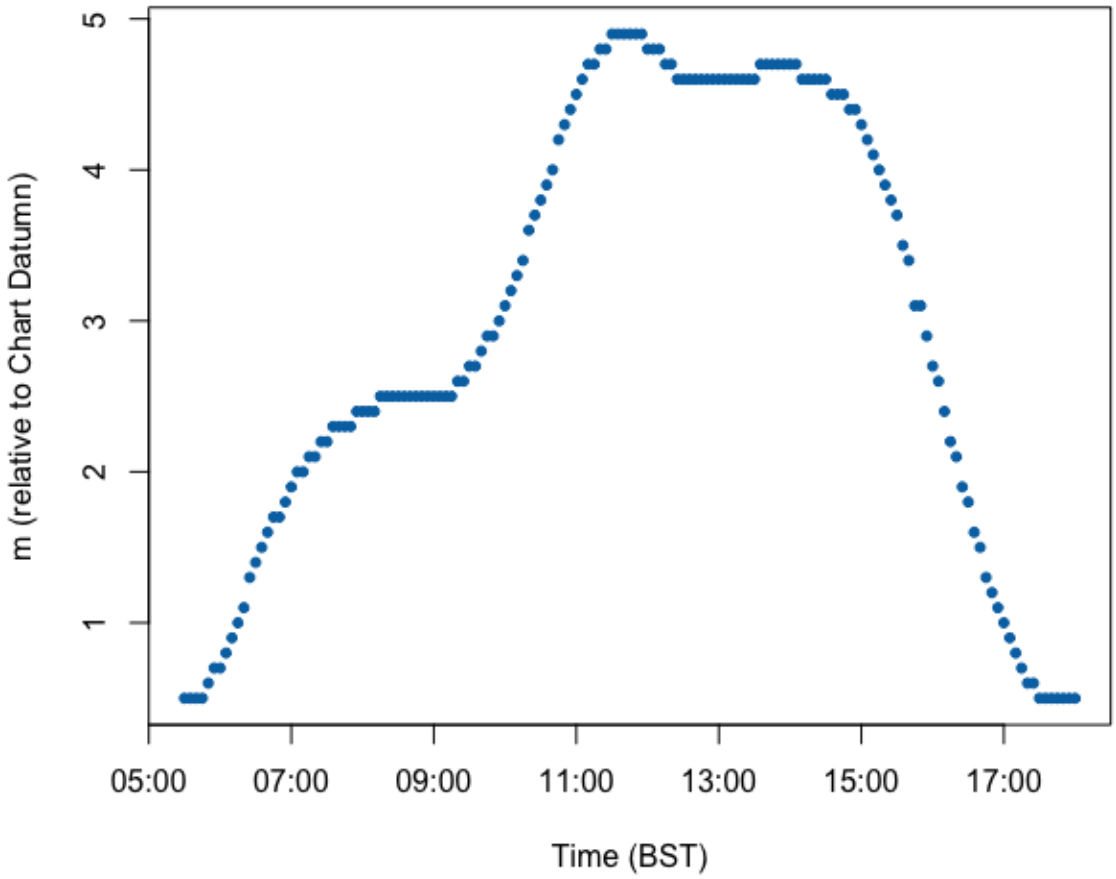

Figure 2-3 A typical spring tide curve for Southampton Water (data from 27/04/2021, data source: sotonmet)

The tides in Southampton Water are controlled by the tidal characteristics of the English Channel (Shi, 2000). As a result of the characteristics of Southampton Water (e.g., its narrow channel and shallow depth, and its irregular shape), the shallow-water tidal constituents are amplified, and in combination with other tidal constituents, this results in the unusual tides experienced – the 'young flood stand' and the 'double high water' (Levasseur *et al*., 2007). The tidal range experienced, of 4.5 m (spring tide) (Levasseur *et al*., 2007), categorises the estuary as macrotidal and is a result of the proximity to the English Channel amphidrome (Price and Townend, 2000). The tidal asymmetry also drives lateral movement of water and suspended particles within Southampton Water, which may drive transport of suspended particles including microplastics from the main channel into the intertidal, providing enhanced trapping potential.

The tidal height curve also shows another feature of the tides in Southampton Water – they are strongly ebb-dominant. The ebb phase of the tide occurs in approximately half the time of the flood tide (4 hours as compared to 9 hours (Levasseur *et al*., 2007)). This produces higher currents on the ebb tide, which provide a mechanism to flush sediments and other suspended and dissolved pollutants out of Southampton Water (Price and Townend, 2000).

As a result of the orientation of the estuary (NW-SE) and the direction of the prevailing winds (SW), the estuary does not usually experience significant wave activity. The effect of swell waves is minimal (Price and Townend, 2000). There may be, at times and in particular locations, increases in wave energy as the result of vessel movements (Hopley, 2014).

The Rivers Test, Itchen and Hamble input relatively small volumes of water annually, with average flows of 11.15 m/s^3 (Test), 5.42 m/s^3 (Itchen), and 0.44 m/s^3 (Hamble) (ABPmer, 2012).The rivers input a small amount of sediment to Southampton Water (Hopley, 2014). The flows from these rivers do not dominate the system, with most material and water exchange occurring from marine sources, meaning that Southampton Water is tide dominated. Collectively, these rivers and smaller rivers drain Southampton and surrounding areas of mixed land use (Figure 2-4)

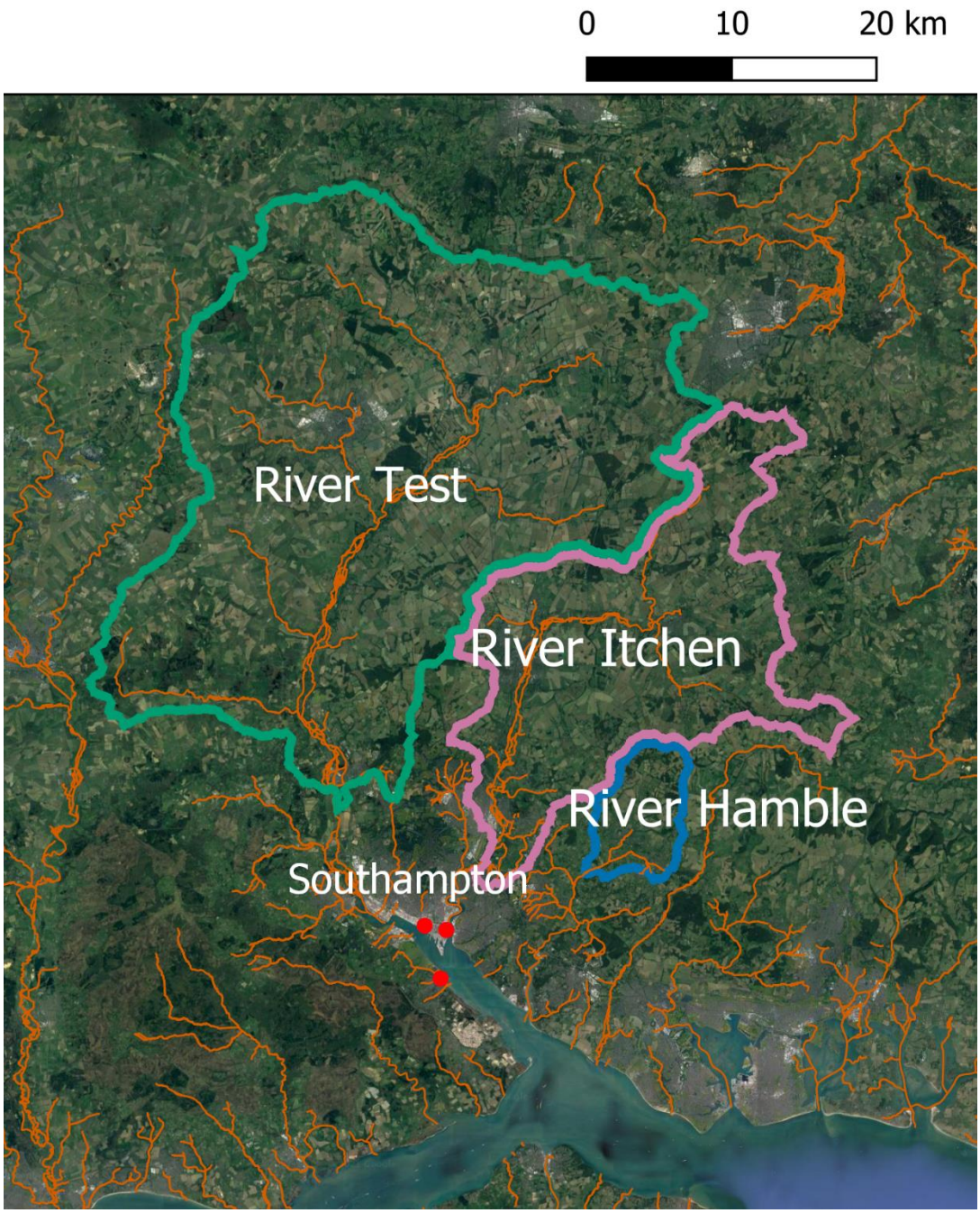

Figure 2-4 The River Test, Itchen and Hamble Catchments

(Imagery: Google).

River catchment outlines data owned by NERC – Centre for Ecology & Hydrology. © Database Right/Copyright NERC. Contains Ordnance Survey data © Crown Copyright and database right 2021. All rights reserved. (Morris and Flavin, 1994, 1990)

River course data owned by Environment Agency, licenced under an Open Government Licence.

Locations of study sites in this thesis are marked with red circles.

2.4 Southampton Water Sediments

Within Southampton Water, sediments are typically composed of mud, or sandy mud, which is derived originally from Tertiary deposits (Lewis, 1997). These form extensive intertidal areas within the estuary, along both the western and eastern shores, including mud flats and salt marshes. There has been considerable change to the extent and locations of these intertidal areas throughout the history of Southampton, and earlier in the mid-late Holocene, well described by Hopley (2014) and Long *et al.* (2000).

The estuary receives inputs of sediment from a variety of sources: the Rivers Hamble, Itchen and Test, from erosion of the intertidal areas including cliffs, remobilised material from the channel, and marine sources. Likewise, there is a variety of sediment sinks in the estuary, including beaches, spit features, mudflats, salt marshes, low cliffs, the channel basin and inland claims (Hopley, 2014). Sediment is cycled in varying quantities between these sources and sinks, as well as exiting to the wider Solent and English Channel. The majority of sediment exiting the system is coarse bedload (ranging from coarse silts to fine gravels), which exits on the stronger ebb tide currents; whereas finer sediment exhibits net transport up estuary and into the various intertidal sinks (e.g., salt marshes) (Hopley, 2014). The 'double high water', or long slack water period, influences this deposition of sediments (Price and Townend, 2000), allowing for a greater period of time in which settling can take place.

2.5 Plastic Pollution within Southampton Water

Two previously published studies have been conducted into the presence of microplastic pollution in Southampton Water (Anderson *et al*., 2018; Gallagher *et al*., 2016). Gallagher *et al.* (2016) conducted plankton net trawls of surface water in the Rivers Hamble, Itchen and Test as well as the main channel of Southampton Water. Microplastics were found in all four estuaries. Quantities were given in microplastics/trawl, which with limited knowledge of trawl variables, does not allow for comparison with other studies of Southampton Water. However, the study identified the existence of microplastic pollution in the surface water of Southampton Water and its tributaries. The most common shapes found in the trawl samples were fibres and rounded particles, and following spectroscopic analysis, the following polymers were identified: cellophane, polyethylene, polypropylene (Gallagher *et al*., 2016), although the authors noted difficulties with the FTIR method and only obtained limited positive identifications of particles with a relatively low (70%) match criteria.

Figure 2-5 Location of previous studies investigating microplastic abundance in Southampton Water.

Locations used in this thesis are marked by red circles, and numbered by the chapter they appear in.

Previous studies are indicated by 'A' for Anderson *et al.* (2018); or 'G' for Gallagher *et al.* (2016).

(Imagery: Google).

Anderson *et al.* (2018) carried out sampling of the sea surface microlayer in the Hamble estuary. Similar to Gallagher *et al.* (2016), the predominant shape of suspected microplastic found was fibres. The average abundance of fibres found was 45.8 microplastics/L. No spectroscopic analysis was performed to confirm the identity of suspected microplastics within this study.

The potential sources of microplastic within Southampton Water are varied and many. As described above, there are a number of industries located around Southampton Water. Spills of primary microplastics – nurdles, or plastic feedstock – have been noted around the River Itchen, and on its shores (Orde, 2020), with several plastics mouldings companies located within Southampton. Macroplastics are also seen on the shores of Southampton Water, including at all field sampling locations visited in the course of this thesis, ranging from food packaging to polystyrene floats used in boating; and will break down into microplastics and mesoplastics as

well as posing a risk as macroplastics. The marinas and port are likely another source, such as by paint chipping, or fragmentation of ropes. Fibres from clothing may be sourced from households or industrial laundrettes, and could input through WWTWs – there are two major WWTWs within Southampton on the River Itchen, and another major WWTW in Millbrook on the Lower Test. Microplastics may be transported into Southampton Water on the rising tide from the Solent and English Channel or may be deposited from the atmosphere. Finally, microplastics may be sourced from outside the estuary, from river flow from upstream of Southampton – the River Itchen, for example, flows through another city (Winchester) before it reaches Southampton – or from coastal inputs on the incoming tide. These sources are poorly understood, and unquantified in terms of their contribution to plastic pollution in Southampton Water. These sources – though generalised – are shown in the estuarine filter diagram in Figure 1-2.

Chapter 3 Seasonal Variation of Microplastics In Southampton Water

3.1 Introduction

Knowledge of how different oceanographic, meteorological and other environmental factors influence microplastic dispersion and localised abundance are essential for effective risk assessment and management. Rarely however do studies consider seasonal or inter-annual variations (Costa *et al.*, 2018). Often only a few samples are taken on one occasion to determine microplastic abundance at a location, when it is clear that microplastic abundances can vary significantly, by orders of magnitude, at just one location (e.g., in an estuarine saltmarsh in the Ou Estuary (China), Yao *et al.* (2019) found microplastic abundance ranged between 9,600 – 130,725 n/m^2). Understanding how different environmental factors interact to drive microplastic dispersion or accumulation, and variations in these over time, will enable greater understanding of distributions of microplastics globally. Knowing, for example, how storm events might influence plastic abundance could enable directed mitigation strategies to reduce inputs. Nel *et al.* (2020) determined that identifying 'hot spots' and 'hot moments' is key to understanding the fate of microplastics, identify likely sources and identify ecosystems that may be vulnerable as a result. Studies have been carried out at various locations, and on various substrates, to investigate factors that might influence microplastic abundance, but they are often limited in scope and consider only, perhaps, two samples taken in different months as a comparison (e.g., Cheung *et al.* (2018)), or take only monthly samples (e.g., Lima, Costa and Barletta (2014)).

Human population has been shown to be linked to increased abundances of microplastics in water and sediment in some instances (e.g., Browne *et al.* (2011)). This is logical, as microplastics are generated by human activity. Whilst microplastics are seen in remote regions long distances from human populations and activity, the highest concentrations are found in regions with large and dense human populations, often with poor waste management (e.g., as modelled by Jambeck *et al.* (2015)). However, there have also been high concentrations of microplastics found a long distance from human populations (e.g., Allen *et al.* (2019)), and so this is not a reliable predictor variable for microplastic abundance, though it can be assumed that locations near and in regions of high population density will also have large concentrations of microplastics.

Seasonal variations have been investigated, mostly at locations in tropical or sub-tropical regions with very distinct rainy and dry seasons. This links to weather conditions, given seasons in

locations such as Brazil or Hong Kong are defined as 'rainy' and 'dry'. There have been correlations drawn between seasons and/or weather, and microplastic abundance, and picking apart the two terms may be difficult. Research into seasonal differences in the tropical regions of South America is well-summarised by Barletta *et al.* (2019), with studies located mostly in estuarine regions of Brazil and Colombia. Less research has occurred at locations with temperate climates, where seasonal differences in weather may be less distinct. Europe, and places with similar climates to the UK, have received little attention in terms of seasonal variation. Galgani *et al.* (2000) found some seasonal variations in macrodebris abundance in the Bay of Biscay; Fanini and Bozzeda (2018) found little seasonal variation in microplastic abundance on Cretan beaches; and Stolte *et al.* (2015) found tourism-linked increases in microplastics in summer on German Baltic beaches. In Portugal, Rodrigues *et al.* (2018) found no seasonal differences in river water and sediment in the Antuã River, although Antunes *et al.* (2018) found rainfall/storm linked increases on beaches in winter. In Finland, Saarni *et al.* (2021) found that the total microplastic flux as measured in a sediment trap set at 3 m depth in a lake was higher during summer (whereas the sediment flux was highest in winter). In the USA, Conley *et al.* (2019) found no seasonal differences in microplastic abundances in WWTWs in North Carolina.

Rivers are reported as main exporters of plastic debris from inland areas (even though a large percentage of the world's population is considered to be coastal (40%) (United Nations, 2017), this still leaves a large population living and producing plastic debris inland) to the ocean. Considering the transition zone between these conduits of debris and coastal seas is of key importance to understanding the dynamics of microplastic transport and fate. As previously discussed, estuaries are understudied in comparison to other environments such as coastal sandy beaches, but a variety of environmental compartments have been sampled – estuarine sediment, estuarine water, estuarine fish – with a variety of findings. Araújo and Costa (2007) found beach macrodebris was slightly higher in the rainy season; Dantas *et al.* (2012) found microplastics in estuarine fish stomach contents were higher in the rainy season; and Lima *et al.* (2014) found estuarine water microplastics were most abundant in the late rainy season. Lima *et al.* (2015) found that the distribution of microplastics in estuarine water changed seasonally, but was more associated with increased rainfall flushing the estuary than with the environmental variation with the seasons. The influence of river flow on flushing was also found by Bailey *et al.* (2021), who did not consider seasonal variation, but did find that in the Raritan Hudson Estuary (USA), low rainfall periods allowed microplastics to accumulate within the estuary due to reduced flushing. In Asia, studies have investigated seasonal variation around Hong Kong. Cheung *et al.* (2016) and Cheung *et al.* (2018) found higher abundances in the rainy season in the water column only on the side of Hong Kong influenced by the Pearl River. Tsang *et al.* (2017) found no differences in microplastics

abundances in sediment, but did find significantly more microplastics at the end of the dry season in water than the beginning of the dry season and the wet season. In the Nakdong River (South Korea), Eo *et al.* (2019) found a majority of microplastics (81% of weight) in the wet season. In summary, seasonal variations in microplastic abundance are sometimes observed, often dependent on the location and often linked to weather conditions. Most commonly, as discussed above, seasonal differences were observed in tropical climates, rather than the temperate climate conditions experienced by the UK.

Tides can be (depending on the tidal regime) a large driver of hydrodynamics in estuarine and other coastal locations. However, little consideration is often given to the effects of tidal currents when sampling for microplastics. The most common consideration is when sampling the intertidal zone; comparisons have been made by a small number of studies of abundances at the low, mid and high tide lines. These studies have shown a variety of conclusions, from no differences across the height of the beach (Besley *et al*., 2017), to significantly more microplastics at the low tide line than the mid or high tide lines (Mathalon and Hill, 2014), to the high tide line having significantly more microplastics than the low tide line (Karthik *et al*., 2018). Tidal cycles also vary, as part of the spring-neap cycle. Few studies have investigated this, but Wu *et al.* (2020) found that microplastics in surface sediments of a tidal flat in the Yangtze Estuary showed more, and larger, microplastics in surface sediments during neap tides. In contrast, using manta trawls for all sizes of plastic debris, Sadri and Thompson (2014) found a lower (not statistically significant) abundance and a smaller size (significant) during neap tides as opposed to spring tides in the Tamar Estuary. Other water sampling campaigns in estuaries focusing on tidal variations have been carried out by Alligant *et al.* (2018), Defontaine *et al.* (2020), Rowley *et al.* (2020), Figueiredo and Vianna (2018), and Sukhsangchan *et al.* (2020). All of these studies have used plankton trawls with various sized nets (300 µm (Alligant *et al*., 2018; Defontaine *et al*., 2020; Sukhsangchan *et al*., 2020), 250 µm (Rowley *et al*., 2020) and both 64 µm and 200 µm (Figueiredo and Vianna, 2018)), at various depths ranging from the surface to 1 m above the estuary bed. While net trawls are common, they sample the upper portion of the water, and the sea surface microlayer, a unique microhabitat that is the interface between the ocean and atmosphere (referred to as the SML, discussed below) together, and they are resource intensive. On the scale of sampling utilised in this chapter (3x per week, for four, four-week periods), trawls are not as feasible an option as sampling from the shore.

Alligant *et al.* (2018) found lowest microplastics abundances at the beginning of the ebb tide, and the highest at the end of the ebb tide in the Seine Estuary (France). Defontaine *et al.* (2020) coupled water sampling with modelling, showing that in the Adour Estuary (France), a salt-wedge estuary, neutrally-buoyant microplastics were flushed out by river flows, but heavier microplastics

were liable to be trapped within the estuary. This supports the hypothesis that the type of estuary and its stratification and hydrodynamics could be a major influence on how estuaries retain or export microplastics, and how this may change over time. Sukhangschan *et al.* (2020) sampled on two tidal cycles, one spring and one neap, in the Chaophraya River (Gulf of Thailand), finding that microplastics concentrations in surface waters were significantly higher on the neap tide than the spring tide, hypothesised as due to the lower mixing on the neap tide. Rowley *et al.* (2020) found, with some minor deviations hypothesised to be due to CSO outflows, that microplastic abundances were lower on the flood tide than the ebb tide in the Thames (UK). This is proposed to be due to diluting of estuarine water with (less polluted) seawater. Contrasting to this, Figueiredo and Vianna (2018) found higher abundances on the flood tide in Guanabara Bay (Brazil). The authors proposed that this was due to the entry of particles on the incoming tide, but the influence of 'clear coastal waters' was also seen in their samples. In summary, though only a few studies have investigated the effects of tidal currents on microplastic abundance, it seems likely that the distribution of microplastics is influenced by local coastal transport processes including tides (Zhang, 2017), and this remains poorly understood to date. Some studies have however, determined that microplastics abundances were influenced by coastal processes and estuarine circulation, such as Zaki *et al.* (2021) in the Klang River estuary (Malaysia).

Thus, how a number of environmental factors might influence microplastic abundance has been investigated, but rarely are multiple factors investigated in one study. However, often they link together, for example, in the case of seasonal variation and precipitation. Understanding how these factors influence microplastic abundance could improve modelling, for example, of river outflows to coastal areas. Several well-known modelling studies use river flow as a predictor of microplastic inputs from rivers to the ocean (Lebreton *et al*., 2017; Schmidt *et al*., 2017), and so understanding how river flow and related environmental parameters influence microplastic abundance has the potential to improve these estimates. In addition, understanding how microplastic abundance varies with the tidal state in estuaries could give an indication as to dominant sources of microplastics – for example, if highest abundances occur on incoming tides, it may be an indication that microplastics are being brought back into the estuary from the sea. The complexity of estuaries has complicated determining clear drivers and patterns of microplastic abundance within estuaries (Dris *et al*., 2020; Nel *et al*., 2020).

Distribution of microplastics within estuaries is complex and understudied, both horizontally and vertically. Some elements of the vertical distribution of microplastics have been investigated, and areas of accumulation of microplastics identified. One of these areas is the sea surface microlayer, or SML. This is defined as the top 1-1000 µm of the ocean (Wurl and Obbard, 2004), though this definition varies dependent on the purpose of research and sampling methods utilised. The SML is

the interface between the oceans and atmosphere, and potentially plays a role in the transfer of microplastics between atmosphere and ocean, given that it is known to play a key role in the distribution of other anthropogenic pollutants, such as POPs (Wurl and Obbard, 2004). It is a key habitat for a variety of small marine organisms, including phytoplankton and fish larvae and eggs (Wurl and Obbard, 2004). Microplastics have been observed at higher concentrations in the SML than in underlying surface water (Anderson *et al*., 2018; Song *et al*., 2014), though the reasons for this are not definite. It is believed that this higher abundance is a result of the properties of both the SML and microplastics. Microplastics are often low-density particles, which have high buoyancy and will hence float at the top of the water column; and the SML has a high organic content with a lot of microbial activity which produces a "sticky" microgel characteristic of the SML (Anderson *et al*., 2018). Microplastics in the SML may pose a risk to the organisms within it, but the risks posed are still poorly understood.

Due to the lack of relatively high-resolution, long-term studies looking at microplastic abundance in estuaries, a year long, seasonal sampling campaign was performed within Southampton Water. Two locations were chosen, for their differing characteristics and water accessibility (described below, 3.2.1.1) and sampled three times a week for four-week periods, four times a year. In addition, environmental variables which may influence microplastic abundance were recorded. This enabled investigation of the effects of meteorological and oceanographic conditions on microplastic abundance alongside calculation of an accurate microplastic abundance in Southampton Water and the range of abundances experienced over a calendar year.

3.2 Methodology

3.2.1 Sampling Methods

3.2.1.1 Field Sampling

Field sampling was carried out three times per week (Monday, Wednesday, Friday) for four four-week periods, which broadly mapped onto the different seasons in northern Europe. These periods were February 4th – March 1st 2019 (winter); May 6th – May 31st 2019 (spring); July 29th – August 23rd (summer); and November 4th – November 29th (autumn). On each sampling day, the Southampton Water Activities Centre (SWAC) was sampled first, then Mayflower Park approximately 25 minutes later. At each site, from approximately 30 cm water depth (around 1 m distance off shore), a bulk water sample was taken; followed by a surface microlayer (SML) sample, weather dependent. The time of sampling was recorded at the start of sampling.

Locations were chosen to provide an overview of Southampton Water, to enable comparability of a more fluvially influenced site which is sheltered from prevailing winds and proximal to a major WWTW (Woolston), to an open estuarine site with less shelter from the wind and in closer proximity to port activity, and for their accessibility to water to enable sampling.

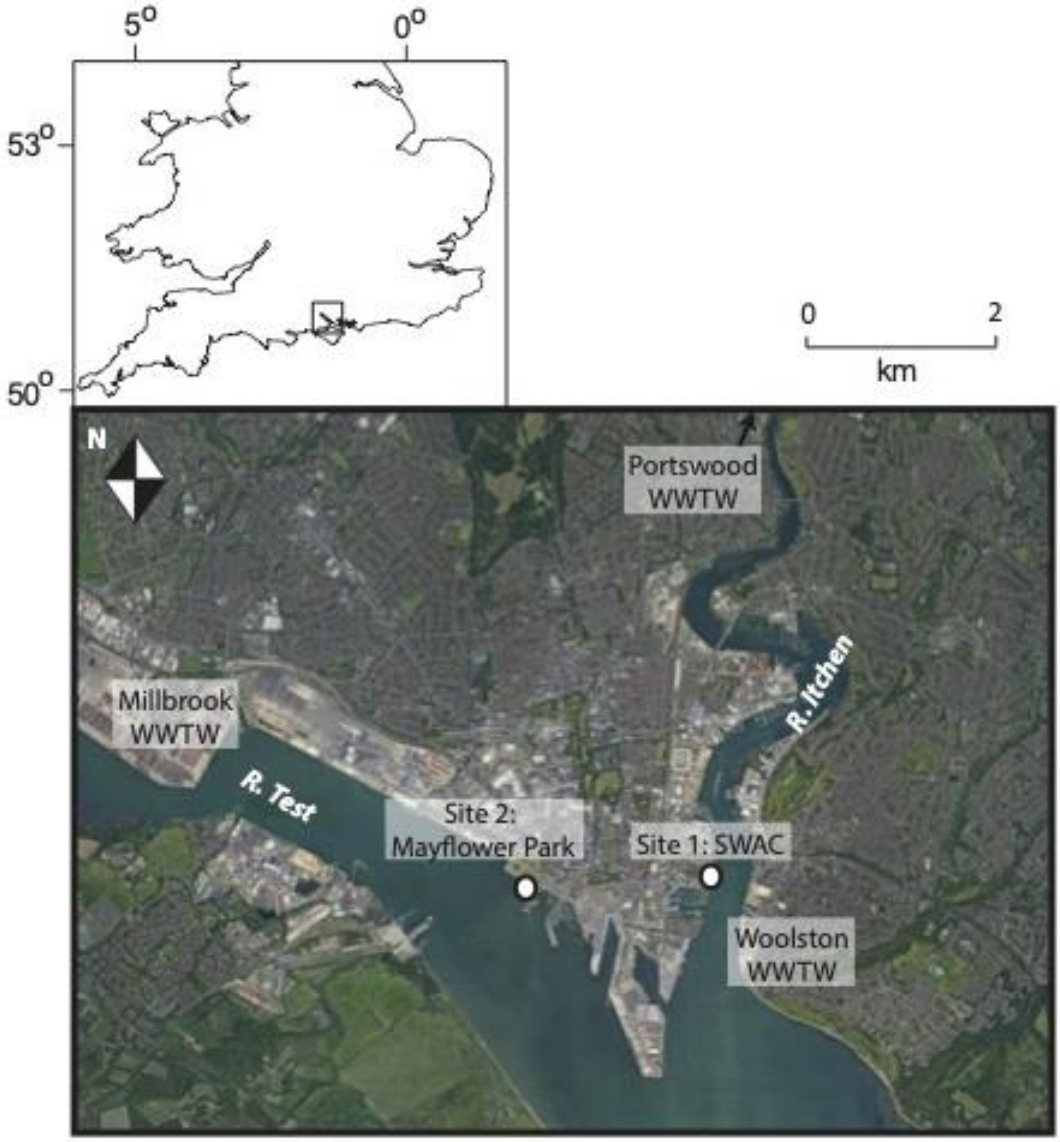

Figure 3-1 Location of Sampling Points and Potential Microplastic Sources (WWTWs) (Imagery: Google).

3.2.1.1.1 Southampton Water Activities Centre (SWAC)

Sampling was carried out from the slipway. The substrate changes from gravel at the high tide mark, to mud below the low tide mark, as can be seen by the visible turbidity in Figure 3-2. The Activities Centre is heavily used during the summer season, with less use over the autumn and winter. Activities undertaken here including sailing, powerboating, and windsurfing, with more frequent usage during the summer season (April-October). There is a pontoon to the seaward side

of the sampling site, which provided some degree of protection from inclement weather conditions (seen to the left in Figure 3-2). The Centre lies on the River Itchen, approximately half a mile before it flows into Southampton Water. The slipway is regularly cleaned of algal growth, although the high tide line is often marked by seaweed and macroplastic debris, and seaweed grows alongside the slipway on the gravel.

Figure 3-2 Southampton Water Activities Centre at low water (source: author)

The photograph shows the change in substrate from gravel to mud at the low water mark (increased turbidity around the low water mark), and the pontoon that shelters the site. Sampling occurred on the left slipway, directly next to the pontoon. The River Itchen flows from right to left in this photograph.

The River Itchen flows from mid-Hampshire, over a total length of 28 miles, and discharges into Southampton Water. The river becomes tidal at Woodmill Bridge (Southampton), approximately 4 miles upstream of the sampling site. It is a Chalk river, nearly entirely fed by groundwater (Giles *et al.*, 1988), with 26 miles of its length designated as a river SSSI. It is notified primarily for the habitats that exist upstream of the sampling site (which does not fall into the area covered by the SSSI notification), including the Chalk river, fen meadows, flood pasture and swamp habitats. The

river is notable for its species-richness, with over 210 invertebrate taxa recorded (*River Itchen Site of Special Scientific Interest Notification*, 2000).

While the SSSI notification for the River Itchen dates to 2001, nutrient enrichment occurs in segments of the river, and this is likely to have continued to date. There are several wastewater treatment works (WWTW) which discharge into the river, including a WWTW located across the river from the site (Woolston), which has recently been redeveloped (Southern Water, 2021a); and one upstream of the site (Portswood). In addition to these potential point sources, and the use of the Activities Centre as a source of microplastics; the river hosts several marinas, boatyards and areas of industry (including plastic mouldings companies and commercial laundries) upstream of the site, and there may be inflow from the main estuary during the flood tide. This site is also located near to Combined Storm Outflows (CSOs), which during high rainfall events can input discharges which are not treated prior to their entry into the waterway.

3.2.1.1.2 Mayflower Park

Mayflower Park is a small park on the shorefront near Southampton City centre. It was reclaimed from mudflats in the 1930s, and has served as a recreational site for the city's population ever since. It consists of a grass park, with facilities including a car park, children's playground and café. Its water access is a small gravel beach, sheltered on one side by the derelict Royal Pier (Figure 3-3). Like the sampling site at SWAC, the substrate changes to mud below the low tide mark. Seaweed grows along the wall at one side of the beach and below the high tide line in the water, and was often present on the beach or floating in the water, with live oysters seen at low tide among the gravel and larger rocks. Macroplastic debris is often recorded here, though appears to be removed on occasion. The beach is used for recreation or swimming, though not frequently. As at SWAC, this recreational activity occurs mostly in the summer season.

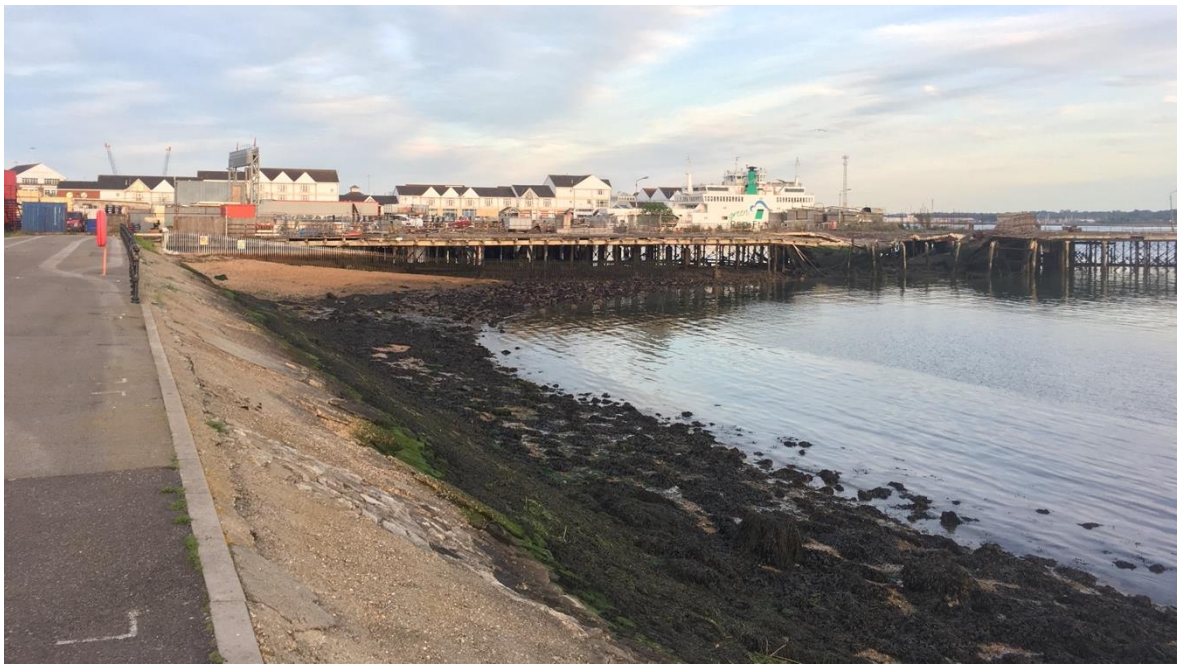

Figure 3-3 The Mayflower Park sampling site at low tide (source: author)

A line of debris can be seen at the top of the beach, at the high tide mark.

Mayflower Park is located on the lower part of the River Test (Southampton City Council, 2021). It is considered to be an open estuarine site for the purpose of this study, which contrasts to the greater river influence at the SWAC site. The Mayflower Park site has a greater commercial shipping influence, being located next to the Red Funnel Isle of Wight ferry terminal, and close to two cruise terminals (City and Mayflower Cruise Terminals) and the Western Docks. During September, the park hosts the annual Boat Show, with pontoons installed near the sampling site prior to the August (summer) sampling period. These pontoons (though reduced in number) remained in situ during November (autumn sampling period), providing an element of shelter to the site. The largest of the WWTWs in Southampton (Millbrook) discharges into Southampton Water close to the site. Like SWAC, there are CSOs located near this site.

3.2.1.1.3 Bulk water

Bulk water samples were always the first sample taken at a site. At approximately 5 cm water depth (which was well below the depth of the SML), a cleaned (washed with detergent, rinsed with DI water) high density polyethylene (HDPE) bottle rinsed in ambient water was opened, filled and closed to produce a sample of approximately 500 mL volume. Bulk water samples were taken on all sample days, at both sites.

3.2.1.1.4 Surface Microlayer

Following prior studies (Anderson *et al*., 2018), glass plate sampling was selected to sample the SML. This method was developed by Harvey and Burzell (1972), described by Wurl and Obbard (2004) and trialled for microplastics sampling by Anderson *et al.* (2018). This method utilises a sheet of glass, without additional treatments to the surface of the glass, which is repeatedly lowered vertically into the water and then raised (Figure 3-4). The plate used was 0.4 cm thick, 18.2 cm wide, and 30.0 cm high. Before sampling began, the plate was immersed perpendicular to the water three times, to remove potential contaminant microplastics from the surface of the glass. As for the bulk water samples, the sample bottles as well as the HDPE funnel used to collect the draining water were also rinsed in ambient water before starting sampling. Following this, the sample was taken, by immersing the plate to a pre-determined depth of 27.5 cm, withdrawing at a steady rate (~5 cm/s) and the adhered water sample collected. This procedure was repeated for a total of 25 plate dips, or, where water depth prevented this, the plate was turned sideways and 30 dips were carried out with a 30.0 cm wide plate to a depth of 16 cm. This produces a sample ranging in volume from 250-350 mL, and samples to an SML depth of approximately 100 µm (Agogue *et al*., 2004). Samplers stood downwind of samples, to reduce contamination from clothing in the field.

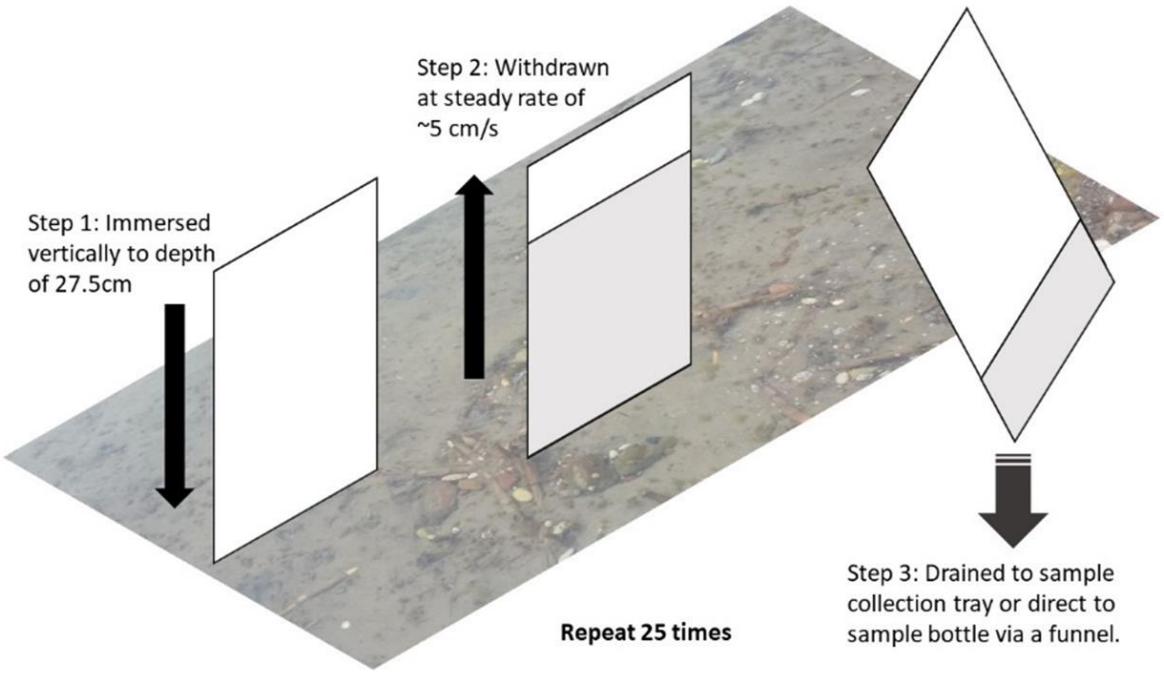

Figure 3-4 SML glass plate sampling method (from Anderson *et al.,* 2018)

Surface microlayer samples were taken if the conditions were calm enough. If breaking waves were observed, conditions were deemed too rough for a SML to exist and be sampled. On these occasions, only bulk samples were taken.

3.2.1.2 Environmental Data

3.2.1.2.1 Rainfall

Rainfall data was requested from the Environment Agency, and is licenced under an Open Government Licence for public sector information (v3.0). The data are quality-checked by the Environment Agency, and only data recorded as 'good' and 'complete' were utilised. The rainfall monitoring site is located in Portswood, Southampton (SU 43562 14775), on the banks of the River Itchen, a short distance upstream from SWAC. Data are recorded in mm/day. Both rainfall on the day of sampling and rainfall on the previous day of sampling were recorded.

3.2.1.2.2 Tidal Height/State (ebb/flood and spring/neap)

Tidal height data were obtained from Sotonmet (sotonmet.co.uk), which utilises data collected by ABP Southampton. The sampling site is located at Dock Head, Southampton, within the Port. It is located approximately half-way between the two sampling sites.

Tidal height was taken at the time of sampling, recorded as sampling commenced. As the resolution of the tidal data is 5 minutes, these were rounded to the nearest 5-minute mark. Determination of tidal state (ebb/flood, and spring/neap) was carried out using the daily graphs of measured tidal height (relative to Chart Datum). Comparison of the tidal height at sampling times with surrounding tidal heights determined whether the tide was rising or falling. The position on the spring/neap cycle was determined using the calculated tidal range on any given sampling day. Mean neap tidal range in Southampton Water is 1.9 m and mean spring tidal range is 4.0 m (ABPmer, 2012). A range of 1 m around these ranges was used to refine, with 1.4 – 2.4 m considered as a neap tide, and 3.5 – 4.5 m considered as spring tide.

3.2.1.2.3 Wind Speed

Wind speed and direction data were recorded by Sotonmet, again at Dock Head, Southampton. Wind speed (knots) and direction (degrees) were obtained for each specific sampling time, as for rainfall, rounded to the nearest 5-minute mark due to the resolution of the data. Daily averaged wind speeds and wind direction were also recorded.

3.2.1.2.4 River Flow

River flow data for the River Itchen was requested from the Environment Agency, and are licenced under an Open Government Licence for public sector information (V3.0). The data are quality-checked by the Environment Agency, and all data from the winter, spring and summer periods are recorded as 'good' and 'complete'. The data from the autumn sampling period are estimated, due to a discrepancy between ADCP gauging and ultrasonic flow figures, as recorded in the metadata for this dataset. The station for these data is located in Riverside Park, Southampton (SU 44474 15337), above the weir at Woodmill Bridge. Data were recorded in m^3/s, averaged over a 24-hour period.

3.2.1.2.5 Dredging

Maintenance dredging is undertaken within Southampton Water during the autumn and winter periods. Information about dredging was obtained via communication with the Association of British Ports, through the harbour manager of Southampton Water. This included information about the location of dredging vessels during the autumn sampling period. This was recorded in terms of presence/absence of dredging in the vicinity of the sampling sites on sampling days.

3.2.1.2.6 Suspended Sediment Concentration

Suspended sediment concentration (SSC) was measured from the bulk water samples. Following filtration of a subsample for microplastics, the sample was utilised for SSC measurements. The sample was homogenised by shaking the sample bottle by hand, with 50 mL then removed by syringe. This was forced through a glass microfibre filter (Whatman GF/C) and dried at 50°C overnight. The filters were weighed before and after filtration/drying to determine the sediment weight, which was then converted to mg/L.

3.2.1.2.7 Salinity

Salinity was measured from the bulk sample remaining after subsampling for microplastics and suspended sediment. A TS probe was used, with salinity recorded in PSU.

3.2.2 Sample Processing

SML and bulk water samples were filtered without additional treatment following storage at room temperature (following previous SML studies (Anderson *et al*., 2018)). The volume of the sample was recorded prior to filtration (to the nearest 5 mL), and for some samples, due to turbidity, the volume filtered was reduced to prevent blockage of the filter paper. For the majority of samples, the entire SML sample was filtered, and for the bulk samples, 0.2 L was filtered. Samples were

filtered onto 0.45 µm cellulose nitrate gridded filters (Whatman, USA), and stored in tight-fitting (polyethylene) Petri dishes (Falcon, USA). Sample bottles (SML samples only) and the measuring cylinder were rinsed with MilliQ[2] (ultrapure) water after use, and this rinse water filtered onto the same filter as the sample. The filter holder was rinsed with MilliQ water before the filter was removed to wash any particles remaining on the glass filter holder onto the sample filter.

Contamination prevention measures are necessary when processing environmental samples for microplastics. Self-contamination, particularly by fibres, is a recognised hazard, and needs to be prevented, where possible, and enumerated. When field sampling, measures were taken to reduce contamination. Samplers stood downwind of the sample being taken, and where possible, wore natural fibre clothing (this was sometimes difficult due to weather conditions). Measures taken in the laboratory included working in a laminar flow hood; wearing cotton clothing and cotton laboratory coats that were cleaned with a lint roller before work; wearing nitrile gloves; and running procedural and airborne blanks.

Procedural blanks comprised a 200 mL sample of MilliQ water processed in the same way as the environmental samples (i.e., measured in a measuring cylinder, filtered, with the measuring cylinder and the filter holder rinsed onto the same filter as the sample). Airborne blanks composed of a filter dampened with MilliQ water were left out uncovered within the laminar flow hood alongside the filtration equipment during the duration of filtration.

Two samples (19th August, SWAC SML and Mayflower SML) were lost due to mislabelling, and a further 11 SML samples were not taken due to high winds observed on the sampling day, leading to a total of 83 SML and 96 bulk water samples across all sampling periods and both sites.

3.2.3 Sample Enumeration

Identification and enumeration of microplastics is a rapidly developing field, however, current techniques are limited and time-consuming, and constrained by access to equipment. In the majority of studies, visual enumeration is utilised as a low-cost tool which is considered acceptable when used in combination with chemical identification techniques such as FTIR (Stanton *et al.*, 2019b). This approach was followed here. Three visual counts were carried out on all filters by three operatives.

[2] Milli-Q refers to water that has been purified via a 0.22 µm membrane filter with a specific resistance of 18.2 micro-ohms.

When enumerating samples for microplastics, the visual criteria described by Qiu *et al.* (2016) and the shape descriptions given by Rochman *et al.* (2019) were followed by all three operatives. Three different individuals counted the filters – the author, and two laboratory assistants. All filters were counted three times, not necessarily by the three different operatives, due to availability. An average of all three counts was utilised. One count was utilised to carry out length measurements of all suspected microplastic particles. Particles were measured using a calibrated microscope camera, and simultaneously photographed for subsequent analysis.

Criteria for visual identification were: no cellular or organic structures are visible in the microplastics; fibres should be equally thick throughout their entire length; microplastics must show clear and homogenous colours; if particles are transparent or white, they shall be examined under a microscope at high magnification to exclude an organic origin (Hidalgo-Ruz *et al*., 2012; Qiu *et al*., 2016).

3.2.4 Spectroscopic Analysis

A subsample of twenty filters were chosen for spectroscopic analysis. The filters were chosen so that four were blanks (three procedural, one airborne) and the remaining sixteen were environmental samples. Four samples, with the highest apparent microplastic abundances, were chosen from each month, two from SWAC (one SML, one bulk) and two from Mayflower Park (one SML, one bulk). This enabled a comparison of polymer types and identities between sites, within the water column, and between seasons. In addition, using spectroscopic identification on blank samples enabled identification of contamination sources.

Samples were reprocessed to move them onto filters suitable for FTIR analysis (stainless steel, 25 µm pore size) and to reduce the sediment in the sample. The Oil Extraction Protocol (OEP) developed by Crichton *et al.* (2017) was used, with modifications. The same contamination control measures were used as for the initial filtration – work was carried out in a laminar flow hood, whilst wearing cotton clothing and a cotton laboratory coat, which were cleaned with a lint roller prior to starting. All filtration equipment was glass, or metal where possible (e.g., it was necessary to use a rubber bung to connect component parts), and was rinsed with MilliQ water prior to starting. Samples were removed from the cellulose nitrate filters using ultrasound, and by shaking the filters with MilliQ water. They were then mixed with a small amount < 10 mL of rapeseed oil, and the mixture left to settle for 10 minutes. The water and sediment fraction at the base was then removed, and the remaining oil and sample mixed with ethanol and filtered onto a stainless-steel filter (25 µm). This filter was then soaked in ethanol for 10 minutes, before being filtered again. Following this, an additional step of soaking the sample post-oil extraction for 72

hours in Decon 90 was added, to remove as many traces of oil as possible following initial FTIR results showing particles coated in oil. Samples were then filtered again, and the filters mounted onto glass sites using double-sided tape, again in a laminar flow hood.

The μATR-FTIR analysis was carried out using a Perkin Elmer Spotlight 400 Imaging system, which was equipped with a μATR accessory. A total of 1746 particles were analysed using μATR-FTIR, against an expected 812 (determined by visual counting). The collected individual infrared spectra were exported into PerkinElmer Spectrum 10 software to carry out identification by comparing the measured spectra to a polymer library of reference spectra (18,711, 460 polymer types; spectra database from S.T. Japan-Europe GmbH, Germany/Japan). Spectra with hit quality >0.8 (on a scale of 0 to 1) were accepted as verified polymer types. A hit quality of 0.8 corresponds to an 80% similarity between the measured and reference spectra. Particles were then classified as 'unidentified' (spectra match < 0.79), 'natural', 'polymer', 'additives' (chemicals which are known to be added to plastics during production), and 'cellulose polymers' (polymers such as cellophane which could be of natural or synthetic origin).

3.2.5 Correction for Blanks and FTIR Results/Uncertainty

Blank samples were examined following the same techniques and protocol as the sample filters. Following observations of degradation of a rubber bung that was part of the filtration equipment used, orange fragments were removed from counts. Colourless fibres occurred in large quantities in the blank samples, and following previous studies (Anderson *et al*., 2018), were removed from sample counts due to a probability that these were derived from sample contamination. Following this, an average count of each type of microplastic particle (e.g., black/blue fibre, red fibre, etc) in the blanks was calculated and removed from the counts of each sample. Black and blue fibres were combined due to their similarity depending on the ambient light when operating the stereomicroscope.

Combining the FTIR results of the 16 environmental samples enabled the calculation of a percentage of the sample believed to be of synthetic origin. 31.47% of the particles in these samples were unidentified. Of the identifiable remainder, 37.48% were of natural origin, and 2.32% were identified as cellulose polymers – polymers such as cellophane or cellulose polyester, which cannot be determined conclusively to be of natural or synthetic origin. Finally, 21.81% were identified as plastic polymers, such as polystyrene or polyethylene, and 6.56% were identified as known plastic additives, such as pentalyn, or decyl oleate; which sums to 28.37 of the tested particles being of a synthetic origin. Assuming the unidentified 31.47% of particles followed the same proportions as the identified portion, the percentage of particles of a synthetic origin was

taken to be 41.41%. This correction factor was used to calculate the abundances used in data analysis in this chapter.

3.2.6 Data Uncertainties, and their Implications

The step of visually identifying suspected microplastics is the first source of uncertainty. Microplastics can look very similar to natural particles within samples, and microplastics could be both undercounted and overcounted within samples. While efforts were made to reduce this error – including triple counting samples, and the use of several operatives, and utilising spectroscopic analysis – the use of visual identification was unavoidable due to the high time and cost requirements of spectroscopic analysis on all samples. Alternative methods of identification have been used in other studies, such as the hot needle test, or Nile Red staining. However, these have significant disadvantages that led to their non-use in this chapter. The hot needle test, while cheap and easily accessible, leads to the damaging or destruction of suspect particles (Cutroneo *et al*., 2020); and Nile Red staining also stains biological particles, leading to overestimation of microplastic abundances (Stanton *et al*., 2019a).

Another source of overestimation of microplastic abundances is contamination of samples (Woodall *et al*., 2015). Contamination was quantified during laboratory work, but not during the field sampling. Measures to reduce contamination were taken in the field, but the practicalities of quantifying field contamination prevented this from occurring. In the laboratory, airborne contamination was quantified by leaving dampened filter papers exposed near the work being carried out; and procedural contamination was quantified by carrying out procedural blanks with MilliQ water. Very small numbers of fibres were observed in the airborne blanks, and larger numbers were observed in the procedural blanks. Contamination could lead to overestimation of microplastics, particularly fibres as these are shed from clothing. Some reduction is achieved by wearing cotton clothing and carrying out spectroscopic analyses. Even with measures taken, plastic fibres were still seen in blank samples which were tested by FTIR. One of the methods of correcting for the contamination seen was to remove all colourless fibres from analysis, to align with other chapters in this thesis (Chapter 4) and previous work (Anderson *et al*., 2018). However, it is likely that not all the colourless fibres in the samples are a result of contamination during laboratory analyses, and this is an underestimation of microplastic abundance.

Four blank samples were reprocessed alongside the environmental samples, and subjected to FTIR. This process introduced additional sources of contamination, as can be seen by comparing the abundance in the visually counted samples, and the abundance in the FTIR results (mean abundance in the visual counts of the blank samples = 151.34; total observed using FTIR = 285).

Some of this increase may also be due to the increased magnification available through FTIR – fibres down to a size of 25 µm were able to be tested, whereas visual identification may be only reliable to a minimum length of 500 µm (Renner *et al*., 2018). The ratio of synthetic:natural particles in the blank samples was 1:4, suggesting that contamination control measures were not perfect – indeed, the presence of any particles in the blank samples proves this. However, given that care was taken to wear non-synthetic clothing and to limit use of plastic in the lab, the 1/5 of particles that were found to be synthetic also suggests that these measures were not perfect. Laboratories used were not solely used for microplastics research, and therefore synthetic laboratory coats and equipment were also in use within the laboratory during sample processing. Additionally, although natural fibre clothing and laboratory coats were worn, these still shed fibres which could contaminate samples.

An assumption can be confidently made that the bulk sampling method will sample all microplastics in the water column at the sampling depth. The bulk sampling method is likely to be less discriminatory and does not bias the resultant sample in the same way the SML sampling method does. The SML is more complicated to sample than the water column in general, due to it being less than 1 mm deep. The glass plate sampling method has been tested in a laboratory study on a range of fibre types, both natural and synthetic, which found an average recovery rate of 26.8% (Birkenhead *et al*., 2020). Recovery rates were affected by salinity, with saltwater treatments showing an average recovery rate of 36.5%, but freshwater treatments showing an average recovery of 19.3%. Observed salinities in this study ranged between 32.4 and 15.5 PSU, and so recoveries are likely to be between 19.3% and 36.5%. Recovery rates were also found to be dependent on fibre type, as acrylic showed significantly higher recovery rates than other types of fibre used (cotton, wool, rayon, polypropylene (PP), polyethylene terephthalate (PET)). Correcting for the effects of polymer type on recovery is difficult, as such a wide range of polymers are used and hence quantifying the recovery rates of all types would be a mammoth task. Only three synthetic fibres were tested (acrylic, PP, PET) in the Birkenhead *et al.* (2020) study, and the polymers identified in this chapter included other common polymers such as polyethylene and poly (vinyl alcohol); and so a correction factor for each polymer type (dependent on salinity) is not possible with the time and resources available. Only virgin microfibres were tested by Birkenhead *et al.* (2020). Fibres in the environment are likely to be altered by processes such as biofouling and weathering, which may have further effects on their sampling by the glass plate method. Exact recovery rates of this method in the field would be very difficult to calculate, but an assumption can be made based on the results of Birkenhead *et al.* (2020) that less than 100% of the microplastics in the SML are sampled using the glass plate method. Using the average recovery of 36.5% suggests that approximately 2/3 of the microplastics in the SML in any given location are

not sampled, and so the stated values here should be revised upwards, by approximately three times, to reduce this underestimation. It is important to note that previous studies comparing SML sampling methods (Anderson *et al*., 2018) show that the glass plate method showed the highest abundances of four sampling methods trialled in the same location, which was why this method was utilised. Recovery using this method is sufficiently consistent to allow comparison of differences at or between sampling locations. When comparing data across river-estuarine transects, or similar, salinity should be monitored in order to be able to account for salinity-induced differences in sampling recovery (Birkenhead *et al*., 2020).

Spectroscopic identification is one method of reducing overestimation of misidentified microplastics. Definitively identifying particles as synthetic or natural will reduce or mitigate the effects of visual misidentification of natural particles as microplastics. However, using a technique that doesn't include scanning of the filter (or a portion of it), and instead choosing particles to test will not reduce underestimation by the misidentification of microplastics as natural particles. Often, only a subsample of samples can be subject to spectroscopic analysis (Frère *et al*., 2017), as was the case here, and therefore assumptions about how to apply the results from this subsample to the whole sample are required. Yet the percentage of the sample positively identified as a polymer within the tested samples in this chapter ranges from 6.3% to 47.4%. Does an average calculated for these samples hold across the whole dataset? This is uncertain and could lead to over- or under-estimation of the microplastics abundance. Additionally, a large percentage of the tested particles were unable to be identified, typically because they did not meet the required hit quality, or because they still retained a coating of oil from the OEP. This ranged from 15.0% to 57.1% - in 2/16 samples, unidentified particles made up half of the tested particles. This is a better ratio than some other studies, including one in the same location (Gallagher *et al*., 2016), although worse than others (e.g., the 100% identification rate reported by Abidli *et al.* (2018)). The percentage of particles successfully identified is likely dependent on a number of factors, including: the number of particles tested, the processing methods used to reduce non-plastic particles within the sample including organic matter, the size of the particles, the shape of the particles and how weathered the particles are. The makeup of this unidentified portion of particles may or may not follow the same ratio as the rest of the sample, but this is another assumption that may lead to over or under estimation of the microplastics abundance. If a correction percentage was averaged from the 16 environmental samples and included the unidentified portion, then 27.5% of particles are assumed to be synthetic; but if these are removed, then 39.6% of particles are assumed to be synthetic.

The FTIR analysis process also introduced another element of contamination. A total of 812 particles (averaged from three visual counts of reprocessed filters) were expected to be subjected

to FTIR analysis. In reality, 1746 particles were tested using the FTIR. This is 215% of the expected particles to be analysed, and represents a significant uncertainty. A portion of this is likely to be a result of contamination, during the re-processing, mounting, and testing process. Whilst this was carried out in a laminar flow (re-processing, mounting) with appropriate precautions taken, the laboratory is also used for other purposes, and full contamination prevention measures – such as the wearing of only natural clothing, or the use of only non-plastic materials within the laminar flow and laboratory space – were not possible. Colourless fibres had previously been identified as a significant contaminant in blank (procedural and airborne) samples, and this proved the same case for the FTIR analysis. A total of 122 colourless fibres were identified visually in the tested samples, but a total of 1143 colourless fibres were tested using FTIR, an increase of 937%. Some of this may be due to an increased ability to identify colourless fibres at a higher magnification, with reduced sediment in the sample. However, given that samples were re-processed in the same environment as the initial filtration, which identified colourless fibres at large quantities in the blank samples; it is likely that a large portion of these fibres are a result of contamination. It may be the case that contamination was a result of natural fibres from, for example, the cotton laboratory coat worn during re-processing. This is supported by 79% of particles on the blank filters that were positively identified being identified as of natural origin; and 70.36% of colourless fibres that were positively identified being identified as of natural origin (compared to 55.21% of other particles being natural). A schematic of these sources of under- and overestimations of microplastic abundance is shown below (Figure 3-5).

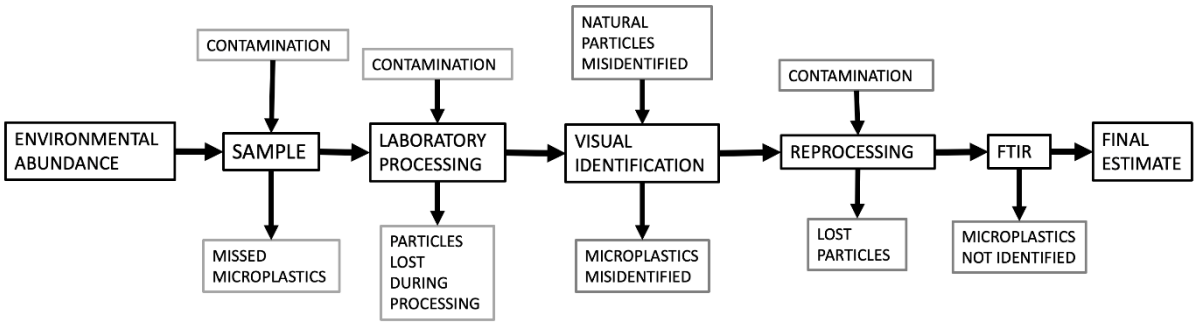

Figure 3-5 A schematic diagram of sources of uncertainties in enumerating microplastics in environmental samples

Of the remaining discrepancy among non-colourless fibres (and non-orange fragments, as orange fragments were previously identified as being the result of contamination from a known source), some is likely to result from the differing magnifications possible between the stereoscopic microscope used for visual identification (which was carried out at x60 magnification), and the FTIR microscope (which was calculated to have a x100 magnification). Visual identification using a

stereomicroscope has been reported as only being useful for particles >500 µm (Renner *et al*., 2018), whereas the FTIR microscope allowed identification of particles down to 25 µm (due to the size of the filter used for the FTIR), and particles smaller than the crystal of the FTIR may be unable to be analysed (Xu *et al*., 2019). In addition to identifying more particles at a greater magnification; a large percentage of the particles are likely to exist in this size range. Studies have shown that microplastic abundance can increase with decreasing particle size (Eriksen *et al*., 2014) and so it should be expected that more particles are observed using FTIR than were under the stereomicroscope. However, a decrease in the number of particles observed using visual methods, and those identified by visual methods during FTIR analysis was found (668 compared to 596). This is likely the result of losses of particles during re-processing, either by way of sticking to the glassware, or through particles being retained within the lower, water fraction of the OEP and being discarded. Therefore, this could have led to an underestimation of microplastics within the samples.

In summary:

$$\begin{aligned} &true\ number\ of\ microplastics\ in\ sample \\ &\quad = [\%\ sampled * correction\ factor\ for\ non-synthetic\ particles] \\ &\quad - contamination + losses\ during\ sampling\ and\ processing \\ &\quad + nonindentification\ of\ plastics\ during\ visual\ identification \end{aligned}$$

In short, despite taking a variety of measures to reduce uncertainty, there are a number of 'partially-known unknowns' surrounding the results. Whilst a correction has been applied, and it is unlikely that the true value is order of magnitudes different, it could be argued that it is more appropriate to use a range of abundances. These abundance ranges are shown in Appendix A. Applying the lowest positive polymer ID along with the highest blank correction values gives a low bound; and applying the highest positive polymer (and additive) identification rate, assuming the unidentified portion follows the same ratio as the identified particles, together with the lowest blank correction values gives a high bound. For the results discussed below, an average (mean) of the blank corrections and FTIR corrections has been used.

3.3 Results

Statistical analysis was carried out using the statistic software R (4.0.0) using the platform R Studio (1.2.5042). When carrying out statistical analyses, a significance level of 95% was used throughout. All variables were non-normal, as tested by Shapiro-Wilk's tests. Log transformations were carried out, which only normalised three of eleven variables: the bulk microplastic

abundance, wind speed and the enrichment ratio. As a result of the non-normality of the variables, non-parametric tests were used throughout.

3.3.1 Microplastic Abundance, Comparison of SML and Bulk, Comparison of Sites

Mean abundance across both sites, and the whole year was 37.4 microplastics/L in the SML, and 9.3 microplastics/L in the bulk water samples. At SWAC, the SML contained an average 46.4 microplastics/L, and the bulk samples contained an average of 10.2 microplastics/L. At Mayflower Park, the SML contained an average 26.2 microplastics/L, with the bulk containing an average 8.4 microplastics/L.

Abundance in the SML and bulk was compared, for each sample. In Figure 3-6, a line has been drawn at y = x. Above this line, microplastics were more abundant in the bulk water sample, and below this line, microplastics were more abundant in the SML. The majority of samples had a greater abundance in the SML than the bulk, as shown by a Mann Whitney U test (W = 1312.5, p = 1.109×10^{14}). The relationship between the two samples was statistically examined using a Spearman's rank correlation test, which showed that there was no correlation between samples taken at the same time and place (Spearman's rho = -0.05132134, p = 0.645). This was shown in all samples, and when the samples were split by site.

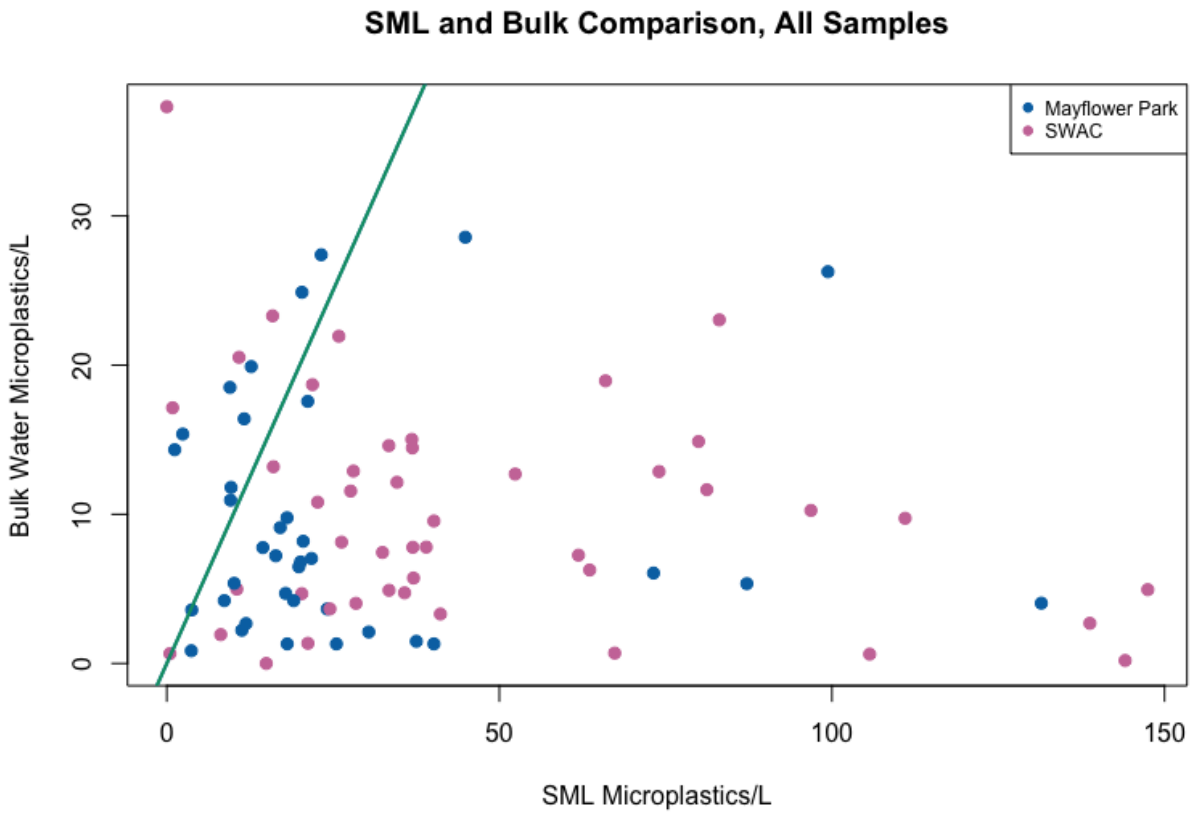

Figure 3-6 A comparison of microplastic abundance obtained from the two sampling methods used

The line is fitted to y = x, or where abundances are equivalent in the bulk water and SML samples.

To further examine the relationship between the SML and underlying water, an enrichment factor was calculated, which is the ratio between the bulk and the SML abundance. A value between 0 and 1 indicated that there were more microplastics in the SML water sample, and a value above 1 indicated that there were more microplastics in the bulk than the SML. The enrichment factor varies between 0.05 and 719.83. Environmental factors and their relationship with the enrichment factor are discussed later in these results.

Differences between the sites (Figure 3-7) were assessed using a Mann Whitney U test. Significant differences were seen in the SML (W = 1219, p = 0.0006189), but not in the bulk water samples (W = 1344, p = 0.1605).

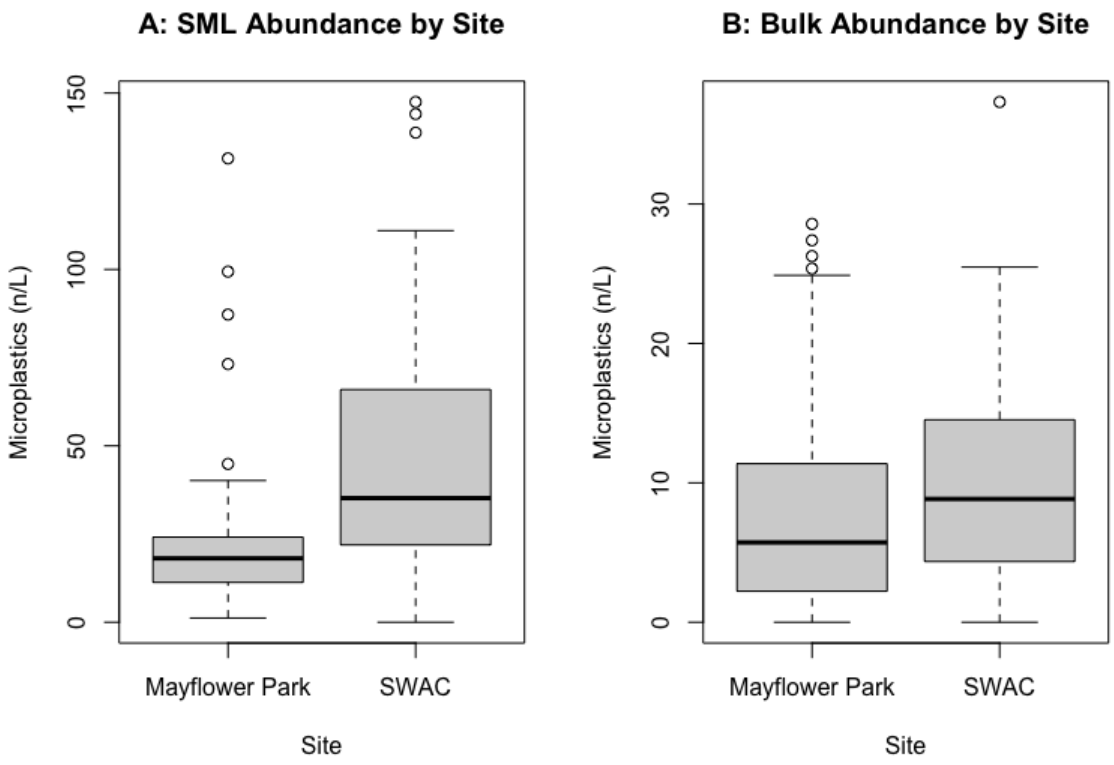

Figure 3-7 Site comparison of microplastic abundance. A: SML, B: bulk water

Whiskers show the maximum and minimum values; the box shows the first and third quartile; and the line shows the median value.

3.3.2 Environmental Variables

Rainfall data are presented in mm/day, and both day of sampling and day prior to sampling were recorded. For rainfall on the day of sampling, autumn showed the highest rainfall, and spring showed the driest season, with a highest value of 2 mm/day. Seasonal differences were seen in rainfall (Kruskal-Wallis chi squared = 12.754, p = 0.005201), but *post hoc* testing (Dunn Test) showed that the only significant differences were seen between autumn and spring. Antecedent rainfall also showed significant seasonal differences (Kruskal-Wallis chi squared = 19.408, p = 0.0002251), with autumn being significantly different from spring and summer. River flow showed significant seasonal differences, (Kruskal-Wallis chi squared = 40.389, $p = 8.814 \times 10^{9}$), with significant differences seen between autumn and spring/summer, and winter and spring/summer.

In graphical form, no trends were seen between rainfall, and river flow. Spearman's rank correlation showed a small but significant correlation between antecedent rainfall and river flow (Spearman's rho = 0.3222628, p = 0.0255), but no significant correlation between rainfall on the day of sampling and river flow. This lag between rainfall and river flow is logical given rainfall may be temporarily stored within the catchment and takes time to flow overland or through CSOs to

the river, and considering that the Itchen is a mostly groundwater-fed river (Giles *et al*., 1988), the small size of the correlation is also to be expected. No correlation was seen between rainfall and salinity.

Tidal conditions were assessed in a number of ways. Tidal height at time of sampling was recorded to the nearest five minutes. As expected, because the same sampling time (13:00, 13:30) was used every sampling day over the course of a month for each season, the same range of tidal heights is seen in each season. Tidal state was also recorded, and did not show any trends with salinity, for either site or both combined. Tidal height did not show any relationship with suspended sediment concentration, although the highest suspended sediment concentrations were associated with the lowest tidal heights, which fits with field observations of increased sediment resuspension due to a change in substrate at the low tide line (from gravel to mud) at both sites. A Spearman's rank correlation showed a significant, but small correlation (Spearman's rho = -0.2140324, p = 0.04163) between SSC and tide height. When the data were split by site, no correlation was seen between the suspended sediment concentration and tide height at SWAC, so this correlation is driven by the correlation observed at Mayflower Park (Spearman's rho = -0.403487212, p = 0.005428).

At SWAC, there was a significant correlation observed between salinity and tidal height (Spearman's rho = 0.6634695, p = 6.795e-07), though no significant differences were seen between the differing tidal states or cycles when tested with Kruskal-Wallis. Salinity at SWAC ranged between 15.5 and 32.4; and at Mayflower Park, ranged between 19.1 and 32.5. At Mayflower Park, no such correlation was seen between salinity and tidal height. A correlation between salinity and tidal height is to be expected, with higher salinity ocean water being moved into the estuary by the incoming tide. At lower tides, when there is less of this higher salinity water mixed into the estuary, salinity would be lower. That there is only a correlation seen at SWAC may be due to the more freshwater influence seen here (from the River Itchen), and the potentially greater mixing seen at Mayflower Park, which is more open than SWAC and further from riverine inputs.

Average wind speed per day showed that the prevailing wind direction in Southampton Water during the course of sampling was south-westerly (which agrees with the overall prevailing wind direction (Croudace and Cundy, 1995)) (Figure 3-8). The majority of wind speeds recorded were less than 13 knots, or no more than a moderate breeze, and maximum average wind speed per day was 26.4 knots, equivalent to a strong breeze (Met Office, 2021).

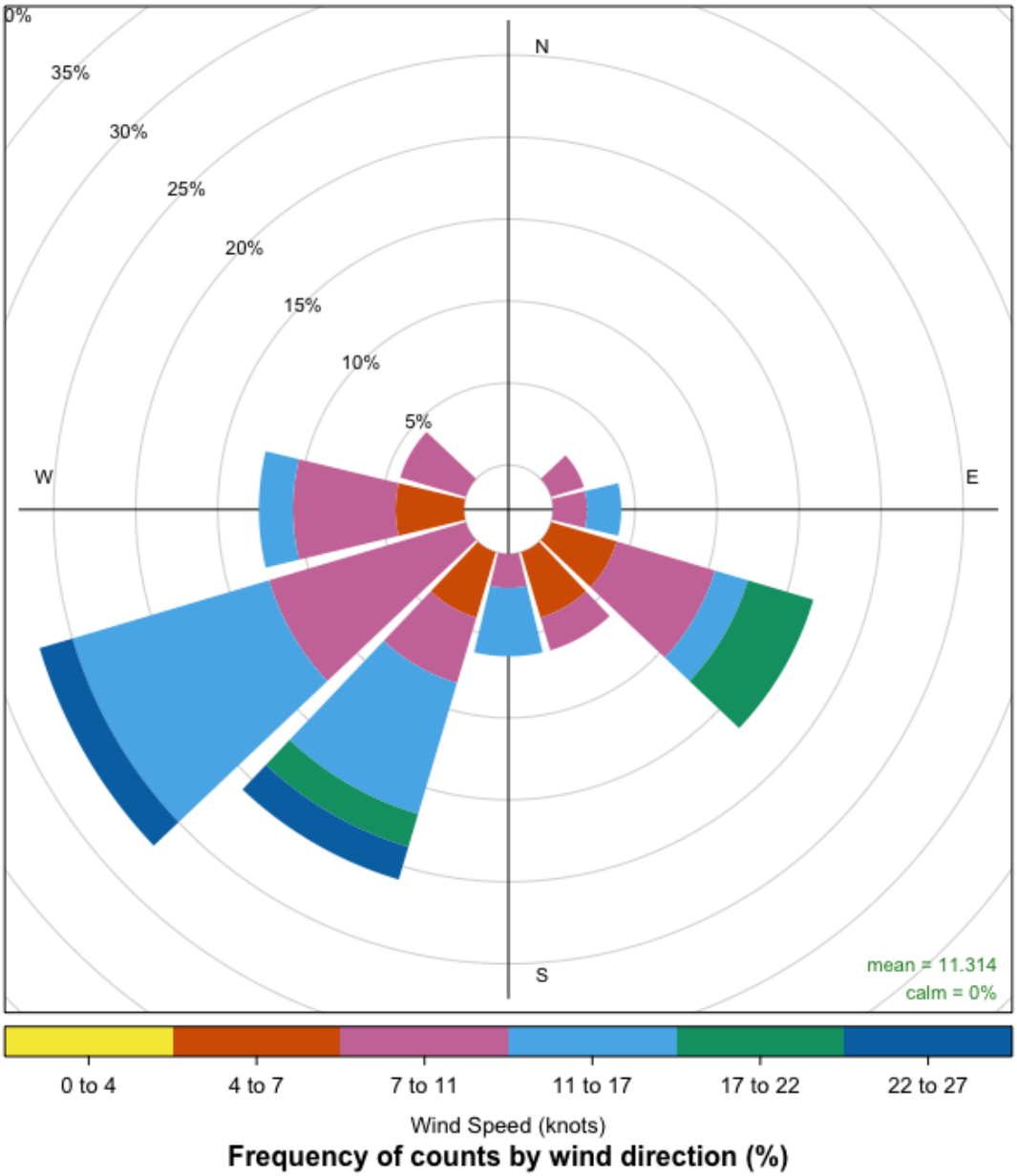

Figure 3-8 Daily average wind speed and direction for all sampling days

Data recorded at Dock Head, Southampton (data source: Sotonmet). Divisions are made to fit the Beaufort Scale.

3.3.3 Comparison of Environmental Variables to Microplastic Abundance

Site comparisons were made first, and where possible, environmental factors were considered with both sites combined, and within each site separately. Mann-Whitney U tests showed a significant difference in microplastic abundance (w = 483, p = 0.0006189) for the SML between sites, but no significant difference for the bulk water samples (w = 960, p = 0.1605). For the SML, SWAC had the greater mean abundance (46.4 microplastics/L as compared to Mayflower Park, 26.2 microplastics/L).

Comparisons were made between microplastic abundance and the measured environmental variables. First, seasonal comparisons were made (Figure 3-9). A Kruskal-Wallis test was carried out, and the SML showed significant differences in microplastic abundance between months (Figure 3-9 A) (Kruskal-Wallis chi squared = 29.749, *p* = 1.558e-06), as did the bulk (Figure 3-9 B) (Kruskal-Wallis chi squared = 21.694, *p* = 7.552e-05). Post-hoc testing using the Dunn Test showed that for the SML, summer (August) was significantly different to the other three seasons, which did not show any differences between them. For the bulk, the Dunn Test showed that only spring and winter were significantly different, and no other comparisons were significant.

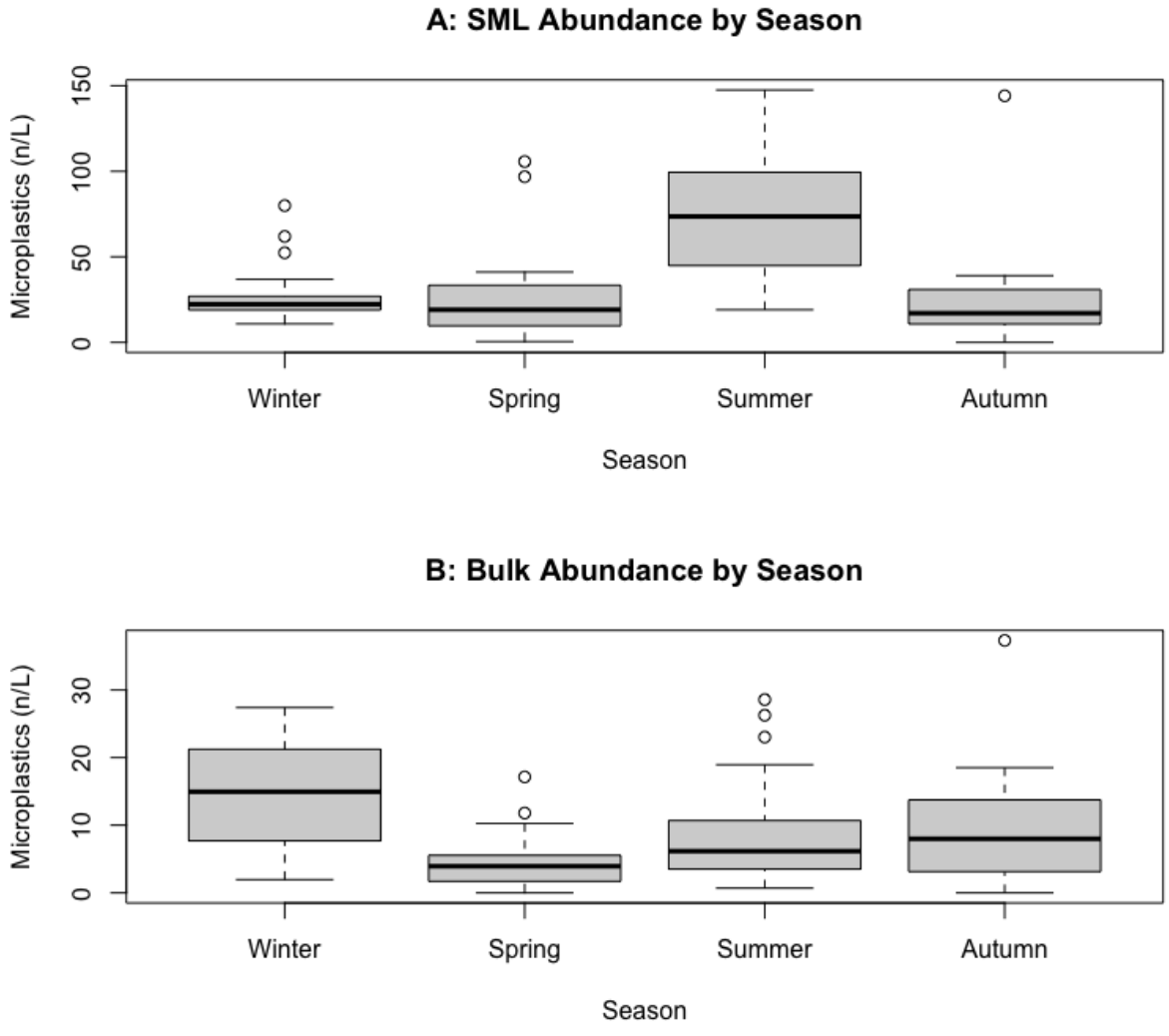

Figure 3-9 Seasonal comparisons of microplastic abundance. A: SML, B: bulk water

Whiskers show the maximum and minimum values; the box shows the first and third quartile; and the line shows the median value.

Spearman's rank correlations were carried out with the environmental variables, or Kruskal-Wallis tests were carried out, dependent on the type of data. For both sites combined, no correlations

were seen between the SML with any of: salinity, rainfall (day of/antecedent), tide height, suspended sediment concentration, wind speed or wind direction. For the bulk samples at both sites combined, the only correlation seen was between the bulk abundance and tide height (p = 0.04412, Spearman's rho = 0.2115484).

When the data were split by site, seasonal differences were observed in the SML and the bulk at SWAC. For the SML, a post-hoc Dunn test showed that significant differences were seen between spring and summer, and autumn and summer; and for the bulk, the only significant differences were seen between spring and winter. At SWAC, correlations were seen between the SML abundance and salinity and river flow (salinity: p = 0.0104, Spearman's rho = -0.3742481; river flow: p = 0.01053, Spearman's rho = -0.3755165); and between the bulk abundance and tidal height (p = 0.04109, Spearman's rho = 0.3057614). Differences in abundance in both the SML and bulk between the various tidal states and cycles, and with dredging, were assessed using Kruskal-Wallis, with no significant differences seen between groups.

At Mayflower Park seasonal differences were observed in the SML and the bulk. For the SML, a post hoc Dunn test showed that significant differences were seen between summer and autumn and spring. These are the same differences seen at SWAC, which is an observation repeated for the bulk water, where the only significant difference was observed between spring and winter. Negative correlations were seen between daily average wind speed and abundance in the SML; and between abundance in the bulk water samples and wind direction at the time of sampling.

Table 3-1 Summary of statistical results between microplastic abundances and measured environmental variables.

Note that grey squares are where no statistical correlation was found; and black squares are for where no statistical tests were carried out as this was not a testable relationship.

Environmental Variables	**Statistical Method**	**SWAC SML**	**SWAC Bulk**	**Mayflower Park SML**	**Mayflower Park Bulk**
Seasons	Kruskal-Wallis	p = 0.001459	p = 0.004388	p = 0.0006614	p = 0.02501
Rainfall (day of)	Spearman's Rank Correlation	Not significant	Not significant	Not significant	Not significant

Environmental Variables	Statistical Method	SWAC SML	SWAC Bulk	Mayflower Park SML	Mayflower Park Bulk
Rainfall (antecedent)	Spearman's Rank Correlation	Not significant	Not significant	Not significant	Not significant
Tide height	Spearman's Rank Correlation	Not significant	$p = 0.04109$ $\rho = 0.3057614$	Not significant	Not significant
Ebb/flood	Kruskal-Wallis	Not significant	Not significant	Not significant	Not significant
Spring/neap	Kruskal-Wallis	Not significant	Not significant	Not significant	Not significant
Wind speed (time of)	Spearman's Rank Correlation	Not significant	Not significant	Not significant	Not significant
Wind speed (daily average)	Spearman's Rank Correlation	Not significant	Not significant	$p = 0.0207$ $\rho = -0.3807492$	Not significant
Wind direction (time of)	Spearman's Rank Correlation	Not significant	Not significant	Not significant	$p = 0.01852$ $\rho = -0.34597$
Wind direction (daily average)	Spearman's Rank Correlation	Not significant	Not significant	Not significant	Not significant
River flow	Spearman's Rank Correlation	$p = 0.01053$ $\rho = -0.3755165$	Not significant	Not applicable	Not applicable
Dredging	Kruskal-Wallis	Not significant	Not significant	Not significant	Not significant
SSC	Spearman's Rank Correlation	Not significant	Not significant	Not significant	Not significant

Environmental Variables	Statistical Method	SWAC SML	SWAC Bulk	Mayflower Park SML	Mayflower Park Bulk
Salinity	Spearman's Rank Correlation	p = 0.01404 ρ = 0.3742481	Not significant	Not significant	Not significant

3.3.4 Comparison to the Enrichment Factor

Of 81 samples where an SML and a bulk sample were taken, the abundance in the bulk water was greater than the SML on 12 occasions (14.81%). Two-thirds of these occasions were recorded at Mayflower Park, although the enrichment factor did not differ significantly between sites. There was a significant seasonal difference seen. Post-hoc testing (Dunn test) showed that summer differed significantly from autumn and winter. No correlations were seen between the enrichment factor and environmental variables.

When data were limited to samples taken at SWAC, the only correlation seen with environmental data was a significant seasonal difference (Kruskal-Wallis chi squared = 0.2588, p = 0.02604). Post-hoc testing using the Dunn test showed that the only significant difference in the enrichment ratio was seen between summer and winter.

When data were limited to samples taken at Mayflower Park, a seasonal difference was seen again (Kruskal-Wallis chi squared = 12.054, p = 0.0072). Post-hoc testing (Dunn test) showed that significant differences were seen between summer and winter, and summer and autumn. At Mayflower Park, there were significant differences in the enrichment factor between tidal cycles – with the spring tide being significantly different from the mid-tide samples, but no other differences between groups. The enrichment factor for samples taken in Mayflower Park showed a correlation with the daily average wind direction (p = 0.04809, Spearman's rho = -0.327167).

3.3.5 Polymer Analysis

A number of polymers were identified across the samples. A greater number of different types of polymer were identified in the SML samples compared to the bulk samples, but a similar range of polymers were identified when comparing sites. Vinyl chloride, for example, was only identified in bulk water samples, with HDPE, polypropylene + vistalon, and polyisoprene only identified in SML samples.

3.4 Discussion

The SML had an average abundance of 37.4 microplastics/L, and the bulk water samples had an average of 9.3 microplastics/L. Two previous studies have been carried out in Southampton Water, one using the same method for the SML as was used in this thesis. Anderson *et al.* (2018) sampled in the River Hamble estuary using the glass plate method, and recorded an average abundance of 53.8 microplastics/L. This is of the same order of magnitude as the SML samples taken at SWAC and Mayflower Park, and at Hythe (Chapter 4), and indicates a low and fairly consistent abundance of microplastics across Southampton Water. It is not possible to compare abundances observed in this study to the other study which has sampled Southampton Water (including the main channel and the Itchen), as Gallagher *et al* (2016) only report abundances in terms of the number of particles per trawl. However, comparisons can be made within that study, given a few assumptions. Assuming similar trawl properties between their trawls (length, speed, amount of water filtered), Gallagher *et al.* (2016) observed a higher quantity of microplastics in the Itchen than in the main channel of Southampton Water. Over the course of the year, a greater abundance of microplastics in the SML was observed at SWAC, which is on the shore of the River Itchen, compared to Mayflower Park, where the main channel of Southampton Water was sampled. While the FTIR analysis in Gallagher *et al*. (2016) was much more limited than in this chapter, three polymers were identified. Polyethylene was identified in Southampton Water and the River Itchen by Gallagher *et al.* (2016), and also at SWAC and Mayflower Park. Polypropylene was previously identified in Southampton Water, although further towards the upper docks than Mayflower Park – and in this chapter at both SWAC and Mayflower Park. Likewise, cellophane was identified in the lower reaches of Southampton Water and at both SWAC and Mayflower Park. This study had a higher threshold for positive ID of particles with FTIR, but achieved a higher positive ID rate than Gallagher *et al.* (2016).

Comparison to other UK estuaries is complicated again by the use of different units and methods, as well as by the differences in estuarine hydrometry. Southampton Water is unique in the UK in having a double-high water with an extended high water period, and therefore a longer period where the intertidal is flooded, and tidal currents are low compared to other estuaries. Sediment sampling in UK estuaries appears to be more commonly used to assess microplastic contamination than water, or biota sampling, but two studies have looked at microplastics abundance in UK estuaries outside of Southampton Water. The River Thames is tidally influenced until Teddington Lock, upstream of the two sampling locations (Putney and Greenwich) used by Rowley *et al.* (2020). They found an average of 19.5 microplastics/m^3, but excluded microfibres from their analysis due to contamination. When converted to microplastics/L, 0.000195 microplastics/L, it is significantly lower than the abundances observed here, as compared to a

bulk water average of 9.3 microplastics/L (as this is more appropriate for comparison with the net trawl methods used by Rowley *et al.* (2020) than the SML-specific sampling method). While some of this difference may be due to the exclusion of microfibres in Rowley *et al*. (2020), or the inclusion of microfibres in this chapter, Southampton Water appears to have a greater abundance of microplastics than the Thames. Removing microfibres from the averages, gives a bulk water average of 3.1 microplastic fragments/L, still several orders of magnitude greater than the Thames. Sadri and Thompson (2014) sampled the Tamar estuary, finding a mean abundance of 0.028 microplastics/m^3 (converted to 0.0000028). Again, this is far lower than the abundances observed here. Differences in methods could account for some of this difference, as both Sadri and Thompson (2014) and Rowley *et al.* (2020) used net trawls to sample, which could have missed a portion of microplastics. Bulk sampling is not size selective, whereas 250 µm and 300 µm nets were used by Rowley *et al.* (2020) and Sadri and Thompson (2014) respectively, and nets will not sample an unknown but likely large proportion of the plastics smaller than their mesh size.

Globally, a number of estuaries have been sampled for microplastics in the water column, but only a few in the SML specifically. These are: Southampton Water (in this study, and in Anderson *et al.* (2018), and two estuaries in South Carolina (USA), which are Winyah Bay and Charleston Harbour (both in Gray *et al.* (2018), and Charleston Harbour only in Leads and Weinstein (2019)). Both Gray *et al.* (2018) and Leads and Weinstein (2019) used a different sampling method (metal mesh screen). These two estuaries showed a very similar – in the case of Winyah Bay in particular – abundance of microplastics in the SML. Average in the SML in Southampton Water was 37.4 microplastics/L, and in Winyah Bay it was 30.8 particles/L (Gray *et al*., 2018). These two studies use different SML sampling and sample processing methods, so although they appear to have very similar microplastic contamination levels, it is likely that this is not the case, supporting calls from the literature to standardise methods in microplastic research. Charleston Harbour was also sampled in terms of abundance in the SML by Leads and Weinstein (2019), who found a similar range of abundances to Gray *et al.* (2018) – from 3 – 36 microplastics/L, which was at the lower range of the abundances seen in Southampton Water in this chapter – which ranged from 0 to 147.5 microplastics/L.

Table 3-2 SML-specific studies in estuaries worldwide

Study	**Location**	**Method**	**Average**	**Range**	**# of samples**	**ID methods**
Anderson *et al.* (2018)	Southampton Water, UK	Glass Plate	53.8 MPs/L	26.3 – 93 MPs/L	Three samples	Visual, SEM

Study	**Location**	**Method**	**Average**	**Range**	**# of samples**	**ID methods**
Gray *et al.* (2018)	Winyah Bay & Charleston Harbour, SC, USA	Stainless steel mesh screen	CH: 6.6 MPs/L WB: 30.8 MPs/L	CH: 3 – 11 MPs/L WB: 6 – 88 MPs/L	Six sites, 1 sample per site	Visual, FTIR (on non-SML samples in same study)
Leads and Weinstein (2019)	Charleston Harbour Tributaries, SC, USA	Stainless steel mesh screen	10.98 MPs/L	3 – 36 MPs/L	Multiple sites per river, multiple replicates per site	Visual, hot needle test, FTIR
Stead *et al.* (2020) Chapter 4	Southampton Water, UK	Glass Plate	76.5 MPs/L (mean)	10.9 – 234.1 MPs/L	One site, multiple samples	Visual, FTIR
Present Chapter	Southampton Water, UK	Glass Plate	37.4 MPs/L (mean)	0 – 147.5 MPs/L	Two sites, multiple replicates per site	Visual, FTIR

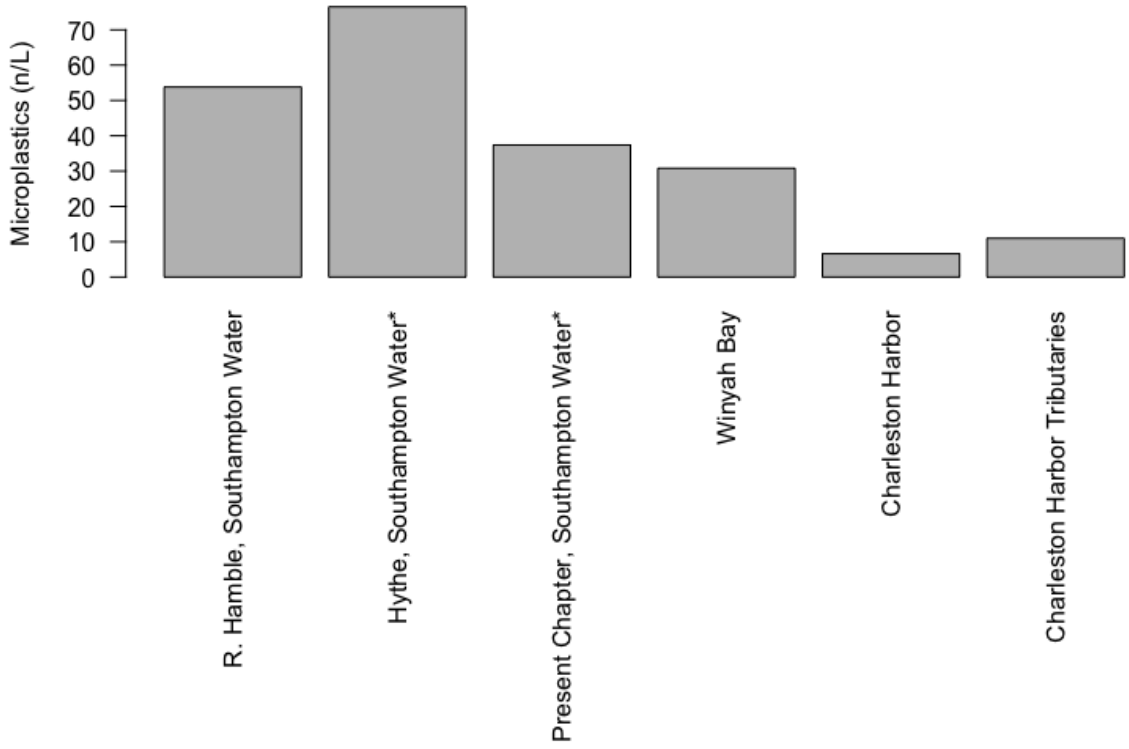

Figure 3-10 Average microplastic abundance in the SML of estuaries worldwide

(*value from work in this thesis, data from Table 3-2)

Bulk/grab samples are commonly used to sample estuarine waters for microplastics, although trawls using a variety of mesh sizes are more often utilised. Bulk samples can be compared relatively directly to the bulk samples here, and for the most part, are lower or the same magnitude than the abundances observed here. An average of 0.94 particles/L were observed by McEachern *et al.* (2019) in Tampa Bay (FL, USA), with a range of up to 7 particles/L. When converting from particles/m^3 to particles/L to enable comparison here, studies in China (1.485 particles/L, (Wu *et al*., 2020); 8.902 particles/L, (Yan *et al*., 2019)) and Argentina (0.139 particles/m^3, (Pazos *et al*., 2018)) all showed a lower abundance than this study. However, one study in California (USA) found an abundance of 641.292 particles/L (Wiggin and Holland, 2019), using grab samples taken in a number of rivers and coastal locations around Long Beach. This comparison suggests that Southampton Water is a moderately contaminated estuary, which fits with a general assessment of its characteristics: it is heavily populated with a large industrial sector, but has a relatively effective municipal waste collection service and local laws restricting, for example, the disposal of industrial waste. Southampton Water is also a macrotidal, ebb-dominated estuary, with a relatively rapid flushing time of 5-10 days (Sharples (2000); Chapter 2) – this rapid flushing of the estuary will move microplastics out of Southampton Water and into the Solent, English Channel and beyond, and decreasing the abundance found within Southampton Water itself.

A number of environmental variables were recorded for each of the sampling days, covering both meteorological and hydrological conditions experienced in Southampton Water. Clear seasonal trends in some of these variables were expected and observed – for example, rainfall – and not expected or seen in others – for example, tides. Unlike some locations that have been previously sampled for seasonal variations in microplastics, Southampton Water does not experience large seasonal variations in climate, with only small differences in total rainfall per month that were not statistically significantly different. A location such as the Atrato Delta in Colombia has an average rainfall of 250 mm/month in the wet season, and 100 mm/month in the dry (Correa-Herrera *et al*., 2017). This is far greater difference between seasons than is observed in Southampton, and may be why very pronounced seasonal differences are not observed in the data presented here. However, seasonal differences were seen in microplastics abundance in the SML and the bulk in Southampton Water. Samples taken in summer (August) showed a significantly greater microplastics abundance in the SML compared to other months, which were not significantly different from each other. However, this increase in summer does not seem to be explained by the measured environmental variables. Rainfall showed seasonal differences, but between spring and autumn; and no correlation was seen between antecedent rainfall or rainfall on the day of sampling and microplastic abundance in the SML. There were no significant seasonal differences in wind speed or direction. Therefore, despite other studies showing links between rainfall and microplastic abundance in other locations, this was not observed in Southampton Water. The increase in microplastics seen in the summer might be linked to increased leisure activity in Southampton Water, including increased use of the SWAC site. Alternately, the summer increase seen in the SML may be linked to annual tidal variations. The highest spring tides are observed at the spring and autumn equinoxes, which for 2019 fell on the 20th March and 23rd September. At these points, the sun and moon are directly over the equator, and cause an increased spring tide range. This increased tidal range and accompanying tidal flows may explain the increased abundance in the SML seen in summer (August, the closest month to the autumn equinox). However, a corresponding increased abundance is not seen in winter (February) associated with the spring equinox, and nor is this seasonal trend seen in the bulk water samples.

Some correlations were seen between the abundance of microplastics and the enrichment factor, and wind speed and direction. These were only seen at Mayflower Park, which was the more exposed site. SML abundance was negatively correlated with the average daily wind speed, which fits well with an interpretation of increased wind mixing breaking up the SML and mixing microplastics downwards. Wind direction at the time of sampling was also correlated to the bulk abundance, with a weak negative correlation. The beach at Mayflower Park is orientated from SW to NW, with the derelict Royal Pier orientated approximately S-SW, the Park itself is North of the

beach, and the Isle of Wight ferry and associated infrastructure is to the west of the beach. Lower microplastic abundances in the bulk water are associated with winds blowing onto the beach. This could be due to a number of reasons, including increased mixing of microplastic to below the sampling depth (5 cm) or winds blowing debris from the beach back into the water (the beach on a majority of occasions had visible plastic debris across the shore and within the debris line). The ratio between the SML and bulk abundances also showed a negative correlation with the daily wind direction at Mayflower Park. The ratio was lower than 1 when abundances were highest in the SML, and above 1 when abundances were highest in the bulk water. Samples for which the highest abundances were seen in the bulk water were associated with winds blowing from behind the beach, over the Pier. Samples for which the SML showed a higher abundance than the bulk were associated with winds blowing onto the beach from Southampton Water. The correlation is weak, and may be related to the variations in wind speed with wind direction, as shown in the wind rose. Additional work investigating the relationship between microplastics in the SML and underlying water column is necessary.

While rainfall and river flow were recorded variables, no data were obtained for the amount of water discharged into Southampton Water and the River Itchen through Combined Sewer Overflows (CSOs). CSOs are a proposed source of microplastics, as they discharge untreated water into water bodies during high rainfall events, when sewer systems are unable to cope with the volume of water entering them (Southern Water, 2021b). While discharges of stormwater during high rainfall events are regulated ("Guidance: Water companies: environmental permits for storm overflows and emergency overflows," 2018), they are not treated, and any plastic debris present, for example, as litter or road debris, may be washed into CSOs and from there, into the estuary. WWTWs can remove 95%+ of microplastics entering them (e.g., 97.6% removal was observed in one WWTW by Conley *et al.* (2019), but as CSOs can discharge untreated (bar the removal of large debris by screens) water during high flow events, they are considered a likely source of microplastics. Investigating the role of CSOs in microplastic inputs to river, estuaries and the coastal environment is difficult, due to the difficulties of sampling storm events, but is a source of microplastics that needs to be better understood, as it could lead to better regulation and laws around outputs from CSOs.

At SWAC, which is the site located at the mouth of the River Itchen, correlations were seen between microplastic abundance in the SML, and salinity and river flow. These correlations were not seen in the bulk, nor at Mayflower Park. As a result, it can be hypothesised that the SML abundance is influenced by river flow, or by tidal influence on the River Itchen. Both correlations were negative (although relatively weak, -0.37 and -0.31 respectively), so as salinity increases, microplastic abundance decreases; and as river flow increases, microplastic abundance decreases.

This is perhaps unexpected, as while river flow has rarely been investigated for links to microplastic abundance, some work has shown that increased rainfall flushing a tropical estuary was associated to microplastic distribution within that estuary (Lima *et al*., 2015). This has significant implications, as modelling studies such as those by Lebreton *et al.* (2017) and Schmidt, Krauth and Wagner (2017) use river discharge as a determining factor for microplastic output from rivers. From the observed abundances and trends, it may be proposed that the River Itchen has a lower abundance of microplastics than Southampton Water and increased river flow dilutes the microplastic abundance. This is supported by the negative correlation seen between salinity and microplastic abundance, although no correlations were seen at SWAC between river flow and salinity. Additionally, a positive correlation was found between tidal height and abundance in the bulk water – suggesting that as the tide enters, it brings with it an increased abundance of microplastics. That no such correlation was seen at Mayflower Park, however, suggests that this trend is locally specific to the River Itchen. These correlations were also not seen in the bulk water samples, despite these being taken at the same time and place as the SML samples. Therefore, the process linking microplastic abundance to salinity and tide height is limited to the SML. One hypothesis for this influence/correlation being seen in the SML only is that it may be limited to low-density polymers. Trials have shown that the glass plate technique recovers more of these low-density polymers (Birkenhead *et al*., 2020), and these low-density polymers are also more likely to occur in the SML as heavier polymers are more likely to sink out of the SML. A correlation was also seen between tide height, and abundance in the bulk water samples, with a weak correlation (Spearman's rho of 0.31) linking an increase in tidal height at the time of sampling to an increased microplastic abundance in the water column. This supports the hypothesis of microplastics being moved into this area by the incoming tide, although no significant differences were seen in abundance between the different states of the tide (e.g., between flood, ebb, and low and high water stand).

As discussed, seasonal variations in microplastic abundance were seen, at both SWAC and Mayflower Park. Summer was seen to be significantly different from both spring and autumn, and winter also when both sites were combined. It was hypothesised that winter would see the greatest abundances of microplastics, particularly microfibres, due to increased laundry during winter (it is hypothesised that this is because of increased clothing worn during the colder winter months; and also due to the increased population of Southampton during winter, as Southampton's large student population typically leaves Southampton during the summer months). However, this was not seen. However, particularly at SWAC, site usage increased during summer. While usage statistics were not recorded, summer schools were run every day during the summer sampling period, compared to autumn or winter, where only limited usage of the site

was observed. This could be why more microplastics were observed at SWAC during the summer, through the shedding of fibres from synthetic clothing used in water sports, but this does not explain Mayflower Park. Activity did increase at Mayflower Park during the summer, with more ferries leaving and more cruise ships, as well as more pedestrian visitors to the park; so perhaps increased boating and leisure activity in Southampton Water is the cause of this observed increase within the main body of Southampton Water in summer.

Southampton Water is known to be a partially mixed estuary, from previous studies investigating estuarine hydrodynamics (Sharples, 2000). The effects of the estuarine hydrodynamics on microplastic abundance can be seen in the limited correlation of environmental variables with microplastic abundance. The strong tidal currents (1 m/s recorded on spring ebb tides (Sharples, 2000) mean that, for example, if large amounts of microplastics are brought into Southampton Water through rivers, this water is rapidly mixed into the main body of Southampton Water, and does not remain a separate unit of low-salinity, high-microplastic water within the estuary. Southampton Water has a flushing time of approximately 10 days (Sharples, 2000), supporting a hypothesis of fairly rapid flushing of microplastics out of Southampton Water and into the Solent and beyond. The links to estuarine hydrometry seen in this study – that there are limited correlations and this may be the result of the partially-mixed nature of the estuary – support the views of Dris *et al.* (2020) that in order to fully understand microplastic abundances and trends in estuaries, a good understanding of the estuary's hydrodynamics is required.

Particularly at Mayflower Park, where the influence of rivers is minimal compared to SWAC, no correlations were seen between environmental variables and microplastic abundance. This supports that the individual inputs of microplastics to Southampton Water are masked by the hydrodynamics within Southampton Water, leading to a fairly consistent abundance of microplastics throughout the year.

The enrichment factor was calculated as a ratio between the abundance in the SML and abundance in the bulk. It was hypothesised that a relationship between these two variables would be seen, however, this was not the case. For the majority of samples (82%), the abundance in the SML was greater than that in the bulk. SML abundance was negatively correlated with wind speed at Mayflower Park, though no corresponding increase was seen in the bulk water samples, suggesting that any mixing of microplastics downwards from the SML by the wind occurs to a depth greater than 5 cm. Except for this, there seems to be no clear environmental variable driving the relationship between the SML and the bulk, and no clear drivers behind when abundance is greatest in the bulk compared to the SML.

3.5 Conclusions

Surface microlayer (SML) and bulk water sampling were employed to assess daily and seasonal variation in microplastics abundance at two locations in Southampton Water. A number of environmental variables were also recorded, and compared to microplastic abundance. Of the two sampling methods used, the SML-specific method recovered a significantly larger number of microplastics (SML average 37.4 microplastic/L, bulk average (9.3 microplastics/L, difference assessed by Kruskal-Wallis), and more clearly highlighted inter-site differences. In general, SML abundances were of the same magnitude as abundances recorded in Southampton Water and estuaries globally, though bulk water abundances were higher than a number of estuarine water studies globally. A wide range of abundances was seen, ranging from 0-147.5 microplastics/L in the SML, suggesting that repeated sampling of locations over a period of time under a range of meteorological and oceanographic (i.e., tidal) conditions is necessary to reflect the variation of abundances at any given site, and to enable an accurate assessment of microplastic abundance in the estuarine system.

Seasonal differences were observed using both methods, and at both sites, though differing trends were shown in the SML compared to the underlying water. For the SML, summer showed a significantly greater abundance of microplastics; and for the bulk, spring and winter were observed to be significantly different from one another with few other observable differences. Few correlations were seen between microplastic abundances and other environmental variables, which were mostly site-specific. No single variable appeared to be a driving factor determining microplastic abundance in Southampton Water. This supports previous (non-microplastic related) studies in Southampton Water which define it as a well-flushed, partially-mixed estuary.

Chapter 4 Intertidal Trapping

This chapter was published in part as (Stead *et al*., 2020), with corrected microplastic abundance values presented in this chapter.

4.1 Introduction

As previously discussed (1.3), the estuarine filter comprises a number of mechanisms, all of which act to moderate the supply of sediment, and dissolved, particle-associated and suspended contaminants, to the sea. These mechanisms act in two directions: i) to retain dissolved and suspended materials in estuarine systems and ii) to move them from and through estuarine systems out to coastal seas and potentially beyond to the open ocean. These modulating processes include those which lead to deposition in short-term or long-term sedimentary sinks within the estuary – specifically sub- and inter-tidal flats, beaches and intertidal wetlands.

A number of studies have been carried out investigating the abundance of microplastics within the sediments of estuaries, worldwide. Most of these focus on estuarine beaches, although some have also looked at wetlands, and estuarine bed sediments. Eight studies have looked at estuarine sandy beaches worldwide (Cheung *et al*., 2016; Clunies-Ross *et al*., 2016; de Carvalho and Baptista Neto, 2016; Fok and Cheung, 2015; Masiá *et al*., 2019; Naidoo *et al*., 2015; Piehl *et al*., 2019; Simon-Sánchez *et al*., 2019). These studies have shown a range of microplastic abundances, ranging from – though comparisons are difficult between microplastics/m^2 and microplastics/kg dw of sediment – a low of 3 particles/m^2 (minimum seen by de Carvalho and Baptista Neto (2016) in Guanabara Bay, Brazil) to 5595 items/m^2 (Pearl River Estuary, Hong Kong (Fok and Cheung, 2015)).

Compared to ocean coastal beaches, this is a very small number of studies. Ocean sandy beaches are frequently sampled for microplastics (Anderson *et al*., 2016; Moreira *et al*., 2016), and are the usual location of citizen science campaigns, including beach cleans. The presence of plastic debris on beaches is attributed both to direct deposition (i.e., as a result of activities on beaches), as well as transport of debris carried on currents (Cole *et al*., 2011) and by transport mechanisms such as alongshore drift (Moreira *et al*., 2016). These transport processes are little quantified in terms of plastic transport and deposition, even in these (relatively) well-studied environments. The same transport processes apply to estuarine intertidal environments, and abundances of a similar scale have been observed on estuarine sandy beaches as compared to open ocean beaches (e.g., Naidoo *et al.* (2015)).

For low-energy environments such as wetlands, or lagoons, there are fewer studies compared to high-energy beaches environments (Lo *et al*., 2018), and so the knowledge gaps are greater. These low-energy environments are important sinks of fine sediment (Wood and Widdows, 2002), and also contaminants (Cundy *et al*., 2005; Gedan *et al*., 2009). Mudflats, which are low-energy environments and dominated by fine sediment, show an increased abundance of microplastics in the mudflats compared to nearby beaches (Liebezeit and Dubaish, 2012; Lo *et al*., 2018). Some studies have shown a correlation between sediment size and microplastic abundance (e.g., Vianello *et al.* (2013)), suggesting that microplastics, as particles in suspension which are very small, and less dense than sediment, require a low-energy environment to be deposited in large quantities. Some of these low-energy environments enhance deposition of suspended particles in other ways. For example, deposition in salt marshes in enhanced by vegetation, partly a result of flow attenuation by plants (Mudd *et al*., 2010). Suspended particles may also deposit directly on vegetation, and this has been observed for microplastics (Cozzolino *et al*., 2020). A range of intertidal and subtidal vegetation has been observed to have a trapping effect on microplastics, be it through direct trapping or through slowed flow and reduced turbulence, including salt marsh (Cozzolino *et al*., 2020; de Smit *et al*., 2021; Lloret *et al*., 2021; Yao *et al*., 2019), sea grass meadows (Cozzolino *et al*., 2020; Goss *et al*., 2018; Huang *et al*., 2020; Jones *et al*., 2020; Unsworth *et al*., 2021) seaweeds (Gutow *et al*., 2016; Sundbæk *et al*., 2018); and mangrove vegetation (Garcés-Ordóñez *et al*., 2019; Li *et al*., 2018; Mohamed Nor and Obbard, 2014). In these studies, microplastic was observed adhered to vegetation (Cozzolino *et al*., 2020; Goss *et al*., 2018), and in increased numbers in sediment in vegetated areas compared to unvegetated areas (Cozzolino *et al*., 2020; Huang *et al*., 2020; Yao *et al*., 2019). While the number of studies on any particular habitat and location is limited, there is increasing evidence that coastal vegetated habitats may trap microplastics. Previous work has been limited to point source sampling, with little investigation into the influence of oceanographic conditions such as the tidal cycle on the fate of microplastics. Conditions change rapidly in the intertidal zone over the period of a single tidal cycle – with intertidal areas going from submerged to exposed on a repeated basis. It is unknown how the effects of changing tidal currents over the period of a tidal cycle – and how these differ, for example, with the spring-neap cycle, which, for example, in Southampton Water, leads to an approximate 2m difference in tidal range – affect microplastic abundance and distribution within the estuary.

During the flood tide, salt marshes are flooded with water from the main estuarine channel, which may be a source of microplastics - and may lead to deposition within the marsh. This inundation occurs initially via creeks. The creeks subsequently overtop to flood the marsh surface if the tidal height is sufficient to do so (this may not occur during neap tides, for example). Thus,

salt marsh creeks probably form the main pathway for sediment and contaminant exchange between marsh and estuary. They also form the main drainage pathway for the marsh, with the drainage on the ebb tide occurring in the opposite direction to the marsh's flooding. Initially, the marsh surface drains first (which, in the marsh interior, occurs into creeks), followed by the creeks themselves draining. As such, salt marsh creeks are the first and last element of marsh systems to interact with the tide, and thus provide a good indicator of temporal microplastic trends over tidal cycles. However, despite the high degree of interconnectivity between salt marshes and estuarine waters, few studies have even investigated the presence of microplastics in intertidal salt marshes. Understanding the threat posed to intertidal saltmarshes by microplastics starts with understanding their exposure, and how microplastics are transported into these environments. As salt marsh creeks are the first point of exposure to the incoming tide, sampling here, and investigating how abundances vary over tidal cycles, particularly in terms of comparing input to the marsh (flood tide) to output from the marsh (ebb tide), is of significant importance to understanding the temporal microplastic trends within salt marshes.

Studies investigating sediment dynamics in salt marshes have utilised inflow and outflow sampling in marshes over a tidal cycle, to determine the direction of transport of suspended particles (Reed *et al*., 1999). Reed *et al.*'s (1999) study found that suspended sediment is brought into marshes by the incoming flood tide, and a decreased concentration is observed on the outgoing ebb tide – supporting the hypothesis of deposition in the intertidal in the salt marsh. This is, as briefly discussed earlier, partly as a result of flow attenuation by plants, and partly as a result of direct deposition on plants. Biofilms on mud surfaces can also trap sediment particles, and decrease resuspension of sediment particles (Decho, 2000). It is also due to reduced flow velocity during the high water stand. Using this technique of sampling inflow and outflow in a salt marsh creek – the first and last element of marsh systems to interact with the tide – will enable the determination of the transport direction of microplastics within the marsh system, as well as allowing an assessment of any trapping processes that may occur in the marsh system. Sampling at high resolution in the creek – every fifteen minutes over the flood and ebb tide – will allow assessment of how microplastic abundance varies throughout the tidal cycle.

4.2 Methods

4.2.1 Sampling Methods

As in previous work (Chapter 3), surface microlayer (SML) sampling was utilised. For this work, SML samples were taken in a salt marsh creek, every fifteen minutes on the flood and ebb tides, and once during the extended high-water period. SML sampling was chosen as this is the first

layer of the water column to interact with the intertidal during the flood tide, and the last layer to drain from the intertidal during the ebb tide, and also contains a high concentration of microplastics relative to the underlying water (e.g., Song *et al.* (2014)).

It is proposed that the SML is involved in remobilising microplastics from mudflats and lower tidal elevations and transporting them to the upper marsh (Anderson *et al*., 2018). Understanding how microplastics abundances change in the SML will give an indication as to its importance in transporting microplastics into the upper intertidal, or exporting microplastics on the ebb tide, for example.

4.2.2 Sampling Location

Sampling took place in a large salt marsh creek in Hythe, Southampton Water, U.K. Southampton Water is discussed in detail in Chapter 2, but further details on the specific sampling site are given below.

The Solent and Southampton Water is designed as a Special Protection Area under Natura 2000, and the Solent is also designated as a Special Area of Conservation. Additionally, the area is a RAMSAR site, with 22 Sites of Special Scientific Interest across the Solent as a whole. Three of these are areas of salt marsh, Eling and Bury marshes; Lincegrove and Hackett's marshes; and the Hythe to Calshot marshes. Of these, it was decided to sample in the salt marsh at Hythe. This decision was made as there is a large tidal creek at Hythe which is easily accessed, as well as being sheltered from passing boat traffic and most (though not extreme) weather conditions and waves. Additionally, this site is located within the main channel of Southampton Water.

Hythe saltmarsh is located on the western shore of Southampton Water, south of the small town of Hythe. The marshes extend to Calshot, the spit at the mouth of Southampton Water, passing by the industrial site of Fawley. Whilst Hythe has previously been *Spartina*-dominant, the marsh is now more mixed, with dominant species comprising *Spartina* sp. (*maritima, alterniflora, townsendii, anglica*), sea purslane (*Atriplex portulacoides*), and saltmarsh grass (*Puccinellia maritima*) (Cundy and Croudace, 2017). The marsh is fringed by an eroded cliff to the seaward side, which marks the boundary between the marsh and an extent of mudflat (Quaresma *et al*., 2007). There are large shell deposits forming chenier ridges which are located mid-marsh, and interrupt the zonation between low-marsh and mid-marsh species. The upper marsh vegetation and zonation ends abruptly where a tarmac road passes parallel to the shore on a low embankment, and at the landward side of this road, the zonation changes abruptly to woodland.

The exact sampling location was located at grid reference SU 43137 07336, on the edge of a large creek (Figure 4-1, Figure 4-2). This creek is partially sheltered by a chenier ridge, reducing the impacts of ship wakes and wind-generated waves, which can be seen in Figure 4-2. While the creeks in this marsh system are largely dendritic in character, the creek here is essentially linear, is accessible and is the main conduit of water from the main channel of Southampton Water into this section of the marsh.

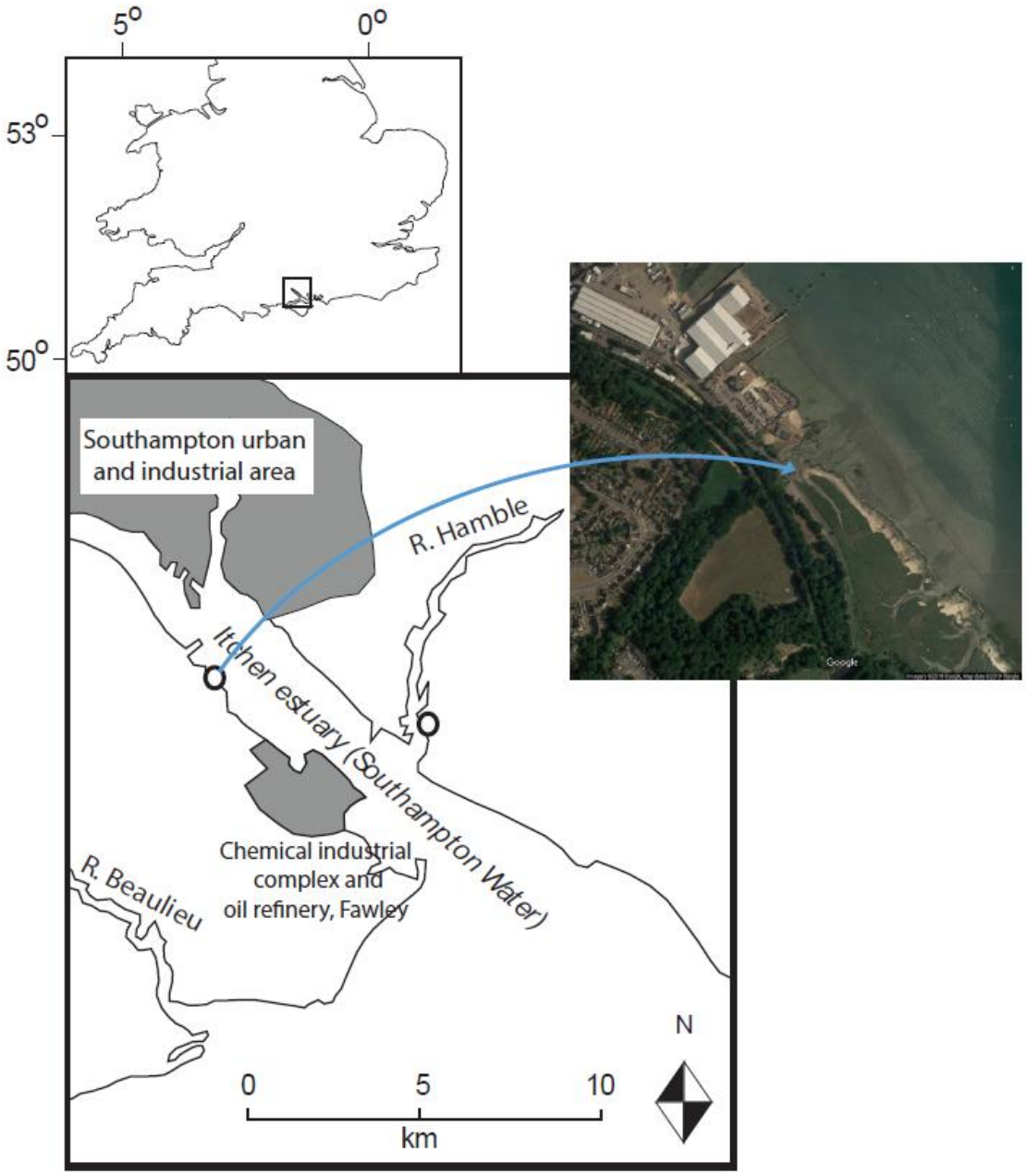

Figure 4-1 Location of the sampling site within the UK and Southampton Water.

(Imagery: Google)

Figure 4-2 The saltmarsh creek sampled in Hythe (source: author)

4.2.3 Field Sampling Methods

Water sampling was carried out every 15 minutes on the flood tide, once during the middle of the slack water period, and every 15 minutes on the ebb tide. Two tidal cycles were sampled, a spring tide (13th September 2018, tidal range 4.30 m) and a neap tide (5th October 2018, tidal range 2.25 m). Two methods of sampling were utilised, simultaneously at each time point: surface microlayer sampling (for microplastics) and bulk water sampling (for determination of suspended sediment concentration).

SML sampling was carried out using the glass plate method. As described in the previous chapter (3.2.1.1.4), glass plate sampling uses a sheet of glass (0.4 x 30.0 x 18.2 cm), repeatedly lowered into the water and drained. A total of 25 plate dips were carried out, or, where water depth prevented this, the plate was turned sideways and 30 dips were carried out with a 30.0 cm wide plate to a depth of 16 cm. The number of dips and orientation of the plate were recorded, with an approximate sample volume of 250-350 mL. As previously (3.2.1.1), HDPE bottles and a HDPE funnel were used, both rinsed in ambient water before sampling. Samplers stood downwind of samples, to reduce contamination from clothing in the field.

Bulk water samples were taken at 5 cm depth, directly into a 2 L PET bottle. This bottle was first rinsed three times in ambient water, before being submerged, opened, filled and closed at approx. 5 cm water depth.

4.2.4 Sample Processing Methods

The Hythe SML water samples were filtered without additional treatment, due to their relatively low suspended sediment concentration. This filtration was carried out at the National Oceanography Centre Southampton, in a fume cupboard. The entire SML sample was filtered,

following previous studies (Anderson *et al*., 2018), onto a 0.45 µm cellulose nitrate filter (Whatman, USA). Those samples with higher SSC were filtered into two fractions, to reduce the sediment load on the filters to enable visual analysis.

Suspended sediment concentrations (SSC) were derived from the bulk water samples taken simultaneously with the SML samples. The samples were first shaken to homogenise them, then a 50 mL aliquot was taken. This was filtered on a pre-weighed glass fibre filter, dried to a constant weight and re-weighed to calculate the SSC in g/Litre.

Alongside the environmental samples, procedural and airborne blanks were carried out. The procedural blanks consisted of 200 mL MilliQ (ultrapure) water filtered using the same procedure as the environmental samples. The airborne blank consisted of a MilliQ-dampened filter left exposed alongside the filtration equipment for the duration of filtration. Additional contamination prevention measures were: the wearing of cotton clothing and laboratory coats when filtering and enumerating samples; wearing nitrile gloves; keeping samples covered whenever possible; and in the field, standing downwind of the sample.

4.2.5 Sample Enumeration Methods

As in previous chapters (3.2.3), visual identification supported by the spectroscopic analysis of a subsample of samples was identified as a suitable enumeration method (Stanton *et al*., 2019). Counts were carried out under an optical microscope (GX Microscopes, GXMXPL1530) at x40 magnification, with increased magnification where necessary. During one of these counts, fibres were measured using a calibrated microscope camera (Dino-Eye, Dino-Lite Eyepiece Camera). The average (mean) of these counts was calculated for each sample, with corrections for the blank (procedural and airborne) samples. As in previous work, three counts of samples were carried out, by two operatives, excluding four samples which were used for FTIR analysis – these were counted twice. This enabled operator counting error to be calculated.

Operator counting error was calculated as one standard deviation as a percentage of the average count, per filter. Counting error is frequently assessed in other fields, including pollen or micropalaeontological analysis (Comtois *et al*., 1999; Patterson and Fishbein, 1989), but is less commonly assessed or reported in microplastics literature. Plotting average counts per filter against counting error shows a relationship with an R^2 value of 0.6881, and a counting error that approaches 10% at higher average count values (Figure 3). The counting error exceeds 60% at lower counts ($n < 10$), and considering the widespread usage of visual enumeration in microplastics research this has significant implications for the accuracy of microplastics data in locations where relatively low number of fibres are observed.

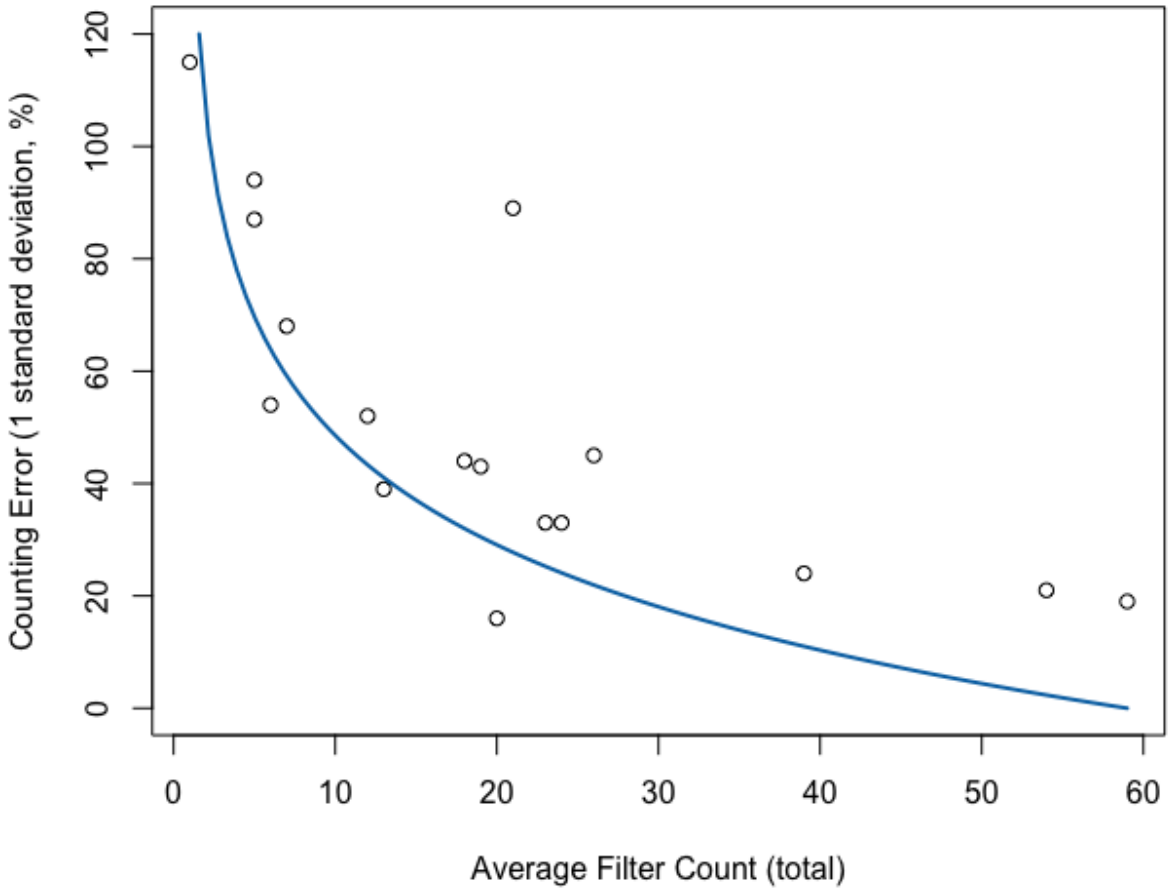

Figure 4-3 Relationship between the average filter count and the calculated counting error

The limit of detection was calculated using the procedural and airborne blank samples collected during filtration. Colourless fibres occurred in sufficient quantities (n > 9 for the airborne blank filter) on these blank samples to exclude them from analysis entirely, following previous studies (Anderson *et al*., 2018) and to align with other work in this thesis (Chapter 3). Coloured fibres were observed on the blank filters. The limit of detection used for this analysis was calculated as the average of these observations + 3 standard deviations. This limit of detection in fibres/filter was then converted into number/m² using the average area sampled.

Abundance per m² of the SML was calculated using the area of the plate and the number and orientation of dips carried out. This was then converted into abundance per litre using the average depth of SML sampled (100µm, (Agogue *et al*., 2004).

4.2.6 Spectroscopic Analysis

Spectroscopic methods are often utilised for microplastic analysis, and should be a vital component of analysis due to their ability to identify polymers (Hidalgo-Ruz *et al*., 2012). µATR-FTIR (micro-Attenuated Total Reflection-FTIR) was carried out on one of the filters (07:15

October), due to time and resource constraints not permitting further analysis, which equated to a total of 32 fibres, or approximately 5% of the total fibres on all filters.

As in Chapter 3.2.4, µATR-FTIR analysis was conducted using a Perkin Elmer Spotlight 400 Imaging system equipped with a µATR accessory. (Polymer library details are available in 3.2.4). Spectra with hit quality >0.8 (on a scale of 0 to 1) were accepted as verified polymer types. A hit quality of 0.8 corresponds to a 80% similarity between the measured and reference spectra. Particles were then classified as 'natural', 'polymer', or 'unidentified'.

4.3 Intertidal Trapping Results

Particles suspected of being microplastics were identified in 100% of the SML samples taken.

Statistical analysis was carried out using the statistic software R (4.0.0) using the platform R Studio (1.2.5042). Following normality tests (Shapiro-Wilks), fibre abundance was log-transformed to fit a normal distribution. A significance value of 95% was used throughout.

4.3.1 Average Abundance

To enable comparison to previous studies, abundances are reported below in both abundance/L and abundance/m^2.

The median abundance over all of the SML samples was 66.3 fibres/L. The minimum and maximum abundances were 29.5 and 234.1 fibres/L on the spring tide, and 10.9 and 80.3 fibres/L on the neap tide.

The median abundance over all of the SML samples was 7.5 fibres/m^2. The minimum and maximum abundances were 1.9 and 22.4 fibres/m^2 on the spring tide and 0.3 and 7.1 fibres/m^2 on the neap tide.

4.3.2 Temporal Trends

Temporal changes in fibre abundance were observed on both sampling days, and are illustrated in Figure 4a and 4b. These subfigures also show the calculated Limit of Detection (4.2.5) (straight line at y = 4.7)), and contain tidal height graphs for both sampling days. The height of the marsh platform is indicated on both Figure 4c and 4d, and shows clearly that the main marsh platform is not flooded by the tide on the neap tide, but that it is on the spring tide.

On both the spring and neap tide sampled, there is a higher abundance of fibres observed on the flood tide than the ebb tide. Additionally, a number of sampling points were close to the limit of

detection, particularly on the ebb tide. An approximate two-thirds decrease in abundance was seen between the flood and ebb tide on both tidal cycles sampled.

To assess the statistical significance of these differences, the fibre abundance was first log transformed to fit a normal distribution. Following this, a two-way ANOVA was carried out, with the factors 'sample day' and 'tidal state'. This showed a significant difference between the two days (F = 18.5052, p = 0.0005486), and a significant difference between fibre abundance on the flood tide and on the ebb tide (F = 10.5553, p = 0.0011939). Differences between the flood and ebb tide were assessed using the non-parametric Kruskal-Wallis test, which showed a significant difference on the spring tide (Kruskal-Wallis chi-squared = 7.4103, p = 0.006485) and on the neap tide (Kruskal-Wallis chi-squared = 5.4634, p = 0.01942).

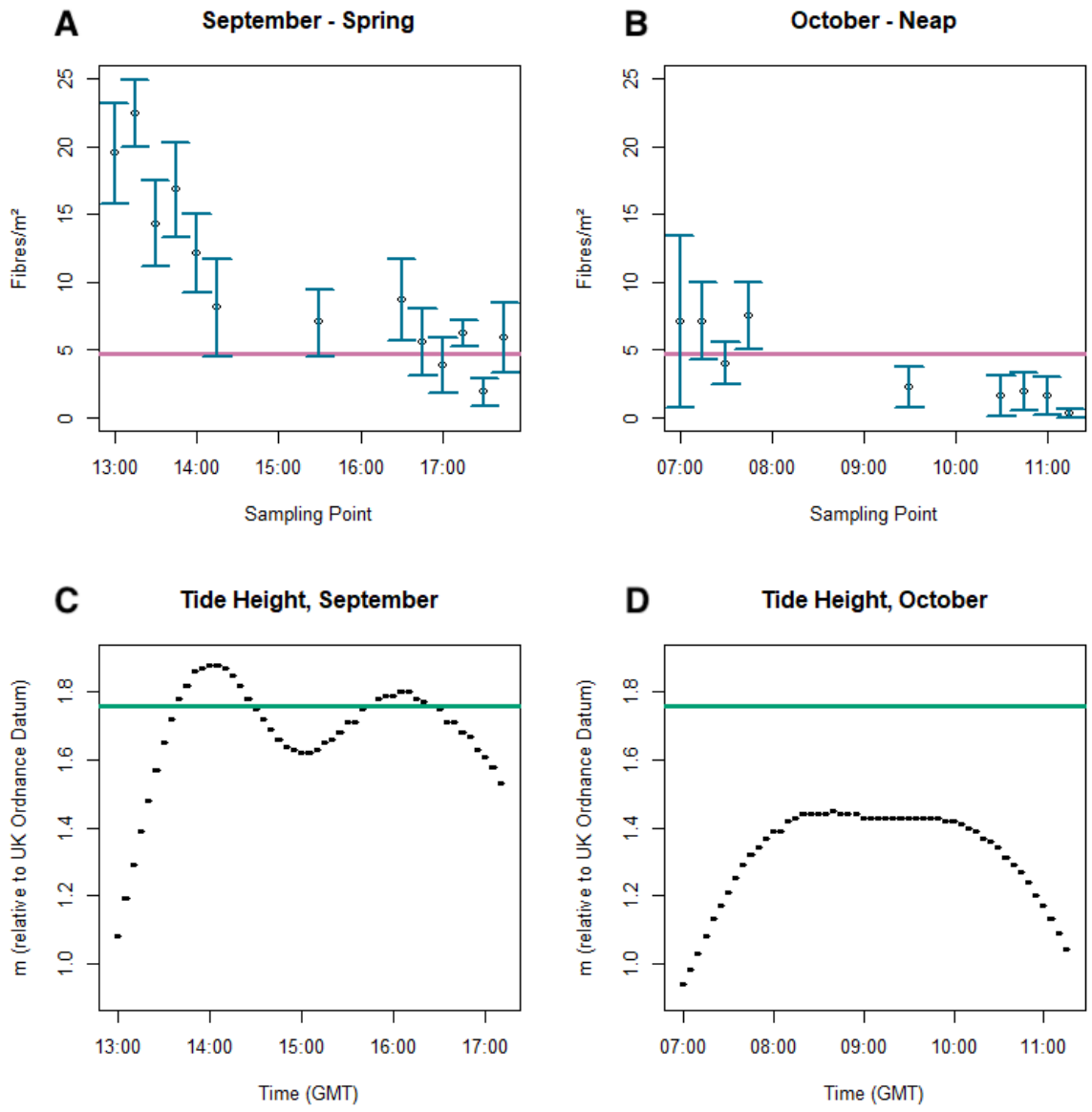

Figure 4-4 Microfibre abundances and tide graphs

A: Microfibre abundance on a spring tide cycle, September 13th 2018.

B: Microfibre abundances on a neap tide cycle, October 5th 2018.

C: Tide curve for September 13th 2018.

D: Tide curve for October 5th 2018.

A/B: horizontal line at y = 4.7 indicates the calculated limit of detection.

C/D: horizontal line at y = 1.76 indicates the elevation of the marsh platform.

4.3.3 Microplastic Characteristics and Polymer Identification

A total of 743 suspected microplastics were identified across both sampling days. A total of 3 of these were fragments, and the remainder were fibres. As they comprised such a small percentage of the total (0.40%), fragments were excluded from analysis.

Using standard light microscopy, the majority of fibres (75%) were identified as black. 22% were blue, and 2% were red.

Whilst most fibres were smooth, some exhibited signs of weathering, such as fraying (Figure 4-5). Fibres were found tangled, both with themselves and with other fibres (Figure 4-6).

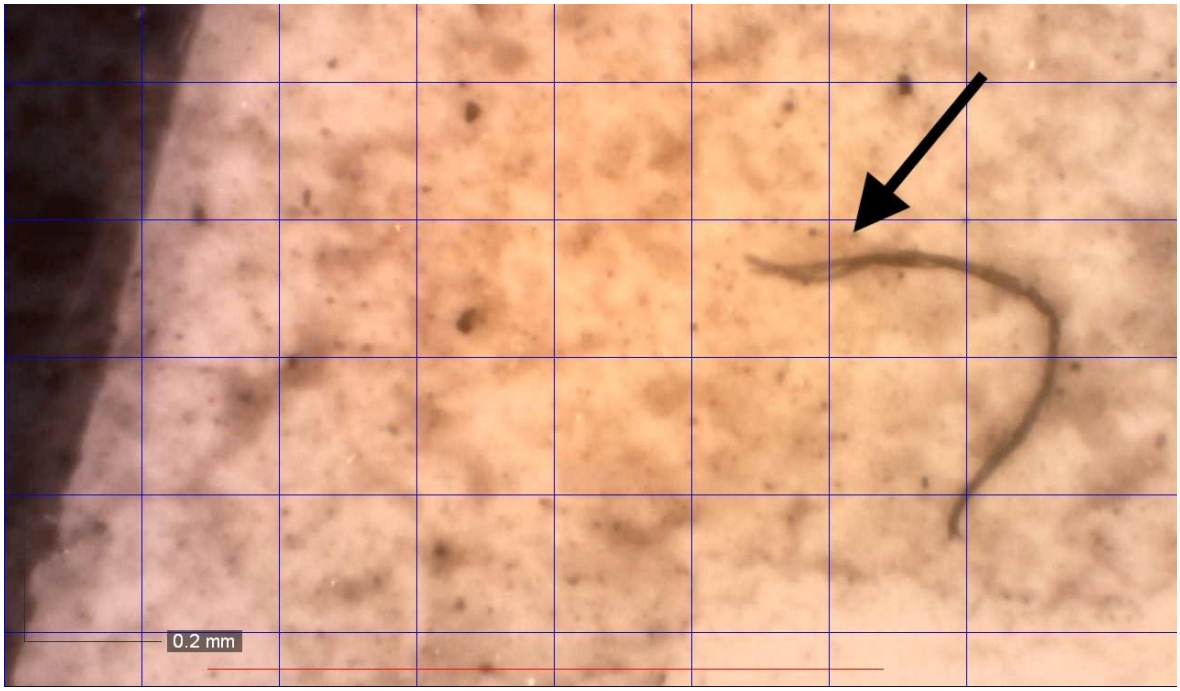

Figure 4-5 A frayed fibre identified in one of the SML samples (source: author)

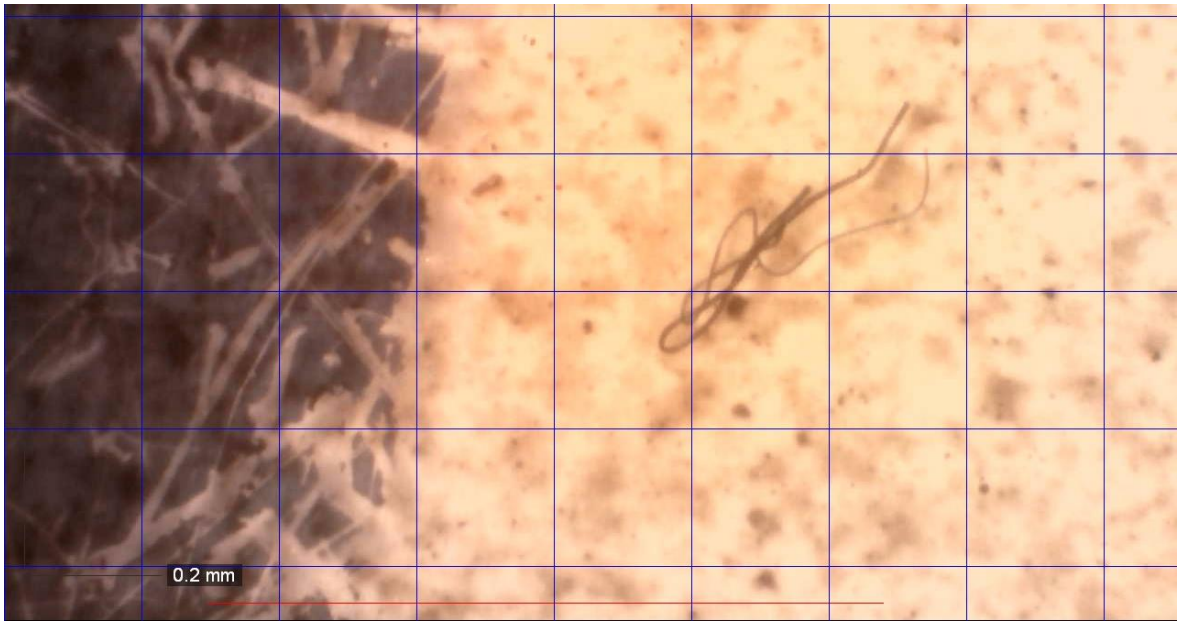

Figure 4-6 A fibre identified in an SML sample which is starting to tangle with itself to form a 'fibre bundle' (source: author)

A sub-set of 32 fibres were analysed by FTIR, all from the 07:15 October (neap flood tide) sample. Twenty-one of these returned spectrum matches to the specified library of >80% and were considered for this analysis. Thirteen fibres (62%) matched to polyethylene (an example is given in Figure 4-7), and one matched to polyvinyl alcohol. One fibre was identified as cellulose nitrate, and was therefore removed as contamination resulting from the processing of the samples for FTIR analysis (the initial filters were composed of cellulose nitrate). Six fibres (29%) were identified as cellulose, or cellulose by-products (but could also be rayon, a regenerated cellulose fibre), and therefore the visual counts (already corrected for the blanks) were again corrected by a 2/3 ratio to account for these natural fibres.

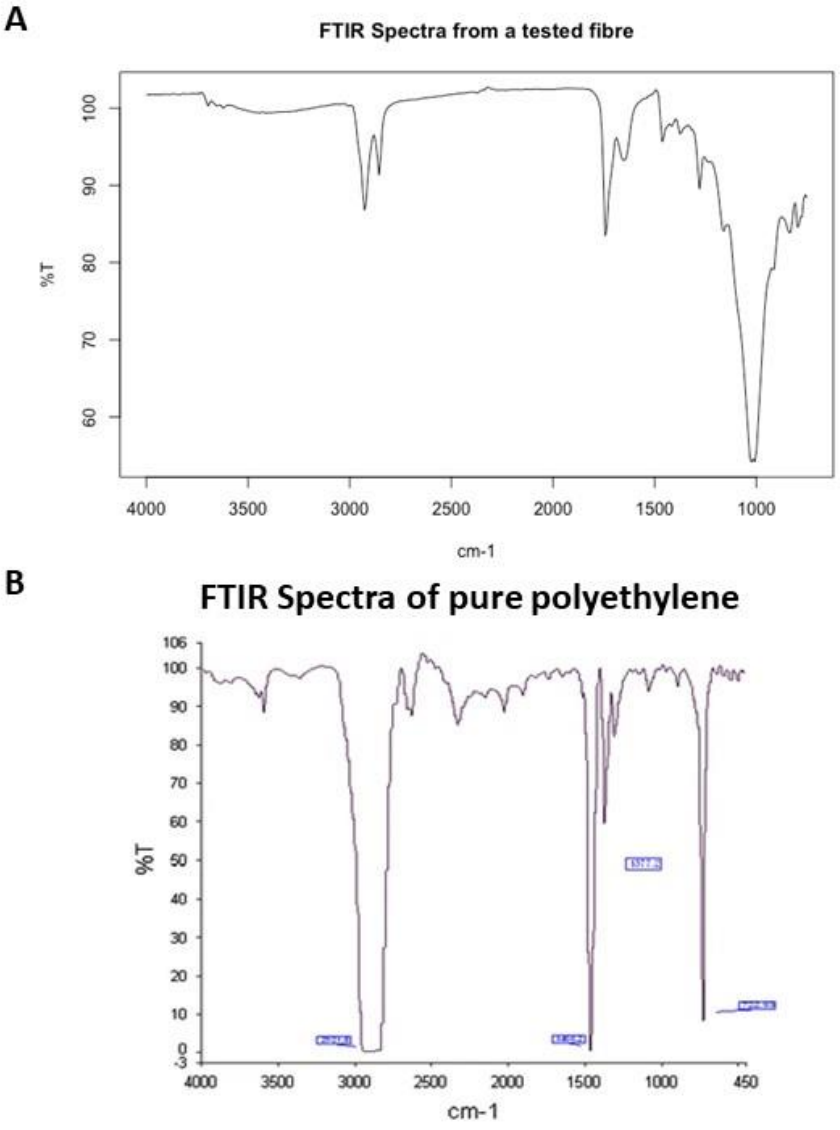

Figure 4-7 FTIR Spectra for a tested particle compared to an FTIR spectra for a pure plastic particle

A: FTIR spectra of a particle returning a 0.82 match to (chlorinated) polyethylene

B: an example FTIR spectra of pure polyethylene (Asgari *et al.*, 2014)

Fibre length was measured once in the three counts. Fibres with a length greater than 5 mm were identified, (n = 4, 0.54%) and removed from the analysis due to falling outside the definition of microplastic utilised here. 81% of fibres were <1 mm in length. Length distribution was found to be quasi-exponential, there was significantly more shorter fibres than longer (Figure 4-8). A comparison of fibre length over the tidal cycle was carried out, assessing for significant differences in fibre lengths between all flood and all ebb tide samples. Data were converted to % < 1 mm, a one-way ANOVA was carried out as data were distributed normally, and there were no significant differences observed in fibre length for the spring or neap tides sampled, and nor was there a difference when all samples were considered together.

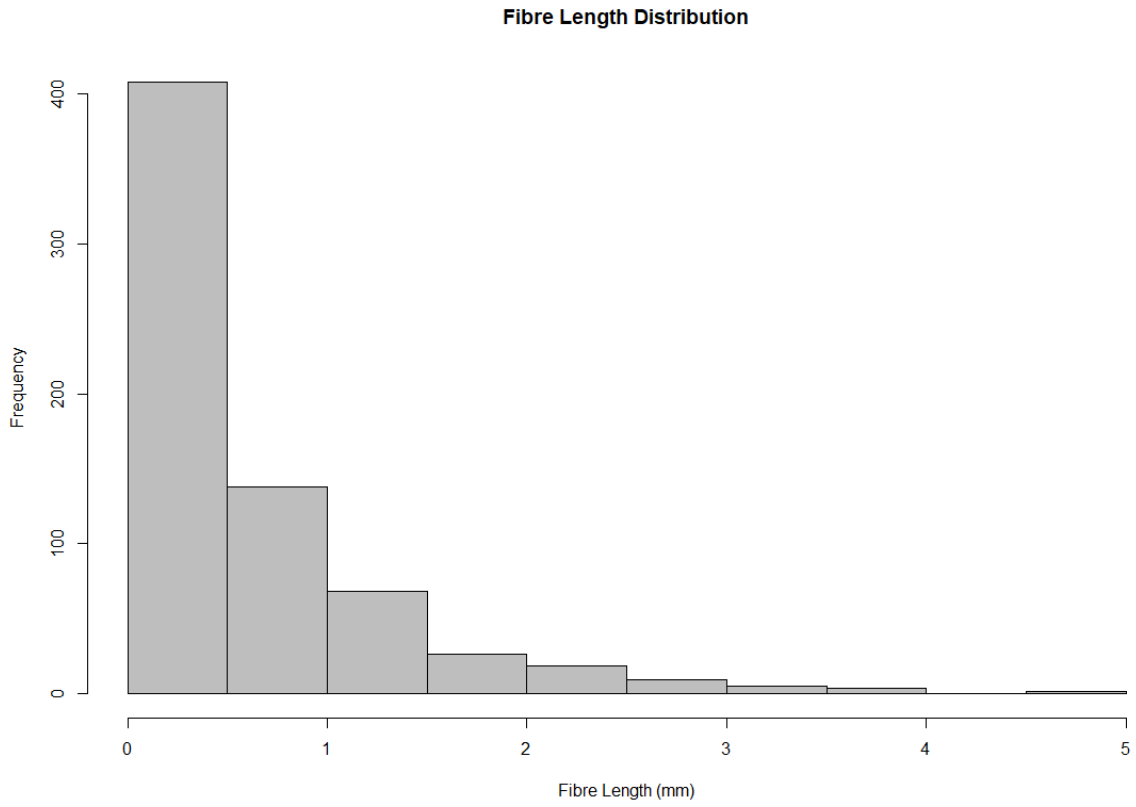

Figure 4-8 Length distribution of fibres in all samples as measured under light microscopy

Note that the x-axis does not extend to 0 mm in length at its smallest, as visual detection and measurement of fibres was not possible below approximately 0.1 mm.

4.3.4 Suspended Sediment Concentration

The suspended sediment concentration (5 cm water depth) and fibre abundance (SML) were both non-normally distributed, as assessed by Shapiro-Wilks (SSC p = 5.505e-06, fibre abundance p = 0.01319). Spearman's Rank Correlation was therefore used to assess for any relationship between

SSC and fibre abundance, which gave a weak positive (ρ = 0.5235, *p* = 0.01241) when considering all samples taken over both days.

Kruskal-Wallis tests were carried out to assess differences in suspended sediment concentrations between the ebb and flood tide. This found a significant difference between the suspended sediment concentrations on the flood and ebb tides, and high water stand, over both sampling days combined (Kruskal-Wallis chi squared = 11.89, *p* = 0.00262). This trend of decreased SSC on the ebb tide is shown inFigure 4-9.

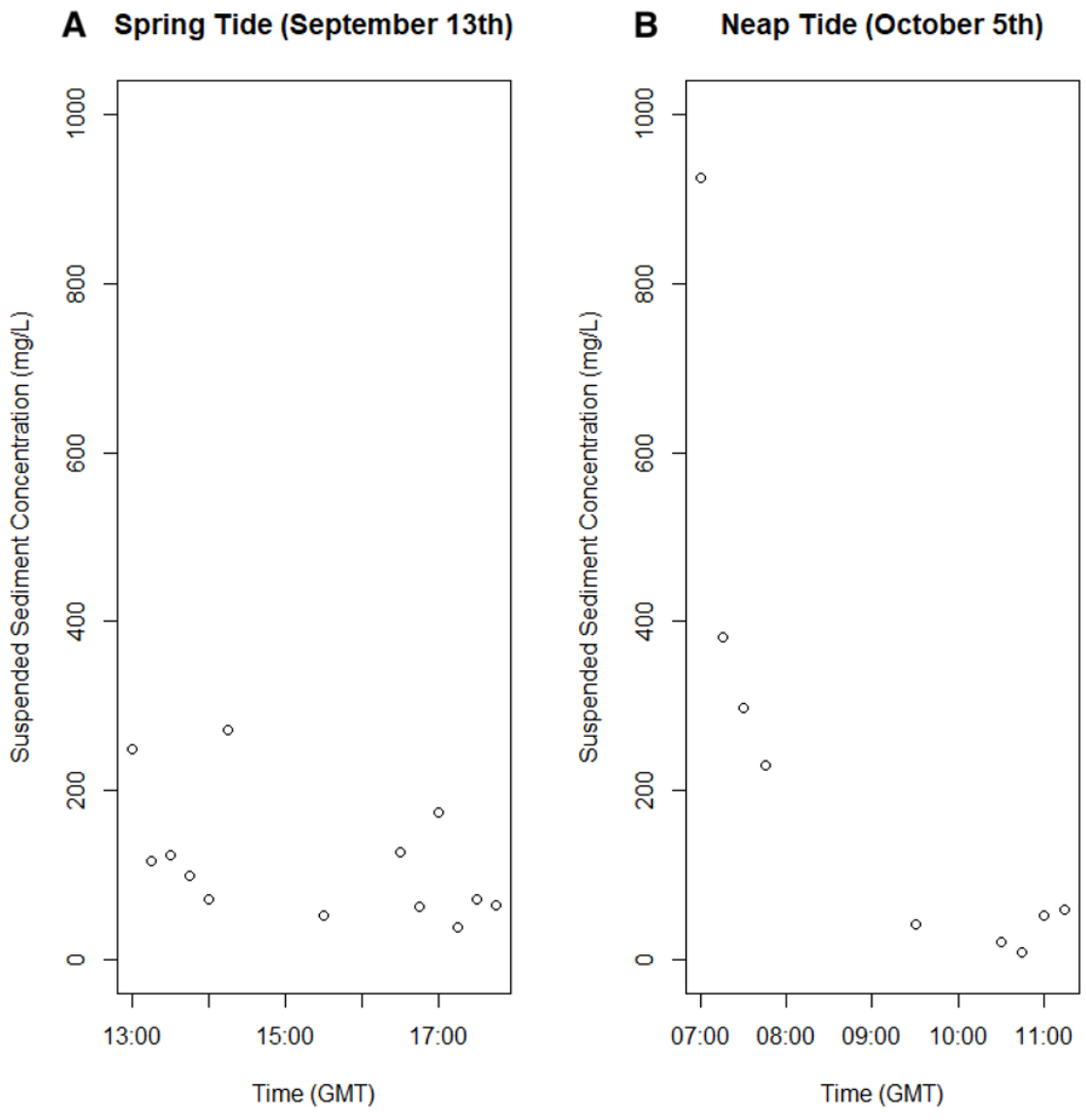

Figure 4-9 Suspended sediment concentration over the two sampled tidal cycles

4.4 Discussion

The abundance of microplastics in Southampton Water is comparable to previous published studies. Whilst this study was located in Hythe, on the western shore of Southampton Water, Anderson *et al.* (2018) sampled on the shore of the River Hamble estuary, which inputs to Southampton Water on its eastern shore. Anderson *et al.* (2018) used the same method as this chapter, the glass plate method, enabling a direct comparison. Median abundance in the Hamble in SML samples was 6.4 fibres/m^2, and in this period of sampling, abundance at Hythe was 6.7 fibres/m^2, indicating a low but consistent presence of microplastics in the Southampton Water estuarine system. Converted to fibres/L, median abundance here was 66.3 fibres/L compared to 42.1 fibres/L in Anderson *et al.* (2018), which suggests that unit conversions may show differences in abundance between samples.

The only other published study which sampled microplastics in Southampton Water is Gallagher *et al.* (2016), who utilised surface water sampling with a plankton net trawl. While these data are not directly comparable here due to the differing methodologies used, they do provide further evidence of a low but relatively consistent level of microplastic contamination in Southampton Water. As this study sampled both the River Hamble estuary and the main body of Southampton Water, it aids in the comparison of these results to Anderson *et al.* (2018). Gallagher *et al.* (2016) found a lower level of microplastics per trawl in the Hamble as compared to the main body of Southampton Water, with this study finding the same trend when considering abundance/L. However, there are many little-understood influences on microplastic abundance, and with both Anderson *et al.* (2018) and Gallagher *et al.* (2016) limited to one or two point samples, this trend may not be reflective of any spatial trends within Southampton Water. Differences were found in abundance between the locations sampled in Chapter 3, however, that study was conducted over a much longer time period than any previous studies in Southampton Water, this chapter included, therefore is able to carry out more robust statistical analyses to examine spatial differences.

Comparison to other studies of the SML beyond the study area is complicated by, as for many microplastic studies, the lack of a standardised method. Studies which have utilised surface microlayer sampling to investigate microplastic abundance have used, in addition to the glass plate sampling utilised here and in Anderson *et al.* (2018), a rotating drum sampler (Ng and Obbard, 2006), a metal sieve (Chae *et al*., 2015; Gray *et al*., 2018; Leads and Weinstein, 2019; Song *et al*., 2015, 2014) and a stainless tray sampler (Song *et al*., 2018). Several of these studies on microplastics in the SML sample the open ocean. Two published studies have investigated microplastic abundance in the estuarine surface microlayer, both in the USA: Gray *et al.* (2018)

who studied and compared Charleston Harbor and Winyah Bay, and Leads and Weinstein (2019), who only sampled Charleston Harbor (all USA). Converting this study in abundance/L gives an average abundance more than double that of the average in Winyah Bay (mean of 76.5 fibres/L as compared to 30.3 microplastics/L in Winyah Bay (Gray *et al*., 2018), a much larger but less industrialised estuary which compares well morphologically to Southampton Water. Charleston Harbor is a more rural estuary, which had lower abundances when sampled, ranging from 3 - 36 microplastics/L (Leads and Weinstein, 2019). However, when considering that microplastic abundance in other media (e.g., sand) can range from 106 to 15,554 items/m^2 in one study (Hong Kong beaches, mean per water control zone, (Fok and Cheung, 2015)), and that these average abundances come from limited studies, so may not be reflective of the abundance over a longer time scale of sampling; the two abundances are of the same magnitude.

A comparison of the microplastic abundance on the flood tide and the ebb tide shows a significant decrease in microplastic abundance from the flood to the ebb. This supports the hypothesis of trapping in intertidal wetlands, through a variety of proposed mechanisms. Both tidal cycles sampled showed an approximate 2/3 decrease in fibre abundance on the ebb tide. On the neap tide, the main marsh platform is not flooded (the elevation of the marsh platform is indicated by the line at y = 1.76 m on the tidal elevation curves (Figure 4-4)), and therefore the amount of vegetation-induced trapping (either by attenuated flow or direct deposition onto stems and leaves) is limited on the neap tide (although some vegetation at the marsh edge is still flooded). However, the still significant decrease in fibre abundance displayed on the neap tide supports the theory of other processes being involved in intertidal trapping of microplastics within saltmarshes. It is probable that there is interaction of suspended microplastics with exposed sediment (e.g., mudflats and other non-vegetated areas, including creek margins) and with algal mats and biofilms on these surfaces (which have been known to decrease the resuspension of sediments (Tolhurst *et al*., 2008)). This may be particularly the case for microplastics suspended in the SML, which is the first layer to pass over these surfaces during the flood tide. Similarly, observations by Cozzolino *et al*., (2020) showed no significant differences in microplastics in superficial sediment of saltmarshes and adjacent unvegetated areas. Other studies comparing vegetated wetland to adjacent non-vegetated mudflat have shown higher abundances of microplastics in vegetated sediment, however, microplastics were still observed in the mudflat sediment (Wu *et al*., 2020). Helcoski *et al.* (2020) found fewer microplastics in denser vegetation in the middle of a freshwater tidal marsh than in the less dense vegetation at the edge of the marsh, suggesting that the marsh edge vegetation reduces transport of microplastics in the dense marsh interior by enhancing trapping at the marsh edge. The current study shows a similar decrease from the flood to the ebb tide on both the spring and neap tides sampled, suggesting an equivalent level of trapping with or

without the marsh platform being entirely flooded. This supports both the conclusion of Helcoski *et al.* (2020) that the marsh edge vegetation plays an important role in microplastic deposition in marshes; and the overall conclusion drawn by Wu *et al.* (2020) and Lloret *et al.* (2021): that there is a degree of trapping of microplastics occurring in the intertidal.

The implications of the trapping of microplastics in intertidal wetlands are significant. While the current study focuses on a temperate saltmarsh, similar processes occur to suspended particles in other wetland ecosystems, such as mangroves. Coastal and estuarine wetlands are among the most productive ecosystems globally (Barbier *et al*., 2011) (salt marshes can have a primary production as high as 3000 g C/m^2/yr, (Klemas, 2013)), and estuaries support a considerable amount of biomass despite often low biodiversity (Elliott and Whitfield, 2011). The presence of microplastics in a variety of locations within these environments as a result of the numerous trapping mechanisms proposed here expose a greater number of species with a variety of feeding modes to microplastic uptake. Trapping on vegetation exposes those species feeding on that vegetation, settling out to benthic sediment exposes benthic organisms, for example; yet there are few if any assessments of the threat microplastics may pose on an ecosystem scale to wetlands.

Alternately, trapping in sediments (potentially aided by bioturbation (Näkki *et al*., 2017)) may remove microplastics from the water column and prevent further transport to coastal seas and exposure to additional organisms. This sequestration may be one contributor to the 'missing plastic' problem (identified by Eriksen *et al*. 2014); and effectively store plastic in marshes and other intertidal areas. However, salt marshes and indeed, many coastal ecosystems are currently under threat due to rising sea levels (Craft *et al*., 2009) and thus these sinks of microplastic may in future or at present, be secondary sources of microplastic due to erosion and marsh retreat. Such exposure may occur in pulses due to storm or flood events, which have previously been recorded to reduce microplastic abundance in sediment (Hurley *et al*., 2018).

Trapping in the intertidal is well-recorded for suspended sediment. Reed *et al.* (1999) utilised a similar methodology (high-resolution temporal sampling) to show a trend of decreased suspended sediment on the ebb tide. This is also observed here on both sampling days (Figure 4-9). Additionally, a weak but significant positive correlation is seen between the SSC and fibre abundance when considering all samples together (Spearman's $\rho = 0.433$, $p < 0.05$). This supports the hypothesis of intertidal trapping for microplastics in a similar mechanism to suspended sediment. However, the weak correlation between SSC and fibre abundance does not provide conclusive evidence to support the modelling of microplastics in the same way as suspended

sediment, as has been previously carried out (e.g., Nizzetto *et al.* (2016), to determine fate or transport of microplastics in estuaries or other environments).

Two recent studies have investigated the trapping of microplastics and macroplastics in saltmarshes, Cozzolino *et al.* (2020) in a *Sporobolus maritimus* marsh in the Ria Formosa lagoon, Portugal, and Yao *et al.* (2019) in a *Spartina alterniflora* dominant marsh in the Ou River, Zhejiang, China. (*Spartina* and *Sporobolus* refer to the same group of cordgrasses, the name of which is under debate (Bortolus *et al*., 2019)). These marshes differ morphologically from Hythe, which is sea purslane (*Atriplex portulacoides*) and *Spartina* (all subspecies) dominated. While the current data suggests a degree of trapping in the intertidal marsh, as demonstrated by the significant decrease in fibre abundance between the flood and ebb tide; this is not seen in the studies examining microplastic abundance on vegetation and in surface sediments in cordgrass saltmarshes and adjacent mudflats. Yao *et al.* (2019) observe a greater abundance of microplastics in marsh edge sediments than marsh interior sediments; and Cozzolino *et al.* (2020) observe no microplastics adhered to the leaves of *S. maritimus.* These observations have led these studies to conclude that considering vegetated areas as traps of microplastics should be done with caution, and that saltmarshes may be a source of microplastics rather than a sink (due to their observed role as a trap of macroplastics, which then fragment). This contrasts with the conclusions suggested here, which imply that saltmarshes can act as a trap for microplastics. Hythe saltmarsh, while previously *Spartina* dominant and still retaining large coverage of *Spartina* swards to date, is dominated by sea purslane *(Atriplex portulacoides).* As such, it may be differing vegetation that influences the trapping seen at Hythe. This effect will vary throughout the year as the marsh changes with the seasons – for example, while sea purslane is evergreen (though sheds some leaves in the autumn/winter), *Spartina* dies back above ground, and sprouts new growth every year. Therefore, over winter, any trapping caused by *Spartina* will be reduced, as it is considerably reduced in size and extent during this season, though remnant material remains standing into spring. Therefore, seasonal variation in vegetation needs to be considered when investigation vegetative trapping of microplastics in salt marshes. Additionally, with trapping seen on both the spring and neap tidal cycles sampled, it could be that deposition is occurring mainly at the edge of the marsh, as observed by Yao *et al.* (2019), especially given that on neap tides in Hythe, the tide does not overtop the creek onto the vegetated marsh platform,. This chapter comprises a spatially integrated study, which may pick up overall trends that are not seen when point sampling sediments in marshes, as was used by Yao *et al.* (2019).

The sampling reported in this chapter is limited to two sampling days: one neap tide cycle and one spring tide cycle. As such, a comparison of spring and neap tides is not particularly feasible, from the limited samples taken. However, the two sampling days did differ significantly, with

significantly more fibres in the spring tide samples than the neap tide samples. This is a trend which may be the result of a number of variables, for example, precedent weather conditions or human behaviour in terms of the supply of microplastics to Southampton Water. However, two previous studies have found trends associated with the spring/neap cycle. Sadri and Thompson (2014) found a (not significant) decrease in abundance of plastic debris in trawled estuarine surface water samples between spring and neap tides. Wu *et al.* (2020) found an increased abundance of microplastics in mudflat and saltmarsh surface sediments during the neap tidal cycle. This can be explained by the reduced flows during the neap cycle permitting greater deposition, with greater abundances in sediments and lower abundances in the water column. Further research is needed into tidal influence on microplastic abundance and location.

Chapter 3 showed a weak positive correlation between the tide height at the time of sampling and bulk water microplastic abundance at SWAC, but not at Mayflower Park, although Chapter 3 only involved a minimal number of samples per individual tidal cycle compared to the high-resolution sampling within this chapter. These sites were both sites with limited or no vegetation and a larger sediment bed grain size (i.e., a higher energy environment than in the present chapter); supporting a view that the composition of the environment will play a key role in determining the fate of microplastics during the course of a single tidal cycle. Additionally, this chapter (Chapter 4) utilised sampling over the same tidal cycle, and therefore the effects of other environmental factors (such as weather, river flow, seasonality) will be limited and the effects of the tidal cycle may be easier to see. Further work on the effects of tidal changes, including more assessment of the spring/neap cycle in particular, and how any effects are determined by the environment of interest, is necessary. Further analysis and discussion of temporal controls in microplastic abundance in Southampton Water are given in Chapter 3.

In terms of microplastic characteristics, the morphology of suspected microplastics identified was dominated by fibres (>700 fibres, 3 fragments). Only the fibre abundance is discussed in this chapter. The dominance of fibres may be a reflection of the shape distribution that exists in Southampton Water, and also globally. Numerous studies in a variety of media (e.g. water column, sediment, biota) in a range of locations globally also show a dominance of fibres over other shapes of microplastic (e.g. Salvador Cesa *et al.*, 2017; Gago *et al.*, 2018). Previous studies in Southampton Water also show a dominance of fibres (Anderson *et al*., 2018; Gallagher *et al*., 2016).

Alternately, the dominance of fibres observed may be methodological. Previous studies utilising the same sampling method also found a dominance of fibres (Anderson *et al*., 2018). Studies sampling the SML in the open ocean found an effect on the abundance of shapes of microplastic

recovered (Song *et al*., 2014). Additionally, the use of visual identification on samples which had not been digested or treated to remove organic material and sediment may also have influenced this. Fibres can be more distinct from other background material, and other microplastics may have been obscured by the presence of organic material and sediment on the filters.

Twenty-one fibres analysed using FTIR returned spectrum matches of >80%. One of these fibres was identified as cellulose nitrate, and deemed to be a by-product of the re-filtration process necessary to utilise FTIR analysis. A further six fibres were identified as cellulose, or cellulose by-products (29%). This suggests that, as in other studies, there is a degree of misidentification and overestimation of microplastic abundance (Lenz *et al*., 2015). This highlights the importance of utilising spectroscopic techniques to positively identify suspected microplastic particles. The cellulose or cellulose by-products have the potential to be polymers such as rayon, which are derived from plant material but heavily modified.

The most common polymer identified was polyethylene (62%, or 13 fibres), and one fibre was identified was polyvinyl alcohol. This likely reflects the proportion of plastics utilised in applications globally. Polyethylene is one of the most in-demand polymers worldwide for a wide variety of uses including plastic bags, ropes and fishing nets. Though fishing activities in Southampton Water are minimal, there is still a great deal of marine activity associated with the numerous docks and marinas. Fibres produced as a result of laundry will also be a source of these fibres, possibly a main source given the quantities estimated through some studies (e.g., a WWTW in Glasgow, UK, was estimated to be outputting 65 million microplastics per day, 18.5% of which were fibres (approximately 12 million fibres/day) (Murphy *et al*., 2016)), entering via waste water. These are all potential sources of the fibres identified in this study, although an absolute determination of fibre origin is impossible. Polyethylene is the polymer identified in the greatest frequency in microplastic studies as reviewed by Burns and Boxall (2018).

Previous studies utilising FTIR on samples collected in Southampton Water identified three plastic polymers from surface water samples (Gallagher *et al*., 2016). Whilst spectrum matches were not greater than 70%, cellophane, polyethylene and polypropylene were identified. Like polyethylene, polypropylene and cellophane are also commonly used polymers, suggesting that microplastic pollution within Southampton Water reflects plastic usage.

4.5 Conclusions

Deposition of microplastics in intertidal wetlands was identified as a potential key process in the estuarine filter, due to their role as a sink of other suspended particulate material. High resolution sampling in a salt marsh creek was utilised to investigate this potential sink of microplastics. A

significant decrease was found between microplastic abundance in the flood tide (entering the marsh) and the ebb tide (draining the marsh), supporting this pathway and sink of microplastics playing an important role in an estuarine filter for microplastics. Specific processes were not identified by the method utilised, but some conclusions can be drawn as the significant decrease in abundance was seen on both tidal cycles, including the neap when the main marsh platform is not flooded. This points to related habitats such as mudflats also playing a key role in microplastic deposition, or marsh edge vegetation. Suspended sediment, from which the hypothesis of microplastic trapping in wetlands was derived, also saw a significant decrease from flood to ebb, but no correlation with microplastic abundance was seen. The deposition of microplastics in intertidal wetlands has significant implications to the health of these important environments, although there are limited effects study from which to assess risk. Coastal wetlands may also be subject to coastal erosion with increased sea levels, and therefore may become a future source of microplastics.

Chapter 5 Resuspension and Flocculation of Microplastics

5.1 Introduction

The estuarine filter in essence is defined by deposition and resuspension within the estuary. This determines if suspended and dissolved components are retained within the estuary or transported out to coastal seas and beyond. While it is fairly well understood how these processes apply to components such as sediment, how deposition and resuspension processes act on microplastics, a relatively recent emerging contaminant, is less clear. For example, little is known about settling rates of microplastics, which are likely to vary widely due to the variety of shapes and densities, which in turn will significantly affect deposition of microplastics (Chubarenko *et al*., 2016). Typical shapes of microplastic include pellets/nurdles, fragments, films and fibres, all of which will have differing transport, deposition and resuspension behaviour. Some settling experiments have been conducted into microplastics of varying shapes, suggesting that some differ significantly from the established settling equations developed from sediment studies (Khatmullina and Isachenko, 2017). This is of particular importance, as fibres in particular are noted to sink at much slower rates than suggested from equations, and they are among the most common shape of microplastic found in environmental samples. This suggests that fibres are more likely to be retained in the water column and transported further, whereas shapes like spheres, which would be faster to sink, are more likely to be retrained within sediment closer to their source, or within an estuary, for example. Understanding how microplastic behaviour differs across the wide spectrum of shapes, polymers, sizes and densities, is essential to understanding the global life cycle of microplastics.

Microplastics do not exist in isolation, however. They are one of many particulate and dissolved components transported by rivers and estuaries, and can and may interact with these other components. Biofilms have been observed on microplastics, increasing particle density (Lagarde *et al*., 2016). Other biological interactions with microplastics include incorporation into faecal pellets by zooplankton (Cole *et al*., 2016), and aggregation of microplastics by algae (Summers *et al*., 2018). Lagarde *et al.* (2016) observed an increased density of microbial microplastic aggregates compared to virgin microplastic density, supporting an increased settling rate of aggregated microplastics. Non-biological interactions can also occur. Microplastics carry a surface charge, which means they (like clay particles) are likely to repel one another in suspension. However, in brackish or salty water, charged ions dissolved in the water can overcome these

surface charges, and enable flocculation of microplastics (here, flocculation refers to aggregation between like particles, as opposed to aggregation (mixed particle types). Flocculation of sediment is known to increasing sediment settling velocity (Mehta *et al*., 1989),and transport of cohesive sediments within estuaries may distribute anthropogenic contaminants input to estuaries from rivers (Markussen and Andersen, 2014). Aggregation of microplastics, including by flocculation, is one mechanism by which microplastic settling velocity may be increased. Whilst this aggregation may take place between two microplastic particles, it is more likely, due to the higher abundance of natural colloids, to take place with natural particles such as suspended sediment or organic matter (Alimi *et al*., 2018). Increased settling velocity will lead to increased deposition closer to the source and shorter transport distances. This is one mechanism by which deposition is enhanced in estuaries, and forms part of the estuarine filter (Figure 1-2). Understanding how this mechanism does or does not enhance microplastic settling will improve estimates of microplastic outputs from rivers, and improve risk assessments in estuaries of the risks posed by microplastics.

Resuspension of microplastics is a new field of study, and brings expertise from sediment dynamic studies, to study how microplastics behave in the environment. Microplastics are found in sediments and in water globally, even in remote regions (e.g., Suaria *et al.* (2020)). There is often an unspoken assumption that once microplastics are deposited, that they are not again moved, with studies stating that microplastics would be 'expected to accumulate over time' in sediment (Gray *et al*., 2018), and that sediments are a long-term sink of microplastics (Van Cauwenberghe *et al*., 2015). But studies looking at river sediments before and after periods of flooding show that there is a change in microplastic abundance and composition as a result of this increased flow (Hurley *et al*., 2018), and like any other particles in rivers, microplastics will be subject to the same forcings as sediments (Horton and Dixon, 2018). However, there is less understanding as to how these forcings act on microplastics and if or how it differs from sediments. It is important to understand the hydrodynamics influencing microplastic resuspension from sediments under flood and also under routine river flow; and also, how tidal and wave influences might act on sediments in estuaries, in order to understand the risks posed, and when they might be posed.

Whether a particle remains deposited or is resuspended and transported further is dependent on the balance between the gravity-based forces towards the bed, and the upwards lift and drag forces which move or keep particles in suspension (Chubarenko *et al*., 2016). If the force of gravity is greater than that of the upwards and lateral forces acting on it, then it will remain deposited. If, for example, these forces increase as a result of an increased current speed, then particles may lift off from the bed and begin moving once again, either as bedload or suspended load. This balance of forces is relatively well constrained for sediment, but is poorly understood, if at all, for microplastics. Several studies document microplastic movement when flow rates are increased

during floods, with increased microplastic abundance in coastal seas (Gündoğdu *et al*., 2018) and decreased or increased microplastic abundance in riverine sediments (Hurley *et al*., 2018) following floods. It seems to be often assumed that once microplastics are deposited, they remain deposited in sediment, given there is so little focus on resuspension of microplastics. However, it is clear that this is not the case, as seen both in the pre- and post-flood comparisons of environmental data, and in the one study of resuspension of microplastics during flood events (Ockelford *et al*., 2020). This study used a laboratory flume to investigate the flux of microplastics over a flood event, showing that flood events released microplastics from a gravel bed, and that the bed changed from sink to source during the modelled flood event. Whilst the conclusions of this study may be applicable on a wider scale, sediments in estuaries are much more likely to be muddy (and thus cohesive) and may interact with microplastics and high flow events differently. Understanding how microplastics are resuspended enables a greater understanding of the potential risks posed, and how these risks differ temporally, and with substrate and changing sediment types. In addition to considering changing river flow conditions, estuaries are subject to tidal currents with current velocities changing direction and magnitude during tidal cycles, and therefore microplastics may be deposited during slack water periods and resuspended during flood or ebb tides. Wave action is particularly also relevant to estuaries, although some estuaries are relatively well-protected from the effects of wave action by their geometry. For those that are not, breaking waves may be a source of both resuspension, and of fragmentation and secondary microplastics (Efimova *et al*., 2018).

In order to investigate flocculation and resuspension of microplastics, two separate experiments were conducted. Settling column experiments were used to investigate the flocculation of microplastic fibres; and a series of annular flume experiments were conducted to study the resuspension of fibres and nurdles with a variety of sediment beds (clay and sand).

5.2 Methodology

5.2.1 Flocculation

Settling column experiments are a long-established method of investigating sediment settling and aggregation. Flocs are very small (maximum observed floc size by Eisma *et al.* (1991) was 600 µm), and thus observing them is difficult. Aggregates mediated by biological processes may reach considerably larger sizes, such as observed in ‘marine snow’ in the deep ocean (e.g., maximum size of aggregates observed by Alldredge and Gotschalk (1988) were 25.5 mm in diameter and 75 mm in length)), but are still difficult to observe in the environment. Settling columns allow for the measurement of settling rates, and a comparison of predicted settling rates to observed settling

rates. In addition, given sufficiently large microplastics, aggregation and settling can be observed without magnification. A series of settling column experiments, utilising microplastic fibres, was set up to investigate if fibres flocculated together, and if they flocculated with suspended sediment (clay) particles, at a variety of salinities and suspended sediment concentrations. Settling columns have been previously used to investigate the settling behaviour of microplastics by Waldschläger and Schüttrumpf (2019a) and Waldschläger *et al.* (2020).

Settling columns were set up in plastic (HDPE) 2 L measuring cylinders, filled to a total volume of 1 L, with a diameter of 83 mm. Three salinities were used (made up of tap water and sea salt (Fluval Sea Marine Salt)), 0 PSU, 4 PSU and 35 PSU. Flocculation is recorded to occur at salinities as low as 0.5 PSU (Sutherland *et al*., 2015), 4 PSU was used as a low-salinity mid-point approximately equivalent to upper estuarine regions, and 35 PSU is the average marine salinity. Kaolinite clay (ACROS ORGANICS) was used at four concentrations (0 mg/L, 5 mg/L, 20 mg/L and 50 mg/L), to align with measured turbidity in Southampton Water (Townend, 2008). Large microplastics (LMPs) were made by cutting used polypropylene rope into 3-4 mm lengths, and sieving between a 1 mm and a 4.5 mm sieve. 100 fibres were used in each settling column, a similar magnitude to measured concentrations in Southampton Water (Anderson *et al.* (2018), River Hamble). Polypropylene rope is commonly used in marine and fisheries settings, and with Southampton Water being the location of several marinas and a large quantity of shipping traffic, it is hypothesised that polypropylene fibres resulting from the fragmentation of this rope is common within Southampton Water (polypropylene was observed in SML and bulk water samples taken in Southampton Water (Chapter 3, Chapter 4)). Household washing-up liquid was used to reduce surface tension that may retain the fibres at the water surface.

The method of Folk (1980) was followed, and is summarised as follows: settling columns were set up with water, sediment and microplastics, in a temperature-controlled room (21˚C). The entire water column was thoroughly mixed, and a timer started. A 10 mL water sample was taken at 10 cm depth at set time intervals (56 seconds; 4 minutes 38 seconds; 51 minutes 35 seconds; 7 hours 44 minutes 16 seconds). Water samples were then examined for microplastics to determine sinking, accompanied by visual inspections of the settling column.

5.2.2 Resuspension

A commonly used method of investigating sediment resuspension in laboratory settings is the use of flumes. While developed for use on environment sediment cores to determine erosion thresholds and sediment properties, the Core Mini Flume (CMF, Thompson *et al.* (2013) is suitable for investigating the resuspension of microplastics and sediment in a ‘model’ unidirectional flow.

Annular flumes have been used on remoulded and artificial beds previously, for example, by Araújo, Teixeira and Teixeira (2010, 2008) to investigate shear stress on sediment beds. Within the CMF, a model sediment bed composed of either sand or clay was set up, and a unidirectional flow applied. The use of a flume enables close replication of natural conditions in terms of stresses applied to the bed (Thompson *et al*., 2013). An annular flume gives a continual channel with an infinitely long flow (Waldschläger and Schüttrumpf, 2019b), ideal for investigating resuspension as there is no disruption to the flow.

The CMF provided consistent results in prior studies using environmental sediment cores (Thompson *et al*., 2013), so should also give consistent results on an artificial sediment bed. While an artificial sediment bed is not truly representative of a natural sedimentary environment, it does limit the variables which will change between experiments by removing biological activity, and thus enabling a determination of the source of any observed changes, i.e., the presence/absence of plastic within the system.

The mini flume generates a current by the use of four paddles, situated at the top of the water column (Thompson *et al.*, 2004). Velocity steps used were based on preliminary control runs of clay (for the clay experiments) and medium sand (used for all three sand sizes), which determined the approximate threshold of bedload motion based on visual observations. A step-wise series of velocity steps were decided upon, starting from two steps below the observed bedload movement, and going several steps beyond it. Velocity steps were arbitrary settings based on the digital stepping motor which controlled the speed of the paddles (Thompson *et al.*, 2004). They were either 15 minutes in length (clay) or 10 minutes in length (sand), with the length of the steps reduced for sand due to the increased number of velocity steps used.

The CMF has an Optical Backscatter Point Sensor (OBS), which measures turbidity, located at approximately 6 cm above the sediment bed, and an Acoustic Doppler Velocimeter (ADV), to measure velocity, located approximately 7 cm above the sediment bed. In addition to data from these two instruments, visual observations were made and several of the experiments were video recorded. To enable calibration of the OBS, 10 mL water samples were taken at a height of 10 cm above the bed to measure suspended sediment concentration (SSC).

Additionally, most experiments were video-recorded (Nixon Coolpix B500). The video footage enabled assessment of sediment and microplastic movement to support visual observations made during the experiments, and enabled more detailed observations to be made than would be enabled by sole use of the OBS.

Kaolinite clay, as used for the flocculation experiments, was used for one set of flume experiments. To prepare the bed, the flume was filled with a clay slurry, which was left to settle for three days to form a flat bed. Three sizes of marine sand were used, fine-, medium- and coarse-grained sand. Fine grained sand was sieved between 150 and 212 µm, medium sand between 300 and 425 µm, and coarse between 600 and 850 µm. Median grain sizes were: 180, 355 and 710 µm. For the coarse bed, an insufficient amount of sand was acquired through sieving, and so the bottom 2/3 of the bed was made from foam to achieve a sufficient bed depth to match previous experiments and maintain consistent flow conditions. For the clay experiments, only polypropylene fibres were used. These were the same fibres that were used for the flocculation experiments, with a virgin density of 0.88-0.92 g/cm^3. For the sand experiments, the polypropylene fibres were used, as well as poly vinyl alcohol (PVA) nurdles (as used by Ockelford *et al.* (2020). The nurdles had a median size (d_{50}) of 3.8 mm (3,800 µm), and a density of 1.33 g/cm^3 (Ockelford *et al*., 2020). The nurdles were used at an abundance of 1500 nurdles/m^2, which was visually lower than observations standardised by search time for citizen science rather than surface area (Fidra, 2021).Approximately the same concentration of fibres was used in the sand experiments (1,500 fibres/m^2), but a greater number were used in the clay experiments (approximately 10,500 fibre/m^2 for experiments with surface fibres, and 150,000 fibres/m^3 for experiments with buried fibres. Converted to weight, 1 g of fibres were used, or 52 g/m^2 and 750 g/m^3). For the clay experiments, two different experimental protocols were used: fibres were settled onto the surface of the sediment bed at the start of the experiment in the first protocol, and were mixed with the clay slurry to be buried within the bed for the second protocol. Fibres were not able to be started on the surface of the sand bed due to the higher starting velocity leading to immediate resuspension of the fibres, so were only used in 'buried plastic' experiments. They were buried under approximately 1 cm of sand prior to the start of the experiments. Nurdles were only used in the sand experiments, and were used for both 'surface plastic' and 'buried plastic' experiments.

Table 5-1 Substrate and microplastic combinations used in resuspension experiments

	Clay	Sand
Surface fibres	Yes	No
Buried fibres	Yes	Yes
Surface nurdles	No	Yes
Buried nurdles	No	Yes

5.2.3 Thresholds of Motion Calculations

Thresholds of motion were calculated according to the literature for sediment dynamics, for both sediment and plastic.

Equation 1 Threshold of Motion (Soulsby, 1997)

$$\overline{U}_{cr} = 7(\frac{h}{d_{50}})^{1/7}[g(s-1)d_{50}f(D_*)]^2$$

With:

Equation 2 Integration of Dimensionless Grain Size (Soulsby, 1997)

$$f(D_*) = \frac{0.30}{1 + 1.2D_*}$$

Equation 3 Dimensionless Grain Size (Soulsby, 1997)

$$D_* = [\frac{g(s-1)}{v^2}]^{1/3}d_{50}$$

With:

$\overline{U}_{cr}$ = threshold current speed (depth average)

h = height (*above the bed?)

d_{50} = median grain size

g = acceleration due to gravity

s = ratio of densities of grain and water, or $s = \frac{\rho_s}{\rho}$ where ρ_s = sediment density and ρ = water density

v = kinematic viscosity of water

Equation 4 Threshold Shields Parameter (Shields, 1936)

$$\theta_{cr} = \frac{\tau_{cr}}{g(\rho_s - \rho)d}$$

With:

τ_{cr} = threshold bed shear stress

g = acceleration due to gravity

ρ_s = grain density

ρ = water density

d = grain diameter

Shield's parameter (θ_{cr}) is plotted against the grain Reynold's number:

Equation 5 Grain Reynold's Number

$$u_{*cr} = \frac{\tau_{cr}}{\rho}^{1/2}$$

Equation 6 Modified Shields Parameter for Microplastic Particles (Waldschläger and Schüttrumpf, 2019b)

$$\theta^*_{c,i} = 0.5588\theta^*_c \left[\frac{D_i}{D_{50}}\right]^{-0.503}$$

With:

$\theta^*_{c,i}$ = critical Shields parameter of the microplastic particle

θ^*_c = critical Shields parameter of the sediment bed

D_i = representative microplastic particle diameter

D_{50} = median grain size of the sediment bed

Equation 7 Depth Averaged Current Speed (Soulsby, 1997)

$$\overline{U} = \frac{1}{h}\int_0^h U(z)dz$$

With:

$\overline{U}$ = depth-averaged current speed

h = water depth

$U(z)$ = current speed at height z

z = height above sea bed

And:

Equation 8 Current Speed at Height z (Soulsby, 1997)

$$U(z) = \frac{u_*}{\kappa} \ln\left(\frac{z}{z_0}\right)$$

With:

u_* = friction velocity

z_0 = bed roughness length

κ = von Karmen's constant = 0.40

5.3 Results

5.3.1 Flocculation

For all combinations of sediment and salinity, no aggregation or settling of the plastic fibres was observed. Settling of the kaolinite was observed, with a clear layer of clay at the base of each settling column at the end of the experiments.

Fibres were left in a salt water solution at room temperature for several weeks, following which sinking and aggregation of some fibres (approx. 5-10%) was observed.

5.3.2 Resuspension

5.3.2.1 Clay

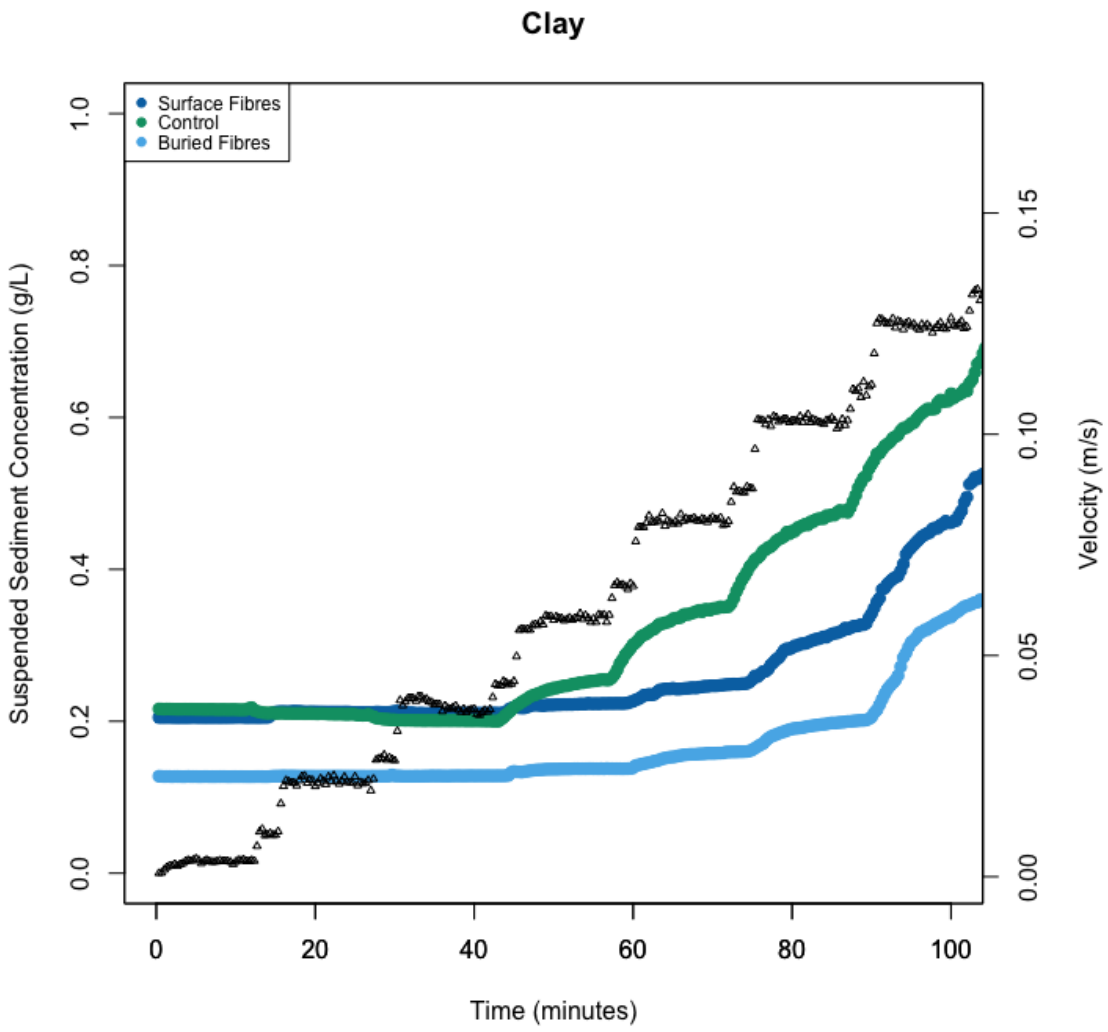

Figure 5-1 Calibrated suspended sediment concentrations and velocity (clay)

Triangles indicate measured velocity (m/s).

Figure 5-1 shows the calibrated suspended sediment concentrations, as measured by the OBS. Initial sediment movement occurs at the same time point in all three experimental runs, and follows a very similar pattern for the two containing plastic fibres. Initial sediment transport by way of suspension is apparent at 45 minutes, or at the fourth velocity step. Following this, there is an increase in suspended sediment in each experiment, which is steeper for the control run (no plastic) than for the two experiments which contained plastic fibres.

Plastic behaviour was observed, and where possible, recorded on video. Fibres on the surface of the clay bed moved immediately as suspended load at a current velocity of 0.02 m/s. All the fibres which were on the surface were in suspension at a velocity of 0.08 m/s. Once fibres were suspended, they remained in suspension and were not deposited on the bed over the remainder

of the experiment. The buried fibres were contained within the clay slurry, and thus, were only eroded when the overlying clay was eroded. No fibres were seen over the course of this experiment, although clay was eroded and moved into suspension. It is likely that the fibres were buried too deeply within the clay bed to be eroded over the course of the experiment.

5.3.2.2 Sand

An instrumental error occurred during the course of the sand experiments, resulting in only a small portion of the ADV data being usable. Therefore, velocities used through these results are derived from a calibration of the data that was of an acceptable quality. This is the case for all sand sizes, with significant deviation from the input pattern of velocity steps with passing time shown in the ADV data. Velocity steps were at ten-minute intervals, rather than the 15-minute intervals used in the clay experiments, to reduce the total length of the experiment, as more velocity steps were used for the sand experiments to better investigate the wider range of grain sizes used for the sand experiments. Velocities as measured by the ADV or as calibrated from accepted ADV data at a height of 7 cm above the bed were converted into bed shear stress (τ_0) and depth-averaged current speed ($\overline{U}$).

5.3.2.2.1 Fine Sand

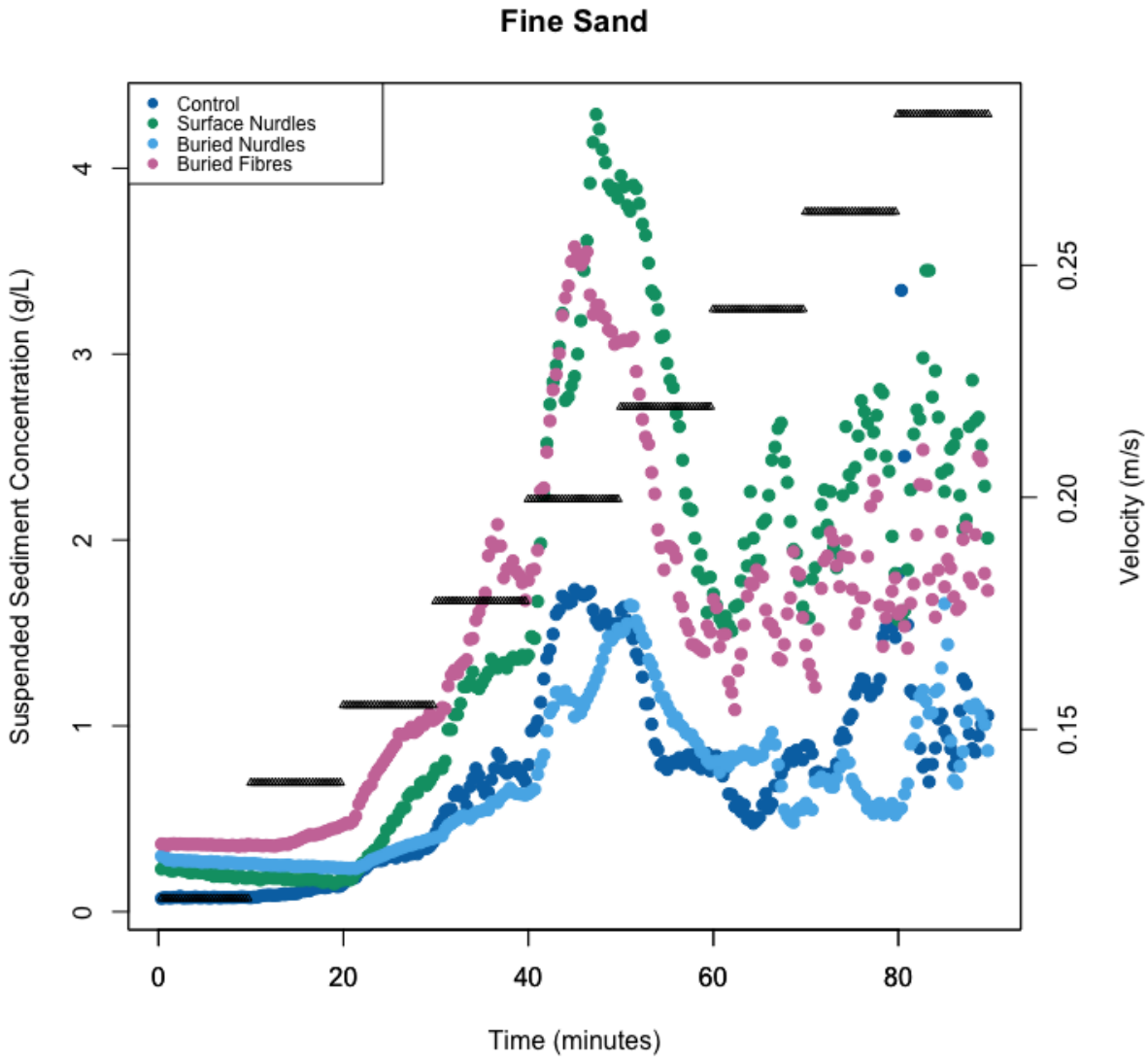

Figure 5-2 Calibrated suspended sediment concentrations and velocity (fine sand)

Triangles indicate calibrated velocity (m/s).

Suspended sediment motion occurs at the same time point in all four experiments (Figure 5-2) during the third velocity step (21 minutes), at a calculated bed sheer stress value of 0.1340 Nm^{-1}. Bedload motion of sediment was observed visually during the second velocity step (bed shear stress of 0.1067 Nm^{-1}). The suspended sediment concentration increases until 45 minutes (5^{th} velocity step, bed shear stress of 0.2217 Nm^{-1}. Following this time point, the OBS data appears to show a fall in suspended sediment concentration, which was not supported by the suspended sediment samples taken for calibration, nor by visual observations. While at a lower temporal resolution, the SSC samples taken at 9 minutes into each velocity step also support a threshold of motion during the third velocity step. The SSC data shows a continued rise in suspended sediment

as the velocity increases throughout the course of the experiments, for all protocols, with the steepest increase occurring after the 5th velocity step. This rapid increase in suspended sediment concentration – visible in the data from the water samples – was also visually observed, with large amounts of sediment being moved into suspension from the top of the bedforms in the flume, which were ripples. Smaller ripples were observed following the start of sediment transport by bedload, during the second velocity step.

Fibres were observed to be suspended immediately on exposure by bedload movement of overlying sediment, and were in suspension before the fine sand was in suspension (fibre suspended during the second velocity step, bed shear stress of 0.1067 Nm^{-1}). They were rapidly moved into the top of the water column, and remained suspended for the remainder of the experiment. All fibres were removed from the sediment bed over the course of the experiment and recovered from the surface of the water column after the experiment was ended and the flume stopped. Nurdles on the surface moved at a similar time to the sediment, although only a few nurdles moved initially. Sliding of nurdles was observed during the second velocity step, but a large portion of the nurdles were initially buried if they were on the surface at the start of the experiment by sediment moving as bedload. Buried nurdles were exposed through the formation of sediment bedforms (ripples) during the third velocity step (bed shear stress = 0.1340 Nm^{-1}), and the majority moved into the lee of ripples and remained circulating in these areas (Figure 5-3 A). Some nurdles began saltating for short time periods along the sediment bed during the third velocity step, and by 40 minutes, during the fifth velocity step, nurdles were observed moving by saltation (Figure 5-3 B), moving further and higher in the water column than previously observed. Although 29 nurdles were in the flume, only around half of these were ever observed on or above the sediment bed at any one time, whether they started on the sediment surface or below it.

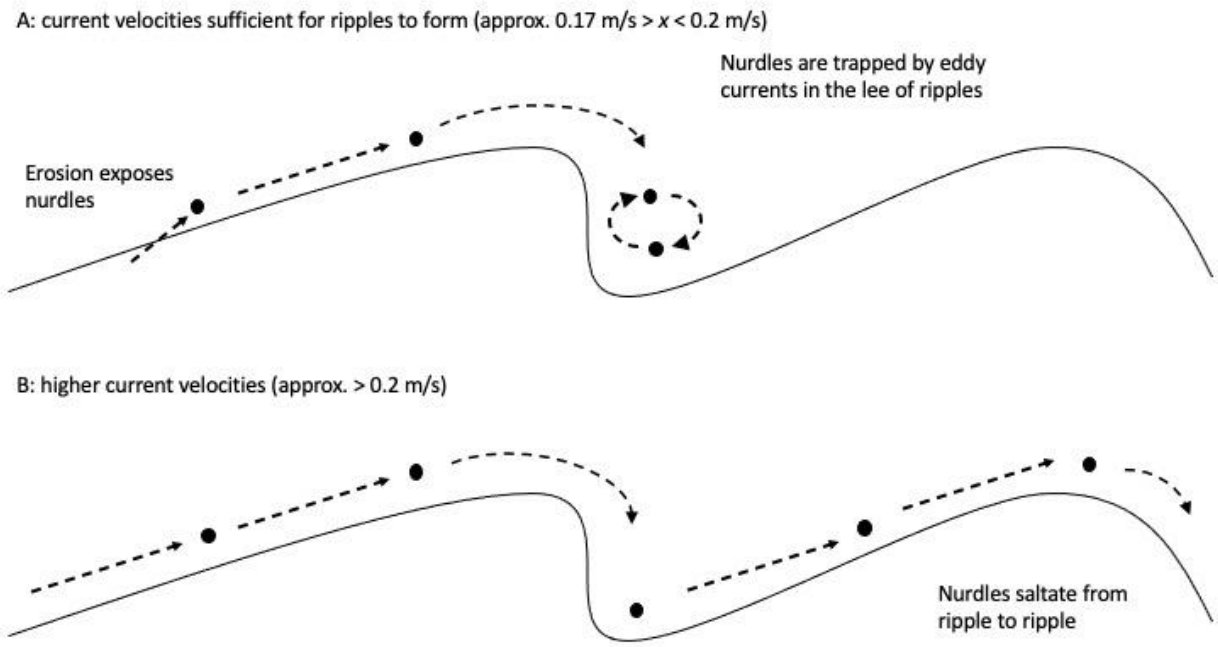

Figure 5-3 Movement of nurdles and interaction with bedforms at different depth averaged velocities

A: current velocities are high enough to form bedforms (ripples). Ripples are exposed by erosion on the stoss side of the ripple, moved by bedload into the ripple trough and retained there by eddy currents, occasionally being buried by sediment deposition.

B: current velocities are high enough that saltation of the nurdles occurs. Nurdles 'hop' from trough to trough, with decreased eddy current influence allowing for this movement and reduced burial of nurdles by sediment.

5.3.2.2.2 Medium Sand

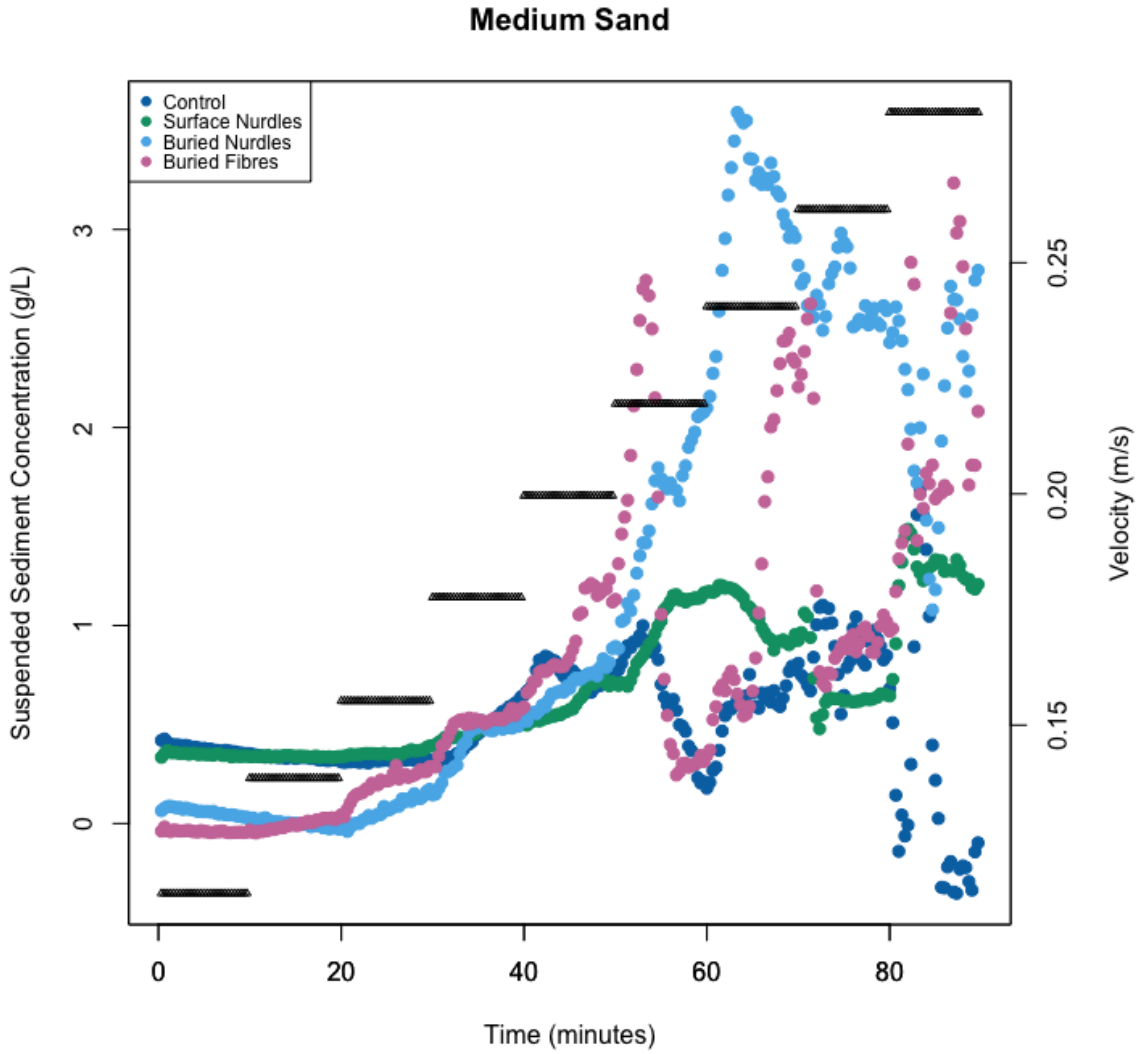

Figure 5-4 Calibrated suspended sediment concentrations and velocity (medium sand)

Triangles indicate calibrated velocity (m/s).

Suspended sediment motion occurred during the same velocity step (third) during all four medium sand experiments, which equated to a bed shear stress of 0.1627 Nm^{-1}. The trends shown in the OBS data, and the suspended sediment samples differ, but do both agree that an increase in suspended sediment is seen during the third velocity step and is indicative of erosion of the bed. Bedload transport of sediment was visually observed one step earlier (second velocity step, bed shear stress = 0.1296 Nm^{-1}). Ripples began to form during the third velocity step (bed shear stress = 0.1627 Nm^{-1}).

Nurdles were, if they began the experimental run on the surface, initially buried by sediment moved as bedload. Some began sliding during the second velocity step (bed shear stress: 0.1296 Nm^{-1}). Buried nurdles were uncovered during the third velocity step by sediment movement, and began to slide along the bed. Saltation of nurdles was observed beginning from the third velocity

step (bed shear stress: 0.1627 Nm^{-1}), and was initially focused in the lee of ripples, before nurdles began to move longer distances after the fifth velocity step (bed shear stress: 0.2692 Nm^{-1}).

Fibres, which were only used in buried plastic experiments, immediately moved into suspension once uncovered by transport of sediment above them. Once moved into suspension, they remained in suspension high in the water column or at the surface of the water, and remained there throughout the experiment. Nurdles were first observed to move by bed load sliding during the third velocity step (bed shear stress 0.1627 Nm^{-1}). The first movement of nurdles by saltation, when nurdles began bouncing, occurred during the fifth velocity step (bed shear stress of 0.2692 Nm^{-1}). No nurdles became fully suspended during the course of the experiments, and approximately 1/2 - 2/3 of the nurdles were buried (either at the start of the experiment, or during the first few velocity steps by moving sediment) and were not in transport at the end of the experiment.

5.3.2.2.3 Coarse Sand

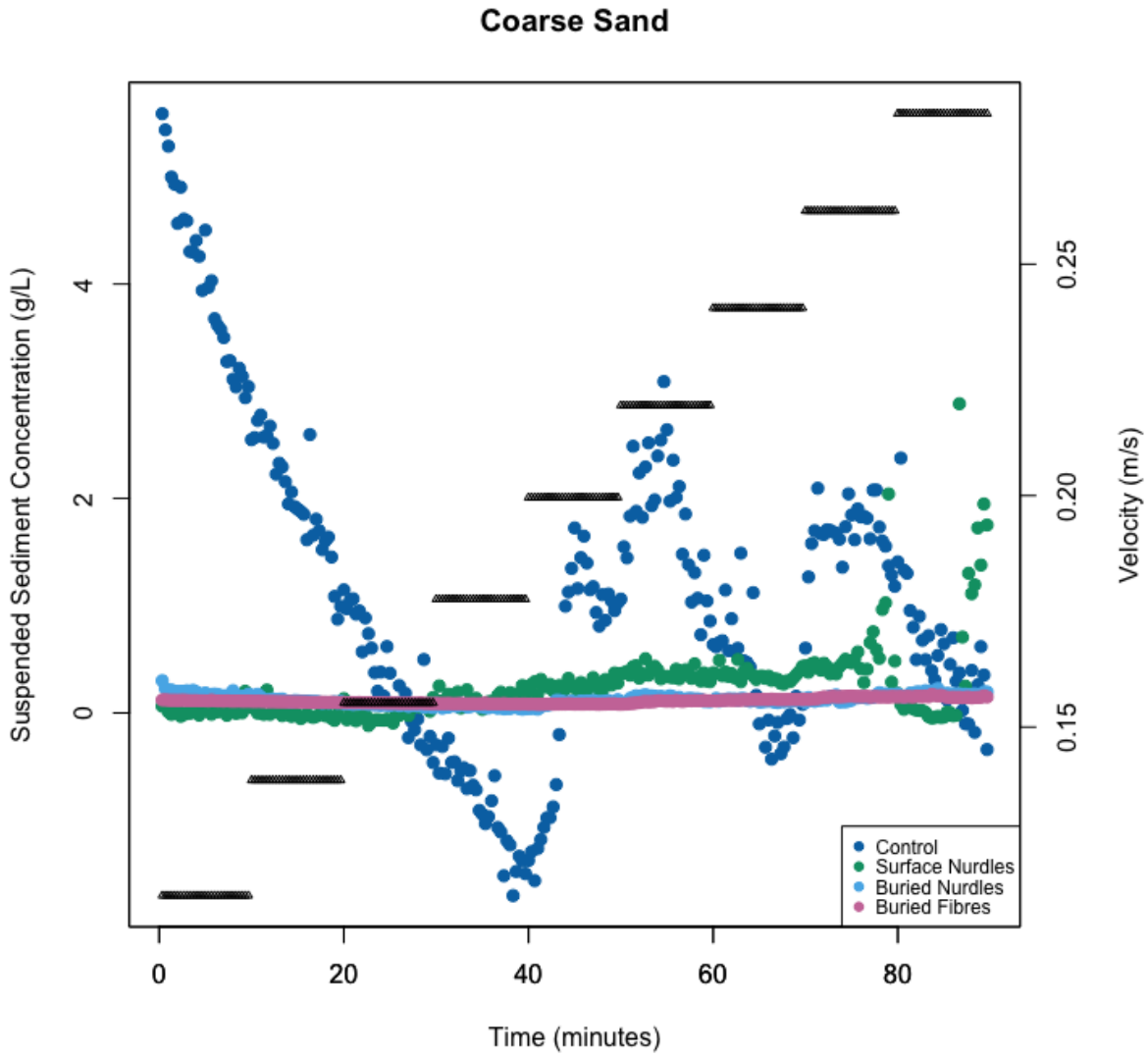

Figure 5-5 Calibrated suspended sediment concentration and velocity (coarse sand)

Triangles indicate calibrated velocity (m/s).

OBS data for this series of experiments was not as expected, and calibrations between the OBS data and the suspended sediment samples taken every 10 minutes had R^2 values ranging between 0.1361 and 0.6915 and for most experiments (coarse sand control, coarse sand surface nurdles, coarse sand buried fibres) produced negative sediment values. As the OBS measurements rely on sediment in the water column to obtain a measurement, lower suspended sediment concentrations as seen with the coarse sand made it more difficult to obtain a robust measurement with this sediment type. As the coarse sand was not suspended, it was not detected by the OBS, leading to these poor-quality measurements. The water samples taken for calibration show large variation and no consistent trends in suspended sediment, likely as there was little suspended sediment. Suspended transport of sediment was observed visually after 40 minutes, in the fifth velocity step (bed shear stress = 0.3281 Nm^{-1}), in both the control run and the

buried fibres run. In the two studies with nurdles, the sediment began to move during the fourth velocity step (so one velocity step down from the other two runs, a bed shear stress of 0.2598 Nm^{-1}). This may be within the variability of the measurements, but may also be a lowered threshold of movement due to the presence of the nurdles. Bedforms (ripples) were observed forming from the fourth velocity step onwards (bed shear stress = 0.2598 Nm^{-1}).

As in prior experiments, surface nurdles were first buried by bedload sediment transport. Buried nurdles were buried more shallowly than in the medium and fine sand experiments, due to the limitations of the amount of sediment available. Nurdles moved in bedload at 40 minutes, and mostly remained in the turbulent flow downstream of the large ripples that formed. Fibres were seen in suspension before sediment movement is observed, and were all in suspension after the sixth velocity step (bed shear stress = 0.3968 Nm^{-1}). They were retained within the sediment bed until overlying sediment was moved, and then were swiftly eroded.

5.3.3 Calculated Thresholds of Motion

5.3.3.1.1 Soulsby (1997):

Thresholds of motions were calculated according to Soulsby (1997)and are as follows:

Fine sand: 0.177 m/s

Medium sand: 0.181 m/s

Coarse sand: 0.206 m/s

Nurdles: 0.181 m/s

Fibres: 0.000253 m/s

5.3.3.1.2 Shields (1936):

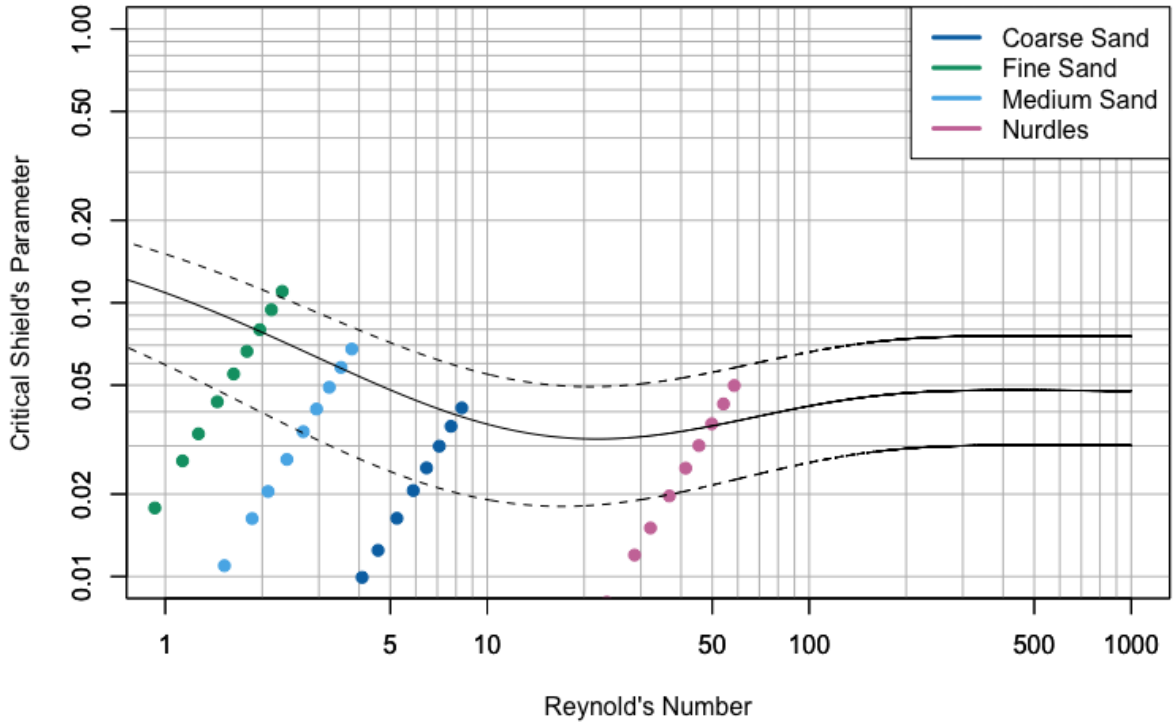

Figure 5-6 Shield's diagram

Shield's diagram is a curve based on experimental erosion behaviour of natural sediments obtained by Shields (1936). It divides behaviour into "motion" (above the curve) and "no motion" (below the curve) (solid line), but also can be plotted as an envelope (dashed lines).

5.3.3.1.3 Waldschläger and Schüttrumpf (2019b) (for nurdles only):

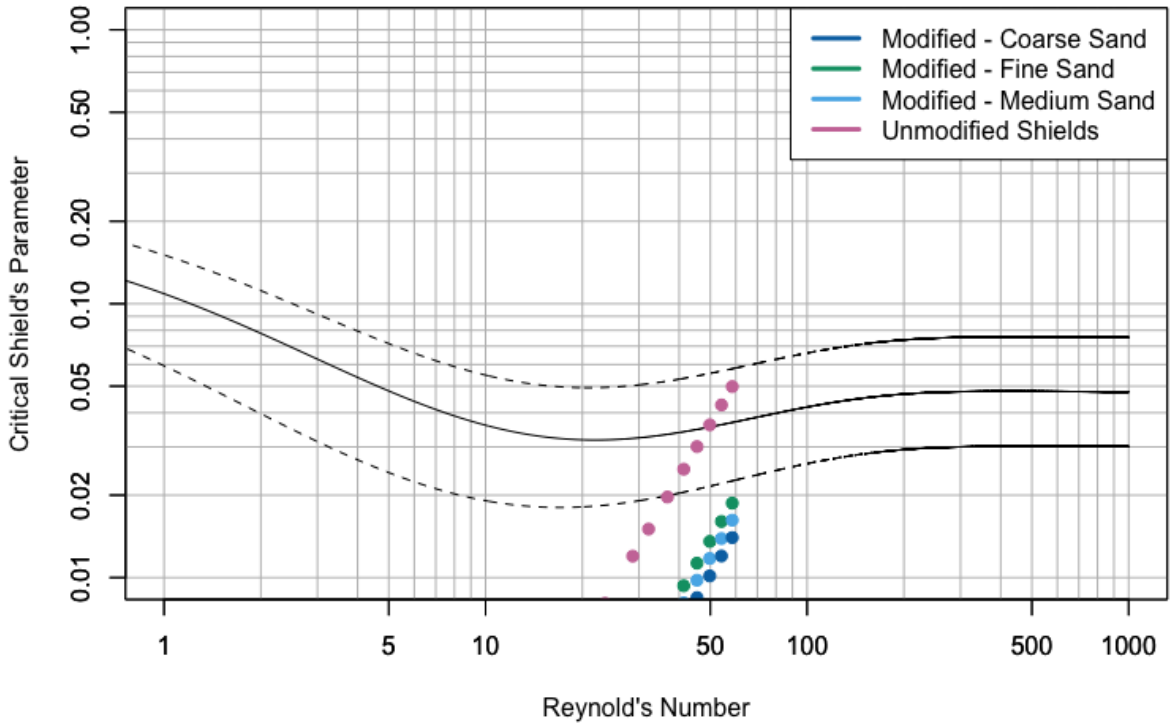

Figure 5-7 Shields diagram, with modified Shields parameters for the PVA nurdles calculated from Waldschläger and Schüttrumpf (2019b)

Waldschläger and Schüttrumpf (2019b) modified the equation for the Critical Shield's Parameter for microplastics, but did not modify the location of the curves.

5.4 Discussion

The flocculation experiments conducted were limited in scope and scale, but showed that new microplastics that are of a density lighter than water will float, until weathering may decrease their buoyancy and cause them to begin to sink. As a result of this, microplastics may travel a long way from their source before they lose sufficient buoyancy to sink below the surface and be deposited. Microplastics have been found a large distance from sources, in remote regions of the ocean such as in the Southern Ocean (Suaria *et al.*, 2020), and the slow sinking of buoyant particles is an explanation for this. This also has implications for the risks to riverine environments posed by microplastics. If buoyant microplastics travel a large distance from source before sinking due to decreased buoyancy as a result of weathering, then the areas to which they pose a risk will differ. As they will be transported out of their source region before sinking, they will not pose a risk to the benthic and pelagic environments in this source region. This may differ depending on how weathered microplastics are when they enter the watercourse, which may depend on their origin and their path to the watercourse. For example, a nurdle released as a result of a spillage

during transport will be less weathered than a fibre that has entered the watercourse as a result of runoff from a field with applied sludge from waste water treatment, and therefore may travel further before becoming weathered sufficiently to aggregate or sink.

In combination with the flume studies on these same fibres, these light microfibres are likely to settle only in regions with a slow flow and little turbulence. Fibres, once resuspended in the flume, were not redeposited and were transported high in the water column, at or near the surface. Following the cessation of the experiment, fibres remained at the surface, and did not sink once the flow had stopped. As such, this has implications for regions at risk from microfibres, namely that they will be regions with low energy, such as deep pools in rivers, mudflats or lagoons. However, the experiments detailed in this chapter used 'new' or nearly new microfibres, generated from little-used rope, and these are similar to very few microfibres in the environment. While 'new' microfibres are being constantly released to the environment, they are rapidly weathered and changed by physical, biological and chemical processes occurring in the environment – their characteristics including their surface charge is constantly changing (Galloway *et al*., 2017). Therefore, the processes observed here may differ for weathered particles, and may differ as microplastics age in the environment.

The flocculation studies (5.3.1) showed little, if any, salt-mediated aggregation of (large) microplastics. The fibres used were large microplastics, >3 mm in length, and their size may be the reason why no aggregation was seen. Smaller microplastics may aggregate due to salt flocculation, but this was not seen in the microfibres used in the experiment. The results of these experiments also suggest that other factors may be of greater importance to causing microplastics to aggregate, such as biologically-mediated aggregation.

In contrast to the experiments carried out in this study, Andersen *et al.* (2021) used smaller microplastics (63-125 μm) and observed microplastics incorporated into flocs with cohesive sediment (<20 μm). The microplastics used in the Andersen study were much smaller than the large microplastics used in this study, and this size difference may be why no flocculation of the nylon fibres used in this chapter was observed. Increases in microplastic settling velocity were observed by Andersen *et al.* (2021), though this again was not observed in this study. Again, this could be due to the size of the nylon fibres preventing flocculation.

One comparison that could potentially be made between these experiments, using microplastics and a cohesive sediment, and studies looking at mixtures of cohesive and non-cohesive sediments. With fine sand and cohesive sediment, this mix of sediment has been shown to produce flocs that have differing characteristics to their component parts (Manning *et al*., 2013). Although integration of microplastics into flocs is not shown in the experiments carried out here,

it has been observed in other experiments using different microplastics (Andersen *et al.*, 2021), and it could have implications for sediment transport processes as well as microplastic transport processes.

While the first half of this chapter looks at deposition of microplastics, the second half looked at the resuspension of microplastics. When referring back to the diagram of the estuarine filter for microplastics (Figure 1-2), we see that the estuarine filter is formed by the deposition and resuspension of microplastics, and its efficiency is determined by the ratio between these two processes. Understanding both processes is therefore vital to understanding if there is an estuarine filter, and how it functions, and how it might balance in favour of one or the other and how that might vary in time and space.

The resuspension of microplastics moves them back into the water column and transport, and may enable their outflow to coastal seas, and further movement into, for example, deep sea sediments, or the open ocean. Understanding how and when this might happen is key to managing the risk posed by microplastics. The experiments carried out in this chapter are a key starting point to understanding the velocities at which microplastics might be removed from sediments, and the processes surrounding this, such as how they interact with bedforms. Within the sediment bed, weathering of microplastics may be slowed, due to lowered mechanical abrasion (compared to moving, say, in suspension or as bedload). Further work is warranted into the modification of microplastics contained within sediments, including the effects of sediment inclusion on the weathering and fragmentation of plastic debris.

Initially, examining how sediment movement occurred, and how it varied from sediment dynamics equations is a good starting point to understanding microplastics resuspension, and interaction with the surrounding sediment matrix.

As a regression was not used to calculate the threshold of motion, the observed threshold can be said to occur between the observed velocity, and the step above it, as thresholds are often ‘envelopes’ rather than a strictly defined value at which erosion will occur. Soulsby’s (1997) calculations for the threshold of motion give a velocity threshold (depth averaged) (5.3.3.1.1). Depth averaged velocities were calculated for each velocity step and bed used. Fine sand moved a velocity step lower than would be expected (during the second velocity step) from Soulsby (1997), with the threshold calculated (0.177 m/s) being above the depth-averaged velocity for the 3rd step (0.172), suggested a threshold velocity between 0.15 and 0.17 m/s (5.3.2.2.1). Similarly, medium sand was observed to move as bedload during the second velocity step (0.153 m/s), compared to a suggested threshold of 0.181 m/s (which would have occurred between velocity steps 3 and 4) (5.3.2.2.2). Coarse sand was observed to move by bedload during the 4th velocity step (0.193 m/s),

which aligns with the calculated threshold from Soulsby (1997) (0.206 m/s), which would have occurred during the 4th or 5th velocity steps (5.3.2.2.3). For fine and medium sand, while the observed threshold of motion was lower than predicted, no observed changes in the threshold were observed between the control experiments, and those which contained plastics. The only sand substrate for which a change in sediment movement is seen is coarse sand, which was observed to move as bedload at a lower velocity when nurdles were either on the surface or buried in the sediment. The implications of plastic altering the erosion threshold of sediment could be significant. With microplastics ubiquitous in many sediments and locations, a decreased erosion threshold would potentially lead to much greater sediment transport than has previously occurred. In addition, large concentrations of microplastics have been recorded in coastal beach sediments (e.g., 27,606 items/m^2 (Lee *et al*., 2013)), where a decreased erosion threshold in the face of rising sea levels (Solomon *et al*., 2007) and increased storm activity due to global warming (Mousavi *et al*., 2011) would lead to increased coastal erosion. However, a potential increased erosion threshold was observed for the clay experiments, contrasting previous studies looking at intertidal mud stability with added plastic fibres (Halliday, 2013; Stead, 2017), though both these studies used higher concentrations of added plastic fibres than was used in this chapter. If an increased erosion threshold is seen at low fibre concentrations, this also has implications for erosion at contaminated sites, but perhaps less concerning. Certainly, this observation justifies further research into the effects of microplastic inclusion on sediment erosion.

Plastic behaviour was also observed during the resuspension experiments. Understanding plastic behaviour and transport is key to understanding the fate of plastic, and to enable accurate assessment of exposure and risk in various environments. Though only two types of microplastic were used, and both were considered “large microplastics” (in the size range 1 – 5 mm), they differed significantly in behaviour and show that when developing models for microplastic transport, transport will differ drastically depending on microplastic characteristics. Fibres in these experiments, once suspended, moved immediately into suspension high in the water column. In contrast, nurdles moved for an extended period of time as bedload and by saltation, and did not move in suspension at the velocities used. As such, fibres will not remain for long periods of time in riverine sediments, and are more likely to be transported through estuaries and out to sea. Nurdles, on the other hand, are more likely to be retained in river sediment, potentially buried by sediment movement at lower current speeds, but a proportion of them could be washed out and transported downstream and through estuaries given high enough flow speeds, such as may occur during storm and flood events. The differing behaviours of different types of plastic has been shown in field studies, where following a flood, the microplastic composition of riverine sediments changed, with fragments reduced and microbeads increased

(Hurley *et al*., 2018). This further supports considering a wide range of microplastic types when assessing the transport and fate of microplastics.

It is not only the microplastic type which has been observed to influence the velocity of flow at which microplastics began to move. For fine sand, nurdle bedload sliding was observed at the third velocity step, of 0.17 m/s, but in coarse sand, this behaviour was observed a velocity step up, 0.2 m/s. This suggests that the sediment bed properties also influence the movement of microplastics contained within the bed. The effect of the grain size of the sediment bed on erosion of microplastics was also observed by Waldschläger and Schüttrumpf (2019b).

A limited number of previous studies have conducted transport experiments on microplastics, and compared these to existing equations for sediment transport. Khatmullina and Isachenko (2017) compared settling velocities of three types of microplastic to modelled settling velocities, and found that while some were well modelled, others were less so. In particular, they found that "fishing line cuts" – which can be described as fibres – deviated significantly from equations. The movement of fibres in particular was not well investigated in this chapter, as the suggested threshold of motion for fibres was significantly lower than the first velocity step used for the sand study and the clay study. However, fibres were not observed to move till the second velocity step (depth-averaged velocity of 0.02747 m/s), which was above the suggested velocity from Soulsby (1997) (0.000253 m/s). This suggests a significant deviation from the existing sediment-based data for some shapes of microplastics, although this may be influenced by the cohesive bed.

Critical shear stresses for the movement of different types of microplastics have previously been determined by Waldschläger and Schüttrumpf (2019b), also using an annular flume, enabling a good comparison to this chapter. A similar approach was taken here, in which the equation from Shields(1936) was used to calculate a threshold of motion. Waldschläger and Schüttrumpf (2019b) also produced a modified Shields equation for microplastics, which again was calculated to compare its suitability compared to the original sediment-based Shields equation. Both Shields and Reynolds numbers were calculated for the nurdles, and the results plotted. The results of this suggests that for the PVA nurdles used in this experiment, their movement into saltation is relatively well-modelled by sediment equations. For the fibres used in this chapter, which were composed of polypropylene, using the density of the virgin polymer gave a negative Shields number. Aged polypropylene fibres were used as they were negatively buoyant, suggesting they had increased in density during the weathering process. This also raises the question of how to best apply transport models to microplastics, which are known to be rapidly altered in the environment (e.g., by biofouling (Kaiser *et al*., 2017)). Fibres have been observed to deviate from existing transport equations – Khatmullina and Isachenko (2017) found that of three tested types

of microplastic (cylinder, spheres and lines), the settling velocities of the cylinders and spheres were well-modelled by existing semi-empirical sediment equations, but lines (or fibres) made of fishing line were less so. Their non-spherical nature and the varying density of microplastics in the environment support the need for more investigation into the transport behaviour of microplastics, particularly microplastics of non-spherical shapes such as fibres, or films. This is particularly important given how common fibres are in environmental samples (Gago *et al*., 2018).

Equations for the threshold of motion were also calculated following the equations of Soulsby (1997) and compared to the observed thresholds. The observed thresholds differed slightly from the calculated threshold, for both nurdles and fibres. Fibres remained on the clay bed for an order of magnitude greater than their predicted erosion threshold, and nurdles first moved at velocities both above and below the calculated erosion threshold, though with only minor differences. The nurdles had a predicted threshold of motion at 0.181 m/s, and moved between 0.17 and 0.2 m/s, although the higher threshold at 0.2 m/s may be because the velocity jumped between 0.17 and 0.2 m/s due to the experimental set up. This similarity to sediment equations has significant implications for the ability of tracking nurdles and modelling their fate. However, these sediment equations are based around sediment particles that are spherical in nature, and particularly for fibres, their shape deviates significantly from this 'ideal particle'. Therefore, the use of these equations to predict fibre movement, as well as other categories of microplastics not used in this chapter including films and fragments, is likely not realistic of their actual transport in water bodies. Therefore, direct measurement of microplastic movement is recommended to close knowledge gaps in understanding the transport of plastics vertically through the water column and horizontally through rivers, estuaries and oceans.

Nurdles, which are often found in only small quantities in comparison to other shapes of microplastics, can still be found in large quantities in the environment (e.g., >1,000 pellets/m^2 found on beaches in Malta, (Turner and Holmes, 2011)), and may be released in large quantities in one location as the result of a spillage. Whilst not entirely spherical, they deviate less from sphericity than other shapes of microplastics such as fibres or films, and this may be why they more closely followed sediment transport equations. Being able to apply sediment models to nurdles could enable a more efficient and reactive response to spillages and accidental releases of nurdles. Fibres did not follow the equations applied to them. This supports the conclusions of Waldschläger and Schüttrumpf (2019b), that theories from sediment transport may not be entirely transferable to microplastic transport.

Waldschläger and Schüttrumpf (2019b) use a relationship between the ratio of grain sizes and the ratio of Shield's parameters for plastic particles and sediment particles to determine if their

modified Shields is applicable (Figure 5-8). These ratios were plotted for the nurdles and types of sand used, and produced ratios that deviate from the majority of plastic/sediment combinations used by Waldschläger and Schüttrumpf (2019b). The deviation of the nurdles/sand combinations – for which the sediment was mostly finer grained than that used by Waldschläger and Schüttrumpf (2019b) – suggests that the use of the modified Shields parameter may not be applicable for this work, and may not be applicable for sediment beds finer than coarse sands or gravels. Indeed, all of the velocity steps were calculated using the modified Shields, including the velocity steps at which movement was observed. Only the higher (6-9th) velocity steps were able to be plotted and all suggest no nurdle motion, which was not the case, as bedload motion of nurdles was observed during the second velocity step, and saltation of nurdles was observed during the fifth velocity step (Figure 5-7). Shields' parameter was also calculated following Shields (1936) and plotted for all sediment bed types and nurdles, and shows a much better prediction of nurdle motion compared to the modified Shields equation.

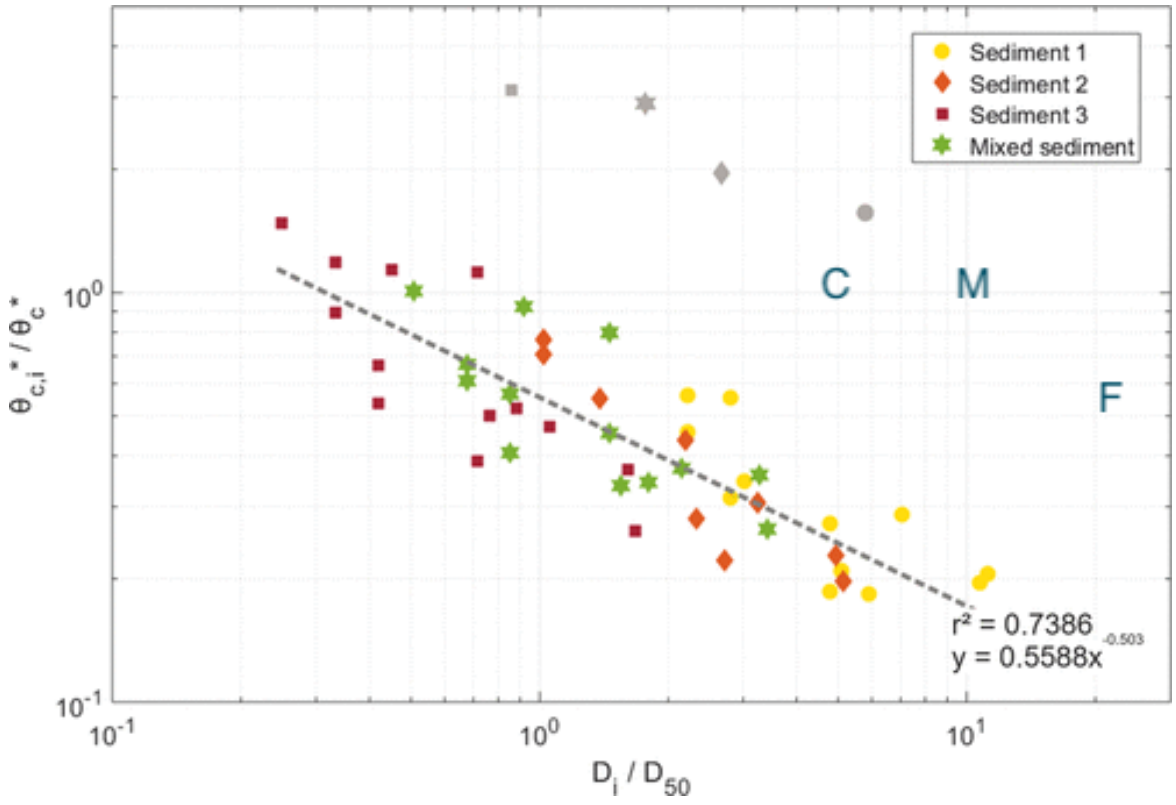

Figure 5-8 Ratios of Shields parameters for sediment and microplastics and particle diameter, from Waldschläger and Schüttrumpf (2019, Figure 7)

(C = coarse sand; M = medium sand; F = fine sand; all plotted with nurdles as the representative microplastic).

At low velocities, nurdles were buried by moving sediment. Burial of microplastics, and their movement within the sediment bed, is not a topic that has received a lot of attention, but has

implications for microplastic budgets. The burial of microplastics within rivers reduces the outflow of microplastics to coastal seas and the global ocean, but increases the risk to benthic habitats in rivers. While studies have shown burial of microplastics within the sediment bed by bioturbation (e.g., Näkki et al., 2017), little investigation has occurred into the burial of microplastics by sediment transport. However, the observed by burial of microplastics by moving sediment suggests that for most of the year, when river flow is low and not increased by storm events or rainfall, river sediments will be a sink for microplastics. In terms of estuaries and coastal areas, these low current velocities will occur during slack water periods, or when there are periods of low wave activity. As such, estuaries and other intertidal areas may be sinks for part of a tidal cycle, and sources for another as tidal currents vary in strength. Tidal asymmetry within estuaries such as Southampton Water may alter the role of the intertidal dependent on tidal current strength.

However, whether regions are sources or sinks is also dependent on the characteristics of the microplastics. Nurdles, which were dense and not buoyant, sank quickly when added to the flume, remained stationary when on the surface of the sediment at low velocities, and were buried by moving sediment and in some cases, remained buried even with significant sediment erosion and movement. Fibres, which were light and buoyant, sank slowly, and could not be used in experiments where they began at the sediment surface, because they were immediately mobilised by the velocities used in the sand studies. Therefore, the role of river sediments as a sink for microplastics is dependent on their characteristics, and also on the local hydrodynamics. Though fibres were moved at very low velocities, it is possible that in very slow flowing areas of the river, such as pools, this velocity may be achieved. Nurdles, and other dense, non-buoyant microplastics, are far more likely to be retained by river sediments, buried at lower velocities, and potentially remobilised during high flow periods. This also brings up the idea of microplastics as a legacy contaminant. Once buried, microplastics may remain with the sediment for an extended period of time, and there, may pose no risk. However, given a sufficiently large event to erode, or move sediment, perhaps through storms or through human activity such as dredging, these microplastics may then be moved back into suspension and transport. Other legacy contaminants include heavy metals and PCBs – chemicals that have been shown in some studies to accumulate on microplastics (Velzeboer *et al*., 2014). This again will increase the risk posed by buried microplastics.

In addition to the implications for microplastic budgets, burial of microplastics transfers their risk to a different compartment. Organisms that live within the sediment bed and feed within the sediment bed may not be at risk from suspended microplastics, but will be at risk from buried microplastics.

However, microplastics may not only be buried. Buried and surface-deposited microplastics can be remobilised by flooding. This is shown in this study and in previous studies, both laboratory (Ockelford *et al*., 2020) and field (Hurley *et al*., 2018) based. Field studies show a reduction in microplastics in riverine sediments following a period of heavy flooding and high river flows (Hurley *et al*., 2018). Ockelford *et al.* (2020) used a differing velocity profile to this study, with a flood wave which peaked and receded, whereas this study used step velocities which peaked and did not then fall. Therefore, this study gives less information on how the microplastics will behave within an entire flood hydrograph, but will indicate how increased flows will move and remobilise sediments.

Microplastics are a suite of contaminants (Rochman *et al*., 2019), and are incredibly diverse. Many plastic polymers have been developed – and are still being developed – and a huge range of additives are included in plastics. Microplastic shapes and sizes vary, and are likely constantly changing due to further fragmentation. As such, assuming they have the same behaviour is a vast oversight, and will lead to inaccurate estimations of microplastic fate. This study, with vastly differing behaviours of microplastic fibres and nurdles, shows the importance of considering the wide variety of microplastics that are in the environment. While this is incredibly difficult, considering how many important characteristics change, it is important not to treat microplastics as one pollutant that behaves in the same manner.

5.5 Conclusions

A series of initial experiments were carried out into flocculation and resuspension of large microplastics. These revealed that microplastics vary in behaviour, dependent on their characteristics and age. Settling of microplastics is increased or enabled by the aging of microplastics, which suggests that, particularly more buoyant microplastics, may travel far from their source before sinking. This may explain why microplastics are seen even in remote regions of the oceans, such as around Antarctica where the sources of microplastics are few.

Resuspension of microplastics was investigated in more detail than flocculation, and revealed that studying how microplastics are resuspended is key to understanding their fate. Microplastics were shown to be resuspended from sediment beds at velocities similar to those which caused transport of a finer-grained sediment, suggesting that sediments in rivers and estuaries may not be final sinks of microplastics. However, microplastics were observed to be buried by sediments at low velocities, and remain buried even during high flow periods with large amounts of sediment erosion, supporting the interpretation of rivers and estuaries as sinks of microplastics.

Inclusion of microplastics within sediments potentially altered erosion thresholds. For coarse sand, the sand began moving a velocity step earlier with nurdles included in the bed compared to the control; and for clay, a lower rate of suspension was observed when microfibres were included in the sediment bed. Future work is necessary to investigate if plastic inclusion has effects on sediment stability, as this has significant implications for sediment budgets globally. Additionally, comparisons were conducted between microplastic behaviour, and equations developed from sediment transport; as well as modified sediment transport equations. These show deviations from the observed behaviour of microplastics in this chapter, suggesting that additional work is required to modify or develop behaviour models for microplastics, which are a diverse suite of contaminants.

Chapter 6 Discussion

This work aimed to further the understanding of the fate of microplastics in estuaries by initially identifying processes acting on microplastics in estuaries. To this end, processes which form the 'estuarine' filter were identified, focussing on the potential for utilising knowledge of other suspended particulates to further understanding of microplastics in estuaries. In particular, given the aim to understand how these processes act in Southampton Water, sampling was focused on sites within Southampton Water and consideration is given to how this increases understanding of the fate of microplastics in Southampton Water as well as estuaries on a global scale.

The 'estuarine filter' is a concept applied to the retention of certain suspended and dissolved particulates within estuaries, including sediment (Biggs and Howell, 1984; Schubel and Carter, 1984) and heavy metals (Cundy *et al*., 1997). It has been proposed that in addition to these particulates, microplastics, a rapidly emerging suite of contaminants, are also retained within estuaries via a series of processes enhancing deposition. Understanding how this filter specifically acts on microplastics is complex as the study of microplastics itself is still a relatively young field, with the seminal paper first defining microplastics published as recently as 2004 (Thompson *et al*.). Applying existing knowledge about, say, suspended sediment transport and fate is difficult, as microplastics are a widely varying group of contaminants that have been shown in initial studies to show differing settling and erosion behaviours to sediment (e.g., Khatmullina and Isachecnko (2017) and Waldschläger and Schüttrumpf (2019b)). Therefore, there is a significant gap in knowledge as to if, and how, microplastics are subject to a 'filter' of sorts in estuaries that modulates their flux to coastal seas and from there, to the global oceans.

The estuarine budget was described in Figure 1-2, and the specific processes identified and investigated during this work are shown below (Figure 6-1). The estuarine filter is defined by part of the estuarine budget that relates to deposition within estuarine sediments. Deposition is enhanced by a number of processes, of which some of the key processes were investigated during this work. Microplastics are formed from a wide combination of polymers and additives, including polymers less dense than seawater. Whilst these may not be expected to sink due to their density alone, they have been found in environmental sediment samples e.g., low-density polymers such as polystyrene have been found in sediment cores in the Arctic Ocean (Bergmann *et al*., 2017; Kanhai *et al*., 2019). This suggests that other processes alter the properties of microplastics to enhance settling and deposition. A number of processes have been identified, including: the aggregation and flocculation of plastics; their incorporation into faecal pellets and marine snow; increased density and decreased buoyancy through biofouling; decreased flow velocities and

turbulence in intertidal wetlands and subtidal vegetation; decreased flow during slack water periods of the tidal cycle; and there are likely others yet to be identified. These processes are well described for other suspended particulates in estuaries, but less so for microplastics. Likewise, in comparison to other environments such as coastal beaches, coastal seas and even the open ocean, estuaries are comparatively understudied when looking at microplastic abundance studies (Akdogan and Guven, 2019).

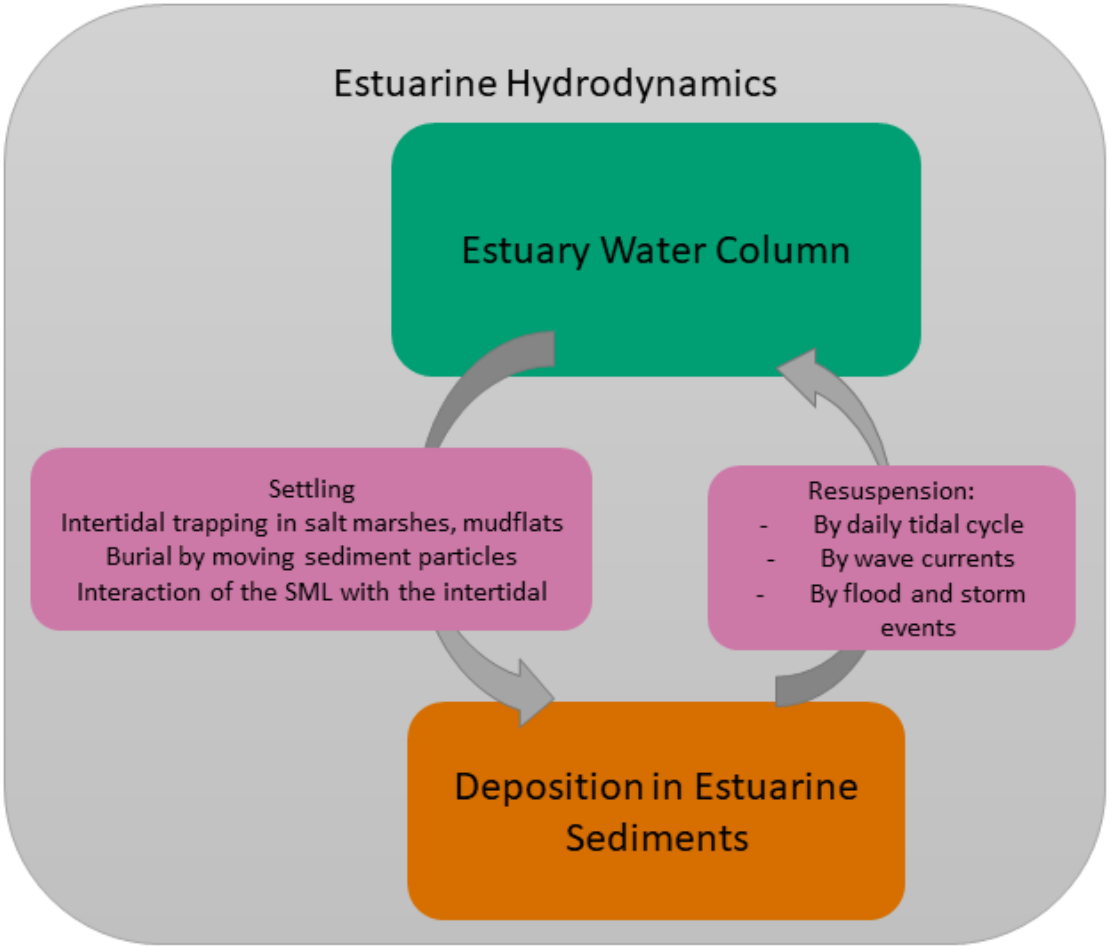

Figure 6-1 The estuarine filter for microplastics, with processes identified by the work in this thesis.

The processes themselves all interact with the hydrodynamics and properties of the estuary itself, including estuarine circulation and mixing.

A number of processes were selected for investigation by this work. Aims 4 and 5 were to investigate how two processes which enhance deposition of suspended material act on microplastics: flocculation, and intertidal trapping in wetlands.

Flocculation is a process by which clay particles aggregate, and is suggested as a process by which microplastics – that also display surface charges in solution – can aggregate and increase their

settling velocity. Chapter 5 showed that for the single type of microplastic used, flocculation was not observed within a short time frame of 24 hours, for relatively "new" microplastic particles. However, flocculation of microplastics has been observed in other studies (e.g., Andersen *et al.* (2021), and aggregation mediated by biological processes has also been observed (e.g., Michels *et al.* (2018)). This supports the importance of using a variety of microplastics (size, shape, polymer etc.) in experiments, and to considering the effects of weathering on microplastics. After a period of the fibres being in salt water solution, it was observed that a portion of the fibres sank and aggregated together (5.3.1). The change in behaviour following aging has significant implications. New microplastics – be it of a primary origin, or microplastics newly fragmented from larger pieces – are likely to behave differently from weathered microplastics, and this needs to be considered when investigating their fate. A majority of the microplastics within estuarine systems, and inputting to them every day, are likely to be weathered to an extent. Enhanced settling of weathered microplastics has implications for estuaries, as while they are subject to direct inputs of microplastics, a significant proportion entering estuaries are likely to have been in the environment for a period of time long enough to begin the weathering process (e.g., if they were transported by rivers, or if they were released from WWTWs). They are also likely to be of a larger size range, including the small microplastic particles (63 µm, so in the same size range as clay particles) that have been observed to flocculate by other authors (Andersen *et al.*, 2021). Therefore, settling of microplastics is likely to be enhanced by flocculation and aggregation in estuaries, supporting the hypothesis of an estuarine filter for microplastics.

Another aim of this thesis (Aim 4) was to investigate how intertidal wetlands affect microplastic fate, using high-resolution sampling in a salt marsh creek. It is hypothesised that specific environments within estuaries will enhance the deposition of microplastics. Coastal wetlands, including salt marshes, mangroves, and seagrasses, are known to accumulate sediment, and have recorded higher levels of microplastics than nearby unvegetated environments (e.g., mudflats, Cozzolino *et al.* (2020)). Understanding how these environments act to enhance microplastic deposition – or not – is key to understanding the risks posed by microplastics to these high-biomass environments, and central for the existence of an estuarine filter for microplastics.

In this thesis, sampling inflow and outflow into a salt marsh gave an integrated view of the processes occurring in salt marshes. A two-thirds decrease in microfibre abundance was found between the flood and ebb tide on two tidal cycles, sampling in Hythe salt marsh, Southampton Water (Figure 4-4). This supports the hypothesis of enhanced deposition, or 'trapping' in salt marshes, which contrasts with studies examining deposition of microplastics on vegetation, and within sediments (Cozzolino *et al*., 2020; Yao *et al*., 2019). In comparison to these point sampling studies, the present study used salt marsh creek sampling, looking at the body of water flowing

into the marsh and then draining the marsh, which provides a more integrated measure of the processes taking place, explaining the differing conclusions. Additionally, a significant decrease in fibre abundance was seen on the neap tide cycle sampled, when the vegetated marsh platform was not flooded. Processes other than the initial hypothesis of vegetative trapping are now hypothesised to be the cause of the decreased fibre abundance observed. This may explain why Cozzolino *et al.* (2020) found that saltmarsh vegetation did not record high abundances of microplastics adhered to them compared to other types of intertidal and subtidal vegetation. The sampling carried out was not designed to determine or quantify the exact processes involved, but the overall effect was well observed using salt marsh creek sampling. Microplastics have been observed by other studies to be deposited within intertidal sediments, including higher energy environments such as beaches and lower energy environments including salt marshes, mangroves and mudflats. That microplastics are trapped and retained within intertidal sediments has important implications, and supports the presence of an estuarine filter for microplastics.

The estuarine filter also includes particles resuspended and moved back into transport, and thus another aim of the project was to improve understanding of the resuspension of microplastics. There are limited studies investigating the resuspension of microplastics, ranging from laboratory flume studies (e.g., Ockelford *et al.*, 2020) to field studies comparing abundances in sediments before and after flooding events (e.g., Hurley *et al.,* 2018). Understanding how or if microplastics are resuspended from sediments is key to being able to understand their fate, and is also an integral input to modelling studies of microplastic transport. Chapter 5 describes the flume experiments carried out, to investigate the resuspension of two types of microplastics. These experiments identified that microplastic nurdles and fibres are resuspended by water currents, including buried microplastics as the flow exceeds the threshold of forming bedforms. Two experiments identified a lower threshold of motion for sediment when nurdles were included within the sediment (coarse sand, 5.3.2.2.3), and though this may lie within the variability of the experiments, further investigation into the effects microplastic inclusion has on sediments is needed. This work identifies that the estuarine filter acts to modulate the transfer of microplastics through estuaries, not only by enhancing deposition, but by removing microplastics from sinks and making them available to be transported out of the estuary.

Chapter 3 does not directly address the processes identified as playing a role in the estuarine filter. Rather, it tackles the project aim (Aim 3) of understanding how microplastic abundance varies in Southampton Water over the course of a year, and how abundance relates to environmental variables, with Southampton Water utilised as a representative temperate estuary. Understanding how environmental changes influence the abundance of microplastics is key to understanding an overall pattern of abundance within an estuarine system, and from there

beginning to understand how the processes occurring in estuaries will affect microplastic transport. There was high variability of microplastic abundances within Southampton Water, which were not correlated with the recorded environmental variables, or only weakly correlated (3.3.3). Seasonal differences were found, with summer recording higher abundances in both the SML and water column, aligning with other studies which have also found seasonal differences in microplastic abundance (e.g., Rodrigues *et al.,* 2018). The variability found within the year and between sites and sampling occasions suggests that inputs are variable, and so the estuarine filter may have differing efficiencies throughout the year and that outputs from estuaries will vary. This work, while it aimed to identify environmental controls on microplastic abundance in Southampton Water, identified that the key control was the hydrodynamic regime of Southampton Water. Southampton Water is a partially mixed estuary, with a strong ebb tide and a flushing time of approximately 10 days (Sharples, 2000), and this was reflected in the limited and weak correlations seen between microplastic abundance and the measured environmental variables. The influence of individual estuaries' hydrodynamic conditions and regime has been identified as a key control of microplastic fate within these systems (Dris *et al*., 2020), and although local scale processes have been identified as the key control of microplastic fate (Vermeiren *et al*., 2016), this work has identified some of those local scale processes acting in estuaries and considered how they will be applicable in the system studied (Southampton Water), as well as how they may be applicable across a wide-range of estuaries, despite differences in their hydrodynamic regimes and characteristics.

The work within this thesis has a variety of implications for Southampton Water. Sampling in Hythe in 2018 (over two tidal cycles) and on a repeated basis at SWAC and Mayflower Park throughout 2019 has provided 105 samples over which to calculate an average abundance of microplastics in the SML in Southampton Water, and 96 samples at SWAC and Mayflower Park to calculate abundance in the water column in Southampton Water (bulk water). As a result, the work likely captures nearly if not all of the range of variability in microplastic abundance which occurs within the surface layers of Southampton Water, and provides an abundance which can be compared – with of course, assumptions needing to be made for the variety of methods in use – with other estuarine systems in the UK and around the world, as well as non-estuarine settings.

Within Southampton Water, the work has identified a moderate level of microplastics (in comparison to global abundances, with assumptions made for comparability purposes). Whilst the risks posed by microplastic exposure to biota are still unclear, laboratory studies have shown that microplastics can have negative effects on species ranging from invertebrates to seabirds and mammals (as reviewed by Anbumani and Kakkar (2018)). This work identifies that there is a potential risk posed to Southampton Water by microplastics, although further work is necessary

to understand the risk of current (and future) concentrations of microplastics and how this can be incorporated into risk assessments. Plastic usage has increased rapidly since the 1950s, and even if production were to stop today, the disposal of plastic items in our homes, buildings and cars, as well as the erosion of landfills; as well as the breakdown of plastic litter already in the environment, would continue to produce microplastics and cause them to enter estuaries such as Southampton Water. Establishing a baseline will enable future work to assess whether abundances are increasing within Southampton Water, and enable global comparisons.

The seasonal sampling identified that there were no clear controls exerted by the measured environmental variables on microplastic abundance (3.3.3). Southampton Water is a partially mixed estuary, as described by its hydrodynamics, and this also describes the microplastic abundances throughout the year. Seasonal differences were observed, with higher abundances in summer (Figure 3-9), and this coincides with increased importance of Southampton Water as a site for breeding seabirds. Increased microplastic abundances in the water column during the summer could pose a risk to these internationally important populations, though effects are still unclear due to data limitations of effects studies. The period between April and November is also the growing period for salt marsh plants, among others, and studies suggest effects on plant growth as a result of microplastic inclusion in soils (e.g., Zang *et al.,* 2020).

The identification of intertidal trapping has significant implications for estuaries such as Southampton Water, which has extensive areas of intertidal wetlands, which are notified as Natura 2000 and Ramsar sites for their environmental importance, particularly to migratory water birds but also to invertebrates and other species. With a large area of intertidal wetland that is trapping microplastics, a significant proportion of the microplastics entering Southampton Water are likely retained in these intertidal areas. This poses a previously underestimated exposure risk to the biota in these areas, including internationally important populations of waterbirds and migratory fish. The effects that microplastic inclusion may have on these sediments is unclear, but studies have found that microplastic inclusion can influence sediment and soil properties (de Souza Machado *et al*., 2018). Additionally, some of these areas of wetland have been recorded to have areas of erosion (e.g., edge erosion was observed at Hythe by Cundy and Croudace (2017)). Although it is likely to be of a significantly smaller magnitude than inputs of microplastics from other sources, erosion could remobilise deposited microplastics, and may be significant if future inputs of microplastics are reduced drastically. As there are significant regions of low-energy intertidal habitats in Southampton Water, the intertidal trapping effect could significantly reduce the microplastic abundance within the water column of Southampton Water, and also the outputs of microplastics from Southampton Water to the Solent, English Channel and beyond.

Flocculation is likely to occur within Southampton Water or further up its tributary rivers as Southampton Water can be considered to be "essentially marine in nature" with respect to salinity (Townend, 2008) and flocculation has been recorded to occur at salinities as low as 0.5 PSU (Sutherland *et al*., 2015). This could enhance deposition of microplastics within Southampton Water, likely enhancing the intertidal trapping occurring, alongside deposition in benthic sediments. Southampton Water is dredged to maintain navigation, and this could remobilise deposited microplastics. It is a heavily industrialised estuary, with a history of inputs of pollutants such as heavy metals (Croudace and Cundy, 1995). Heavy metals have been observed to concentrate on microplastics (Brennecke *et al*., 2016), and a combination of benthic sediments with high metal concentrations and microplastics could lead to microplastics with high pollutant concentrations adsorbed onto them. This is an additional risk if these are then remobilised during, for example, dredging.

Additional resuspension of deposited microplastics is likely to occur during high river flow periods, periods when wave activity is high, or during the ebb tide. Resuspension of microplastic fibres and nurdles into suspended (fibres) or bedload (nurdles) transport was observed in flume studies at a velocity of 0.15 m/s at 6 cm above the bed (5.3.2); and bottom layer velocities in Southampton Water were observed to vary between 0 and 1 m/s by Levasseur (2008). This suggests that there will be resuspension of microplastics deposited on the surface of the sediment bed during higher flow periods of the tidal cycle. Seaward transport of coarse sediment is known to occur on ebb tides (when tidal currents are stronger, as Southampton Water is an ebb-dominant estuary) (Hopley, 2014), and it is likely that even larger, dense microplastics are also moved seawards during these periods. This supports the conclusion that the relatively short residence time of Southampton Water (5-10 days (Sharples, 2000)) means that microplastics within the water column are moved out of Southampton Water within a short time period.

The work within this thesis has implications beyond the system studied (Southampton Water). Estuaries are key worldwide transfer zones of microplastics to the marine environment (given that rivers are seen as the main source of plastics reaching the marine environment (e.g., Lebreton *et al.* (2017), and yet relatively little research has occurred in these environments. In the UK, estuaries form a major component of the natural environment, with a total area of ~530,000 ha, covering almost half the total UK shoreline length (Davidson, 2018), making wider implications significant on a country-wide scale. This work has shown evidence for the existence of an estuarine filter for microplastics, and shown that microplastics can be trapped within the intertidal zone. That this retention of microplastics can occur may be one of the processes that is behind the so-called "missing plastics problem", where estimated abundances of microplastics in the surface waters of the global oceans are on the order of magnitude of estimated annual inputs to the oceans, whereas

inputs of plastic have been occurring through any pathway to the oceans for decades (e.g., Gregory (1978) found what are now today termed 'nurdles' on a New Zealand beach in 1978). Retention of microplastics in estuaries would reduce inputs from rivers into the oceans to below that estimated, as none of the modelling studies conducted have considered a degree of trapping of plastics within estuaries (e.g., Lebreton *et al.*, 2017; Schmidt *et al.*, 2017); and this retention could be particularly significant for the UK, as well as globally.

Improving knowledge of how microplastics are transported through or retained within estuaries will be key to being able to better constrain global plastic budgets; especially as microplastics are known to be deposited within river sediments (Bellasi *et al*., 2020), so it is not just estuaries that are retaining microplastics before they can reach the oceans. Estimates of total global abundance of plastic debris in the surface oceans is of the same magnitude as estimates of global annual input of plastic debris to the oceans, yet plastic debris has been entering the oceans for decades. Therefore, plastics must be being either retained before they enter the oceans, or moving elsewhere within the oceans. Some of this missing plastic is likely to be sinking, be it within the water column (Pabortsava and Lampitt, 2020) or to bottom sediments (Bergmann *et al*., 2017); but there is also, as the work conducted within this thesis show, considerable potential for plastic to be retained and trapped within estuaries. Estuaries globally are important environments for biota, and this work suggests that there is potentially an underestimated risk posed to this biodiversity.

The global applicability of this work is likely to vary within the general conclusions of the modulation of microplastics outputs by estuaries, but general conclusions can be drawn and applied globally. Southampton Water is a temperate, macrotidal, partially mixed estuary. Its hydrodynamic regime differs from other estuaries. For example, some estuaries in Western Australia are rarely if ever connected to the sea; and the Adour estuary (France) which has been modelled for microplastic transport is a salt-wedge estuary, with much less mixing than Southampton Water. Likewise, abundance across sites within Southampton Water (at Hythe (Chapter 4), SWAC and Mayflower Park (Chapter 3) and in the tributary River Hamble (Anderson *et al*., 2018) was not statistically significantly different, supporting the hypothesis of a partially-mixed estuary; whereas distribution within a tropical salt-wedge estuary (Goiana Estuary, Brazil) was found to be influenced by the seasonal migration of this salt wedge (Lima *et al*., 2015). This highlights the importance of future work on the transport of microplastics within and through estuaries, as while work on Southampton Water suggests a filtering effect, this may differ with the differing hydrodynamic regimes. The conclusions drawn from the work in this thesis will hold across varying hydrodynamic regimes, and even outside of estuaries, for example, when considering intertidal trapping in wetlands, or the processes of resuspension and flocculation.

Intertidal trapping will occur regardless of the mixing within the estuary as water containing microplastics – as any riverine inputs, the estuary itself and the surrounding coastal seas will all contain microplastics – floods intertidal wetlands. In microtidal estuaries, this process may be less important, but one of the processes hypothesised to be involved – vegetative trapping – will occur within subtidal vegetation also (e.g., in seagrasses (Cozzolino *et al*., 2020)). Flocculation, either between microplastics or between microplastics and natural colloids including suspended sediment, can be salinity dependent (Dyer, 1995), however most estuaries will have a salinity above that where flocculation of clay particles has been recorded (0.5 PSU (Sutherland *et al*., 2015)). Though this is unstudied, the impact of flocculation on microplastic settling may be small compared to biologically mediated aggregation. For sediments, studies report that flocculation as a result of surface charges overcome as a result of oppositely charged salt ions in the water column is of a much smaller magnitude than biologically mediated aggregation (Eisma, 1986). Therefore, the flocculation of microplastics, while a topic in need of further investigation, is likely to play a minimal role in enhancing microplastic deposition compared to other processes. The seasonality and links between environmental variables are likely to vary with the estuary type. For example, seasonal links are observed in Southampton Water, but with no clear driving factor behind this variability. Contrasting this, seasonality with clear links to rainfall have been observed in other estuaries (e.g., in the Goiana Estuary, Brazil (Lima *et al*., 2015)).

Additional potential risks are identified as a result of the seasonal and resuspension work (presented in Chapter 3, Chapter 5). Seasonal differences in abundance were found, as well as the resuspension of deposited microplastics. This supports previous studies which have found seasonal differences in tropical estuaries, and the resuspension of microplastics during flooding events in rivers. Seasonal differences in previous studies have been in regions with distinct rainy and dry seasons, and the resuspension work shows that the increased abundances in the water column during the rainy season may be a result of increased erosion of microplastics during high river flow events. It should be recognised that as a result, the risks posed by microplastics will vary throughout the year as their abundances change within the water column. Indeed, the risks may change on a much more frequent basis than seasonally, as for example, deposition may occur during slack tide periods (increased risk to benthic organisms) and resuspension may occur during periods of higher tidal flow (increased risk to pelagic organisms).

That microplastics are deposited, or 'trapped' within intertidal saltmarshes and mudflats (abundance decreased by 2/3 between flood tide inputs and ebb tide outputs from Hythe salt marsh, 4.3.2) has implications for intertidal wetlands and other low-energy intertidal environments globally. These exist in estuaries and along coastlines worldwide, as well as occurring in freshwater, and they are very productive environments. Wetlands are key for

coastline stability, reducing coastal erosion; they are nursery habitats for fish as well as other species, as well as providing many other ecosystem services. That microplastics are deposited in these environments, which are also under threat from other anthropogenic pressures such as sea level rise, is another threat to their health. The presence of microplastics in these environments may also pose an economic risk to fisheries and shell fisheries, if it is proved that microplastics have a negative impact on these species, particularly given the role of many estuaries and wetlands as nurseries for commercially and recreationally important species. If, as suggested by Chapter 5, there are destabilising effects to natural sediments, the role of wetlands and intertidal areas as natural sea defences may be negatively impacted, which could have significant economic impacts to coastal regions.

In summary, the work within this thesis provides support to the hypothesis of the existence of an 'estuarine filter' for microplastics. It identified processes involved in increasing microplastic abundance in estuaries, and how this may influence the ultimate fate of microplastics. This was considered in context of the system studied (Southampton Water), and also in terms of the global implications for estuaries. The findings have significant implications for the fate and transport of microplastics not only in the system studied, but globally. They have suggested that microplastics may have otherwise unstudied effects on sediments; and may be retained with estuaries and intertidal wetlands, posing risks to these unique and vulnerable environments that have otherwise been little considered.

6.1 Limitations

Chapter 3 considered seasonal variation in microplastics abundance, and how environmental variables influenced abundance. While sampling occurred twelve times during each season, sampling was still limited. Balancing investigations into tidal and meteorological conditions meant that sampling was conducted at the same time every day, and not at the same point in the tidal cycle. Therefore, untangling tidal and meteorological influences was complicated. Additional sampling to increase temporal resolution was not possible, due to the time needed to process each sample, which, as visual identification was necessary, was considerable. Some environmental data was not available, namely information on outputs from local WWTWs and CSOs. Given their potential role as a source of microplastics to the estuary and in particular, the closeness of Woolston WWTW to SWAC, this would have been useful information to aid interpretation of abundance observations. Additional environmental data also could have been obtained, such as the presence of cruise ships berthed near Mayflower Park.

There was a reliance on visual identification in both Chapter 3 and Chapter 4, which can be subject to significant bias and false identification, and only a subsample of the samples in each chapter were subject to spectroscopic identification due to equipment time restrictions. No digestion or separation techniques were utilised (except for the OEP for the FTIR samples), due to the relatively low organic and sediment contents, but the use of digestion or separation techniques may have improved visual identification.

For the laboratory experiments in Chapter 5, it was only possible to use a very limited range of microplastics – fibres and nurdles, both of which were classified as Large Microplastics (> 1 mm). The use of a wider range of microplastic particles (in terms of shape, size, polymer and age) was not possible given the variability seen in microplastics characteristics and the range of experiments conducted. Additionally, only a limited number of substrates were considered, all with a fairly narrow grain size range and without consideration of organic content or biological effects. This was effective for considering microplastic resuspension and potential effects on sediment, but is unrealistic of natural sedimentary environments.

Chapter 7 Key Conclusions and Suggestions for Future Work

7.1 Key Conclusions

The overarching aims of this study involved furthering our knowledge of the transport and fate of microplastics in estuarine systems. In particular, the study aimed to identify processes involved in determining the fate of microplastics in estuaries, in particular, within the study system of Southampton Water. Following the identification of processes in Chapter 1, a number were selected for further study to determine if they played a role in the 'estuarine filter' which was identified as being a potential cause for retention of microplastics in estuaries. Processes which enhanced deposition (flocculation, intertidal trapping in wetlands) and those which return microplastics to the water column from being deposited in sediment (resuspension) were studied in laboratory and field studies. Additionally, this study aimed to investigate the seasonal variation of microplastics in Southampton Water, and how environmental variables influenced abundance. From this, it was also possible to consider how estuarine hydrodynamics influenced abundance in Southampton Water. By drawing the results and conclusions of individual chapters together, it was possible to consider the transport and fate of microplastics in Southampton Water, and also to evaluate how this advanced understanding of estuarine microplastics on a global scale.

Two field sampling campaigns and two series of laboratory experiments were undertaken. A detailed literature review identified a significant knowledge gap around microplastics in estuaries, and in particular, identified the possibility of a so-called "estuarine filter" for microplastics (1.3). From this, aims were developed to investigate the fate of microplastics in estuaries and in particular, the presence of a filter in estuaries for microplastics (1.6). Various aspects of this filter were investigated for the first time using novel approaches, focussing on the enhanced deposition, and resuspension of microplastics. Southampton Water, a macrotidal, partially-mixed estuary located on the southern coast of the UK, was used as a case study, with consideration given as to how findings may apply on a global scale (Chapter 6, Aims 7 and 8).

Chapter 3 outlines how use of seasonal sampling found significant variation in microplastic abundance in Southampton Water over the course of a year, with abundances ranging between 0 and 141.7 microplastics/L, successfully achieving part of Aim 3 (1.6). Consequently, it is recommended that current microplastic sampling strategies should be redesigned to require sampling in a wide range of conditions to fully enumerate variability in microplastic abundance at

any given location. Seasonal differences were observed in microplastic abundance; inter-site and inter-seasonal differences were greater in the SML (Figure 3-9). More consideration should be given in future to sampling this key interface between atmosphere and ocean. The SML is a key global environment that is often considered along with underlying surface water when enumerating microplastics, or excluded from surface samples which may, for example, use a bulk water sampling method to sample below the water surface (e.g., Li *et al.* (2020)). It has distinct properties and its own microbiota that can enhance microplastic abundance within it, as seen in this thesis where the SML showed a significantly greater abundance of microplastics compared to underlying water (Figure 3-7).

SML sampling was utilised to investigate intertidal trapping in a salt marsh in Southampton Water (Chapter 4), which achieved Aim 4. This showed that intertidal wetlands and associated low-energy environments (mudflats) can retain microplastics that are transported into these regions on the flood tide, with a significant decrease seen between the flood and ebb tide samples (approximately a 2/3 reduction in fibre abundance was seen, Figure 4-4). This reduction occurred on both tidal cycles sampled, even when the vegetated marsh platform was not flooded, supporting an interpretation of additional processes to vegetative trapping being responsible for this deposition of microplastics. These processes could include increased deposition as a result of reduced flows during slack water, or the interaction of the SML with the intertidal as the intertidal is gradually flooded by the SML first during a tidal cycle. The trapping of microplastics in intertidal wetlands has significant implications for hazards posed to the health of these ecosystems, as microplastics may pose a risk to biota, from fish larvae to plants, (where effects to these species are indicated by laboratory exposure studies) although these risks remain poorly understood and research into the extent of the hazard posed by microplastic exposure remains limited.

Chapter 3 identified seasonal trends in microplastic abundance, and some correlations with measured environmental variables, considering the second part of Aim 3. No single environmental factor was determined to be the determining factor controlling microplastic abundance. Rather, the complex hydrodynamics of Southampton Water, which is a partially-mixed estuary, are likely the driving factor behind microplastic distribution within the estuary, both temporally and spatially. The hydrodynamics of any estuary therefore need to be considered, for example, when estimating microplastic inputs to the oceans from rivers or assessing estuarine health and risks posed within the estuary from microplastics.

In addition to the field studies carried out, laboratory studies investigated microplastic behaviour in transport processes (Chapter 5), tackling Aims 5 and 6. These studies, of flocculation and resuspension, enable interpretation of environmental observations, and improve knowledge of

the behaviour of microplastics. Flocculation was not observed between the microplastic fibres used in this study, although flocculation has been observed in other studies between smaller microplastics. Some aggregation of fibres was observed after a period of several weeks (5.3.1), suggesting that weathering in suspension alters microplastics and permits aggregation of particles. This has significant implications for the fate of microplastics; as aggregates they may have a higher sinking velocity despite potentially having a lower density, reducing microplastics in surface waters and increasing abundances in deeper waters and in sediments.

Resuspension of microplastics was investigated. Knowledge of how deposited microplastics are moved throughout aquatic systems is key to understanding their ultimate fate and risk, and could enable existing knowledge of suspended particulates to be applied to microplastics which would rapidly improve estimates of transport and fate. Flume studies investigated the resuspension of microplastic fibres and nurdles from clay and sand sediment beds. Fibres and nurdles were moved by flowing water at velocities similar to sediment of a smaller grain size, and are relatively mobile contaminants in aquatic systems (5.3.2). However, burial of microplastic nurdles by moving sediment was observed; this has significant implications for microplastic fate by moving microplastics deeper into the sediment bed and providing an element of protection from erosion. Potential effects of microplastic inclusion were seen on sediment erosion thresholds, for the clay bed, and coarse sand bed.

Chapter 6 considered the local and global implications of the work, tackling Aims 7 and 8. Southampton Water showed a moderate level of contamination, and abundances were controlled by the hydrodynamics of the estuary. Intertidal trapping was shown in one of the numerous intertidal saltmarshes fringing Southampton Water, which could have significant implications for the health of these ecosystems. These findings have global implications, drawing focus onto the output of microplastics from estuaries and rivers and providing evidence for the retention of microplastics in estuarine sediments and intertidal wetlands. The study also supports a view that estuaries globally have an influence on microplastics output and retention within these systems, through their unique hydrodynamics. Consideration should therefore be given, particularly when conducting modelling studies for riverine output to the oceans of plastic debris, as to how estuarine hydrodynamics may influence the fate of microplastics across the terrestrial-marine interface.

Overall, the work presented within this thesis has advanced knowledge of microplastic transport and fate in estuaries, provided evidence for the existence of an “estuarine filter” for microplastics; and considered how its findings have local and global implications for microplastics.

7.2 Suggestions for Future Work

Microplastics research has rapidly developed since the early 2000s. However there are still large knowledge gaps, some of which have been addressed by the work in this thesis. Each chapter has identified significant scope for further work to better understand the transport and fate of microplastics in estuaries and beyond.

The importance of estuaries as potential sinks or conduits for microplastics has been identified by previous authors, but studies are limited and rarely able to be linked (e.g., due to methodological differences) to draw conclusions about the role of estuaries in microplastics transport. Estuaries have been proposed variously as sinks of microplastics, or conduits of microplastics to coastal seas and beyond. Additional studies are necessary to determine the role estuaries play, and determine estuarine budgets of plastic debris; which will in turn improve estimates of plastic debris inputs to the marine environment. Considerations of the effects of estuarine hydrometry on microplastic abundance and distribution are necessary to enable a global overview of the role estuaries play in microplastic transport pathways.

Chapter 3 utilised a four-month long sampling campaign, and identified large variation in microplastic abundance within Southampton Water. Future studies investigating microplastic abundance should consider sampling over a longer period of time and enable sampling under a wider variety of environmental conditions, such as weather conditions, seasons, and tidal conditions. This will improve the accuracy of microplastic abundance studies, and enable greater interpretation of the heterogeneity of abundances. There is a need to understand microplastic variability over a number of time scales, including tidal, seasonal, decadal and even longer term as plastics continue to be used at an increasing rate despite awareness of their hazard (and potential unquantified hazards) to the environment. There are different requirements of sampling regimes that can accomplish these outcomes.

This chapter, along with Chapter 4, looked at the sea surface microlayer, and identified that there is significant scope to investigate this unique environment. Considering how the SML is involved in deposition in the intertidal range will be an important process to investigate in future; along with effects on the biota within the SML. The SML is very rarely the focus of microplastic studies and is often sampled along with underlying water, for example, by surface net trawls. However, as seen here and in other SML studies, it shows a higher abundance of microplastics than underlying water. Given that it is a key interface between the atmosphere and oceans, the key role it plays in the global distribution of other pollutants including being an accumulation zone for range of persistent organic pollutants which may interact with plastics to potentially pose a combined risk; and that it is a key zone in contact with biota over a tidal cycle as the tide rises and falls through

the intertidal, and is a habitat for plankton and microbes, along with other biota; there is significant scope for further study on microplastics in the SML.

Chapter 4 identified the process of trapping of microplastics in intertidal wetlands. The method used, sampling inflow and outflow in a salt marsh creek, has potential to be used on a wider scale. It enables the consideration of all the processes occurring in an environment, to determine the overall direction of movement of microplastics into or out of these environments, in particular, the assessment of the direction of movement with tidal cycles. Studies investigating the abundance of microplastics in low-energy wetland environments such as saltmarshes and mangroves will be key to understanding the exposure to microplastics in these high-biomass environments. Coupling these studies with detailed hydrodynamic measurements will enable better understanding of the role of current velocities, direction and turbulence on these processes.

Intertidal wetlands are potentially a key component of the estuarine filter. There is significant scope to investigate microplastic abundance within these vulnerable environments, and to work from a process viewpoint to understand what happens to microplastics within them. Here, flume studies could be utilised, including in situ flumes such as those used by de Smit *et al.* (2021), and could also be linked to further work to understand the erosion and resuspension of a wider range of microplastics and substrates (including how these are impacted by biota, for example), and potentially used to consider effects of microplastic inclusion on sediment properties.

The resuspension studies showed potential effects on sediment erosion thresholds when microplastics are included in the sediment bed. Few studies to date have considered the effects microplastic inclusion has on sediments, yet if microplastics affect properties such as erosion thresholds, this has wide-ranging implications globally given microplastics are ubiquitous in sediments. As a result, there is a need to carry out studies to investigate if microplastic inclusion changes sediment properties, at what concentration if they do, and how this depends on sediment and microplastic characteristics. The studies here only considered “artificial” sediment beds, and there is further scope to consider how natural sediment beds, with great variability and organic content will behave with microplastic inclusion. In particular, cohesive sediment beds would be of particular interest, as microplastics are hypothesised to accumulate in low-energy environments where cohesive sediment also accumulates. Flocculation of microplastics, and aggregation with cohesive sediment, also need to be considered in environments dominated by fine-grained sediment.

To summarise, there is significant scope to build on the work in this thesis to decrease the knowledge gaps around microplastics, not only in estuaries but in other environments including

rivers, lakes, coastal wetlands, and marine and terrestrial environments. Microplastics are an emerging contaminant which were only given their name in 2004 – less than 20 years ago. As a result, it is not surprising that there are so many unknowns regarding how they move and interact with their environment, which need to be considered to understand how and where they pose risk. In twenty years, significant process has been made in understanding microplastics in the environment. If this previous and ongoing work and the work in this thesis can be built on, expanded and applied, then better risk assessments and cost-benefit analysis can be developed to reduce harm from microplastics and strategically target mitigation measures.

Appendix A Seasonal Data

Appendix A Table 1 Microplastic Abundance Data

Sampling Date	Season	Location	SML Low Range	SML - Value Used	SML High Range	Bulk Low Range	Bulk - Value Used	Bulk High Range
04/02/2019	Winter	SWAC	1.5	15.9	357.5	2.2	23.3	4.5
06/02/2019	Winter	SWAC	0.9	10.9	239.0	1.9	20.5	3.9
08/02/2019	Winter	SWAC	N/A	N/A	N/A	2.5	25.5	5.1
11/02/2019	Winter	SWAC	1.7	21.9	555.3	1.7	18.7	3.6
13/02/2019	Winter	SWAC	9.3	61.9	1998.8	0.0	7.3	1.4
15/02/2019	Winter	SWAC	10.5	79.9	2179.3	0.2	14.9	2.8
18/02/2019	Winter	SWAC	5.3	36.8	1004.2	0.5	15.0	2.9
20/02/2019	Winter	SWAC	7.3	52.4	1453.1	1.2	12.7	2.4
22/02/2019	Winter	SWAC	3.5	26.3	678.6	0.7	8.1	1.6
25/02/2019	Winter	SWAC	4.0	27.6	766.8	0.6	11.6	2.2
27/02/2019	Winter	SWAC	4.5	25.9	766.8	0.0	21.9	4.2
01/03/2019	Winter	SWAC	2.5	22.7	563.9	0.9	10.8	2.1
04/02/2019	Winter	MAY	N/A	N/A	N/A	0.0	2.0	0.4

Appendix A

Sampling Date	Season	Location	SML Low Range	SML - Value Used	SML High Range	Bulk Low Range	Bulk - Value Used	Bulk High Range
06/02/2019	Winter	MAY	1.4	12.7	291.5	1.5	19.9	3.8
08/02/2019	Winter	MAY	N/A	N/A	N/A	0.0	2.0	0.4
11/02/2019	Winter	MAY	2.7	21.8	551.4	0.5	7.0	1.3
13/02/2019	Winter	MAY	1.9	11.6	361.7	1.5	16.4	3.1
15/02/2019	Winter	MAY	3.1	20.3	583.3	2.4	24.9	4.8
18/02/2019	Winter	MAY	3.7	24.1	726.9	0.1	3.7	0.7
20/02/2019	Winter	MAY	N/A	N/A	N/A	0.7	25.4	4.9
22/02/2019	Winter	MAY	3.1	23.2	577.5	1.9	27.4	5.4
25/02/2019	Winter	MAY	3.5	19.9	683.0	0.5	6.5	1.2
27/02/2019	Winter	MAY	2.9	21.2	656.3	0.1	17.6	3.4
01/03/2019	Winter	MAY	2.3	18.0	475.7	0.7	9.8	1.9
06/05/2019	Spring	SWAC	4.6	37.1	887.0	0.5	5.7	1.1
08/05/2019	Spring	SWAC	3.2	24.5	621.6	0.2	3.7	0.7
10/05/2019	Spring	SWAC	14.0	105.7	2627.9	0.0	0.6	0.1
13/05/2019	Spring	SWAC	0.9	8.1	186.2	0.0	1.9	0.4
15/05/2019	Spring	SWAC	6.3	41.1	1180.4	0.0	3.3	0.6
17/05/2019	Spring	SWAC	4.0	32.4	775.5	0.4	7.4	1.4

Sampling Date	Season	Location	SML Low Range	SML - Value Used	SML High Range	Bulk Low Range	Bulk - Value Used	Bulk High Range
20/05/2019	Spring	SWAC	4.9	33.4	942.7	0.3	4.9	0.9
22/05/2019	Spring	SWAC	12.9	96.8	2408.3	0.9	10.3	2.0
24/05/2019	Spring	SWAC	1.2	10.5	266.7	0.0	5.0	1.0
27/05/2019	Spring	SWAC	2.8	20.3	533.7	0.2	4.7	0.9
29/05/2019	Spring	SWAC	0.0	0.5	11.9	0.0	0.7	0.1
31/05/2019	Spring	SWAC	0.0	0.9	23.8	1.5	17.1	3.3
06/05/2019	Spring	MAY	2.3	18.1	450.3	0.0	1.3	0.3
08/05/2019	Spring	MAY	N/A	N/A	N/A	0.0	2.2	0.4
10/05/2019	Spring	MAY	4.7	37.5	915.0	0.0	1.5	0.3
13/05/2019	Spring	MAY	1.2	8.6	252.2	0.3	4.2	0.8
15/05/2019	Spring	MAY	2.0	17.9	410.0	0.2	4.7	0.9
17/05/2019	Spring	MAY	1.2	10.1	251.9	0.2	5.4	1.0
20/05/2019	Spring	MAY	2.7	20.1	529.2	0.5	6.8	1.3
22/05/2019	Spring	MAY	0.5	11.3	108.0	0.0	2.2	0.4
24/05/2019	Spring	MAY	3.8	30.4	740.7	0.0	2.1	0.4
27/05/2019	Spring	MAY	N/A	N/A	N/A	0.0	0.0	0.0
29/05/2019	Spring	MAY	1.1	9.7	240.3	1.1	11.8	2.3

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Sampling Date	Season	Location	SML Low Range	SML - Value Used	SML High Range	Bulk Low Range	Bulk - Value Used	Bulk High Range
31/05/2019	Spring	MAY	0.4	3.7	95.1	0.0	0.9	0.2
29/07/2019	Summer	SWAC	17.8	138.8	3318.7	0.0	2.7	0.5
31/07/2019	Summer	SWAC	14.7	111.0	2760.5	0.8	9.7	1.9
02/08/2019	Summer	SWAC	9.8	74.0	1840.5	1.2	12.9	2.5
05/08/2019	Summer	SWAC	10.1	66.0	1892.7	1.9	18.9	3.6
07/08/2019	Summer	SWAC	10.2	67.3	1932.3	0.0	0.7	0.1
09/08/2019	Summer	SWAC	21.6	147.5	4020.4	0.0	4.9	0.9
12/08/2019	Summer	SWAC	12.5	83.1	2343.9	2.2	23.0	4.4
14/08/2019	Summer	SWAC	8.4	63.6	1611.5	0.5	6.3	1.2
16/08/2019	Summer	SWAC	12.0	81.2	2368.7	1.0	11.6	2.3
19/08/2019	Summer	SWAC	N/A	N/A	N/A	0.0	2.9	0.6
21/08/2019	Summer	SWAC	5.6	40.2	979.4	0.8	9.5	1.8
23/08/2019	Summer	SWAC	4.6	37.0	937.5	0.4	7.8	1.5
29/07/2019	Summer	MAY	18.1	131.5	3395.6	0.1	4.0	0.8
31/07/2019	Summer	MAY	12.7	87.2	2377.3	0.3	5.4	1.0
02/08/2019	Summer	MAY	6.3	44.9	1180.4	2.9	28.6	5.5
05/08/2019	Summer	MAY	2.7	19.1	529.2	0.0	4.2	0.8

Sampling Date	Season	Location	SML Low Range	SML - Value Used	SML High Range	Bulk Low Range	Bulk - Value Used	Bulk High Range
07/08/2019	Summer	MAY	N/A	N/A	N/A	0.5	7.0	1.3
09/08/2019	Summer	MAY	N/A	N/A	N/A	0.3	5.4	1.0
12/08/2019	Summer	MAY	13.9	99.4	2622.9	2.5	26.3	5.0
14/08/2019	Summer	MAY	N/A	N/A	N/A	0.0	2.0	0.4
16/08/2019	Summer	MAY	N/A	N/A	N/A	0.9	7.5	1.5
19/08/2019	Summer	MAY	N/A	N/A	N/A	0.1	3.0	0.6
21/08/2019	Summer	MAY	10.6	73.2	1994.7	0.0	6.1	1.2
23/08/2019	Summer	MAY	4.6	40.2	960.4	0.0	1.3	0.3
04/11/2019	Autumn	SWAC	4.1	21.2	771.0	0.0	1.3	0.3
06/11/2019	Autumn	SWAC	5.0	35.7	957.5	0.0	4.7	0.9
08/11/2019	Autumn	SWAC	21.1	144.1	3996.5	0.0	0.2	0.0
11/11/2019	Autumn	SWAC	5.4	36.9	1059.6	1.0	14.4	2.8
13/11/2019	Autumn	SWAC	6.5	39.0	1137.8	0.6	7.8	1.7
15/11/2019	Autumn	SWAC	5.4	34.6	1092.4	1.2	12.1	2.3
18/11/2019	Autumn	SWAC	4.3	28.4	843.2	0.0	4.0	0.8
20/11/2019	Autumn	SWAC	4.8	28.1	965.9	1.2	12.9	2.6
22/11/2019	Autumn	SWAC	2.7	16.0	544.0	1.2	13.2	2.5

Sampling Date	Season	Location	SML Low Range	SML - Value Used	SML High Range	Bulk Low Range	Bulk - Value Used	Bulk High Range
25/11/2019	Autumn	SWAC	2.3	15.0	443.6	0.0	0.0	0.0
27/11/2019	Autumn	SWAC	0.0	0.0	0.0	3.7	37.3	7.1
29/11/2019	Autumn	SWAC	6.1	33.4	1149.4	1.2	14.6	2.8
04/11/2019	Autumn	MAY	3.1	25.5	622.0	0.0	1.3	0.3
06/11/2019	Autumn	MAY	1.5	11.9	307.6	0.0	2.7	0.5
08/11/2019	Autumn	MAY	1.4	16.4	313.4	0.0	7.2	1.4
11/11/2019	Autumn	MAY	N/A	N/A	N/A	0.0	0.0	0.0
13/11/2019	Autumn	MAY	1.9	14.4	386.9	0.7	7.8	2.2
15/11/2019	Autumn	MAY	1.5	9.6	307.3	0.7	10.9	2.1
18/11/2019	Autumn	MAY	2.4	17.1	456.8	0.0	9.1	1.8
20/11/2019	Autumn	MAY	0.8	9.5	177.2	1.5	18.5	3.5
22/11/2019	Autumn	MAY	0.9	20.5	196.2	0.2	8.2	0.8
25/11/2019	Autumn	MAY	0.4	3.8	109.6	0.0	3.6	0.7
27/11/2019	Autumn	MAY	0.1	1.2	43.3	1.3	14.3	2.8
29/11/2019	Autumn	MAY	0.2	2.3	68.7	1.3	15.4	2.9

Appendix A Table 2 Meteorological Data

Sampling Date	Season	Location	River Flow Data (m^3/s)	Rainfall (mm/day)	Antecedent Rainfall (mm/day)	Wind Speed (knots)	Wind Direction (degrees)	Daily Average Wind Speed (knots)	Daily Average Wind Direction (degrees)
04/02/2019	Winter	SWAC	6.0	2.0	8.0	16.4	253.0	15.5	227.0
06/02/2019	Winter	SWAC	5.9	6.0	7.6	8.3	193.0	11.4	209.0
08/02/2019	Winter	SWAC	6.1	12.8	3.4	26.7	218.0	26.4	229.0
11/02/2019	Winter	SWAC	6.3	0.0	0.8	9.9	2.0	9.0	273.0
13/02/2019	Winter	SWAC	7.1	0.0	0.0	N/A	N/A	9.9	167.0
15/02/2019	Winter	SWAC	7.3	0.2	0.2	11.2	142.0	8.7	132.0
18/02/2019	Winter	SWAC	6.2	3.0	0.0	10.8	219.0	10.6	235.0
20/02/2019	Winter	SWAC	6.3	0.0	0.0	20.3	234.0	12.2	215.0
22/02/2019	Winter	SWAC	5.9	0.2	0.0	6.3	171.0	10.4	127.0
25/02/2019	Winter	SWAC	6.0	0.0	0.0	7.0	155.0	6.5	111.0
27/02/2019	Winter	SWAC	5.7	0.0	0.0	9.2	133.0	4.2	155.0
01/03/2019	Winter	SWAC	5.6	1.8	2.6	7.9	253.0	8.9	255.0
04/02/2019	Winter	MAY	N/A	2.0	8.0	12.9	252.0	15.5	227.0
06/02/2019	Winter	MAY	N/A	6.0	7.6	11.6	200.0	11.4	209.0

Sampling Date	Season	Location	River Flow Data (m^3/s)	Rainfall (mm/day)	Antecedent Rainfall (mm/day)	Wind Speed (knots)	Wind Direction (degrees)	Daily Average Wind Speed (knots)	Daily Average Wind Direction (degrees)
08/02/2019	Winter	MAY	N/A	12.8	3.4	33.2	220.0	26.4	229.0
11/02/2019	Winter	MAY	N/A	0.0	0.8	9.5	357.0	9.0	273.0
13/02/2019	Winter	MAY	N/A	0.0	0.0	N/A	N/A	9.9	167.0
15/02/2019	Winter	MAY	N/A	0.2	0.2	13.1	142.0	8.7	132.0
18/02/2019	Winter	MAY	N/A	3.0	0.0	13.3	239.0	10.6	235.0
20/02/2019	Winter	MAY	N/A	0.0	0.0	15.3	223.0	12.2	215.0
22/02/2019	Winter	MAY	N/A	0.2	0.0	6.0	156.0	10.4	127.0
25/02/2019	Winter	MAY	N/A	0.0	0.0	6.7	154.0	6.5	111.0
27/02/2019	Winter	MAY	N/A	0.0	0.0	8.9	162.0	4.2	155.0
01/03/2019	Winter	MAY	N/A	1.8	2.6	8.9	250.0	8.9	255.0
06/05/2019	Spring	SWAC	4.7	0.0	0.0	3.8	304.0	8.2	282.0
08/05/2019	Spring	SWAC	5.3	0.0	17.0	23.3	237.0	20.0	202.0
10/05/2019	Spring	SWAC	4.9	0.0	0.4	9.5	213.0	6.0	220.0
13/05/2019	Spring	SWAC	4.5	0.0	0.0	16.2	154.0	11.7	104.0
15/05/2019	Spring	SWAC	4.4	0.0	0.0	16.2	152.0	10.7	109.0

Sampling Date	Season	Location	River Flow Data (m^3/s)	Rainfall (mm/day)	Antecedent Rainfall (mm/day)	Wind Speed (knots)	Wind Direction (degrees)	Daily Average Wind Speed (knots)	Daily Average Wind Direction (degrees)
17/05/2019	Spring	SWAC	4.5	0.8	0.0	5.8	20.0	9.0	81.0
20/05/2019	Spring	SWAC	4.5	0.0	0.0	4.9	310.0	6.8	271.0
22/05/2019	Spring	SWAC	4.3	0.0	0.0	13.2	133.0	8.1	212.0
24/05/2019	Spring	SWAC	4.2	0.0	0.0	5.7	290.0	9.1	305.0
27/05/2019	Spring	SWAC	4.1	1.2	0.0	13.5	272.0	10.8	286.0
29/05/2019	Spring	SWAC	4.3	1.2	0.0	11.4	200.0	10.0	244.0
31/05/2019	Spring	SWAC	3.9	0.0	0.0	10.8	238.0	10.8	237.0
06/05/2019	Spring	MAY	N/A	0.0	0.0	7.7	309.0	8.2	282.0
08/05/2019	Spring	MAY	N/A	0.0	17.0	28.1	224.0	20.0	202.0
10/05/2019	Spring	MAY	N/A	0.0	0.4	10.1	237.0	6.0	220.0
13/05/2019	Spring	MAY	N/A	0.0	0.0	16.0	147.0	11.7	104.0
15/05/2019	Spring	MAY	N/A	0.0	0.0	16.9	151.0	10.7	109.0
17/05/2019	Spring	MAY	N/A	0.8	0.0	10.1	48.0	9.0	81.0
20/05/2019	Spring	MAY	N/A	0.0	0.0	10.6	304.0	6.8	271.0
22/05/2019	Spring	MAY	N/A	0.0	0.0	9.4	224.0	8.1	212.0

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Sampling Date	Season	Location	River Flow Data (m^3/s)	Rainfall (mm/day)	Antecedent Rainfall (mm/day)	Wind Speed (knots)	Wind Direction (degrees)	Daily Average Wind Speed (knots)	Daily Average Wind Direction (degrees)
24/05/2019	Spring	MAY	N/A	0.0	0.0	3.2	269.0	9.1	305.0
27/05/2019	Spring	MAY	N/A	1.2	0.0	16.3	293.0	10.8	286.0
29/05/2019	Spring	MAY	N/A	1.2	0.0	11.5	180.0	10.0	244.0
31/05/2019	Spring	MAY	N/A	0.0	0.0	10.6	242.0	10.8	237.0
29/07/2019	Summer	SWAC	2.5	5.6	0.0	17.3	126.0	11.0	168.0
31/07/2019	Summer	SWAC	2.8	0.0	6.2	23.4	256.0	14.9	254.0
02/08/2019	Summer	SWAC	2.7	0.0	0.0	7.4	14.0	6.6	110.0
05/08/2019	Summer	SWAC	2.7	0.0	1.4	8.6	257.0	14.1	237.0
07/08/2019	Summer	SWAC	2.7	0.4	0.0	19.8	238.0	13.4	249.0
09/08/2019	Summer	SWAC	3.1	2.2	3.0	27.8	204.0	23.0	211.0
12/08/2019	Summer	SWAC	2.7	2.6	0.0	4.9	241.0	6.8	276.0
14/08/2019	Summer	SWAC	2.9	3.2	2.0	16.6	209.0	13.5	223.0
16/08/2019	Summer	SWAC	3.2	12.2	0.0	16.8	214.0	16.8	223.0
19/08/2019	Summer	SWAC	3.1	1.6	0.0	5.2	267.0	11.1	254.0
21/08/2019	Summer	SWAC	2.9	0.0	0.0	8.0	209.0	6.2	220.0

Sampling Date	Season	Location	River Flow Data (m^3/s)	Rainfall (mm/day)	Antecedent Rainfall (mm/day)	Wind Speed (knots)	Wind Direction (degrees)	Daily Average Wind Speed (knots)	Daily Average Wind Direction (degrees)
23/08/2019	Summer	SWAC	2.9	0.0	0.0	7.8	132.0	6.0	155.0
29/07/2019	Summer	MAY	N/A	5.6	0.0	16.6	125.0	11.0	168.0
31/07/2019	Summer	MAY	N/A	0.0	6.2	13.7	269.0	14.9	254.0
02/08/2019	Summer	MAY	N/A	0.0	0.0	8.2	31.0	6.6	110.0
05/08/2019	Summer	MAY	N/A	0.0	1.4	15.1	247.0	14.1	237.0
07/08/2019	Summer	MAY	N/A	0.4	0.0	18.8	238.0	13.4	249.0
09/08/2019	Summer	MAY	N/A	2.2	3.0	27.4	223.0	23.0	211.0
12/08/2019	Summer	MAY	N/A	2.6	0.0	1.9	248.0	6.8	276.0
14/08/2019	Summer	MAY	N/A	3.2	2.0	19.9	208.0	13.5	223.0
16/08/2019	Summer	MAY	N/A	12.2	0.0	26.9	211.0	16.8	223.0
19/08/2019	Summer	MAY	N/A	1.6	0.0	3.5	249.0	11.1	254.0
21/08/2019	Summer	MAY	N/A	0.0	0.0	6.8	158.0	6.2	220.0
23/08/2019	Summer	MAY	N/A	0.0	0.0	9.9	134.0	6.0	155.0
04/11/2019	Autumn	SWAC	5.8	5.0	5.6	5.8	168.0	7.8	150.0
06/11/2019	Autumn	SWAC	6.0	17.4	0.6	9.2	204.0	8.3	197.0

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Sampling Date	Season	Location	River Flow Data (m^3/s)	Rainfall (mm/day)	Antecedent Rainfall (mm/day)	Wind Speed (knots)	Wind Direction (degrees)	Daily Average Wind Speed (knots)	Daily Average Wind Direction (degrees)
08/11/2019	Autumn	SWAC	5.8	0.0	0.0	10.6	10.0	9.7	273.0
11/11/2019	Autumn	SWAC	5.8	0.0	4.4	22.1	297.0	15.5	264.0
13/11/2019	Autumn	SWAC	5.5	6.0	6.0	N/A	N/A	9.5	235.0
15/11/2019	Autumn	SWAC	5.3	2.0	2.0	21.1	7.0	14.4	135.0
18/11/2019	Autumn	SWAC	5.1	0.0	0.0	N/A	N/A	8.1	249.0
20/11/2019	Autumn	SWAC	5.3	0.0	0.2	30.1	120.0	21.7	133.0
22/11/2019	Autumn	SWAC	5.6	3.2	7.0	19.0	116.0	17.9	135.0
25/11/2019	Autumn	SWAC	6.3	6.0	2.6	10.5	209.0	13.2	190.0
27/11/2019	Autumn	SWAC	6.8	3.8	4.0	5.3	272.0	11.2	231.0
29/11/2019	Autumn	SWAC	6.0	0.0	0.6	5.4	28.0	7.7	55.0
04/11/2019	Autumn	MAY	N/A	5.0	5.6	7.1	161.0	7.8	150.0
06/11/2019	Autumn	MAY	N/A	17.4	0.6	7.2	192.0	8.3	197.0
08/11/2019	Autumn	MAY	N/A	0.0	0.0	12.2	359.0	9.7	273.0
11/11/2019	Autumn	MAY	N/A	0.0	4.4	26.9	285.0	15.5	264.0
13/11/2019	Autumn	MAY	N/A	6.0	6.0	N/A	N/A	9.5	235.0

Sampling Date	Season	Location	River Flow Data (m^3/s)	Rainfall (mm/day)	Antecedent Rainfall (mm/day)	Wind Speed (knots)	Wind Direction (degrees)	Daily Average Wind Speed (knots)	Daily Average Wind Direction (degrees)
15/11/2019	Autumn	MAY	N/A	2.0	2.0	15.2	4.0	14.4	135.0
18/11/2019	Autumn	MAY	N/A	0.0	0.0	8.8	6.0	8.1	249.0
20/11/2019	Autumn	MAY	N/A	0.0	0.2	23.8	122.0	21.7	133.0
22/11/2019	Autumn	MAY	N/A	3.2	7.0	23.6	124.0	17.9	135.0
25/11/2019	Autumn	MAY	N/A	6.0	2.6	7.8	211.0	13.2	190.0
27/11/2019	Autumn	MAY	N/A	3.8	4.0	5.8	291.0	11.2	231.0
29/11/2019	Autumn	MAY	N/A	0.0	0.6	6.7	20.0	7.7	55.0

Appendix A Table 3 Tide and Other Environmental Data

Sampling Date	Season	Location	Salinity	SSC (mg/L)	Dredging	Tidal State	Tidal Height at Sampling Time (OD)	Tidal Range	Time in Cycle
04/02/2019	Winter	SWAC	30.3	54.0	N/A	flood	1.3	1.8	neap
06/02/2019	Winter	SWAC	24.8	32.0	N/A	flood	1.2	1.6	neap
08/02/2019	Winter	SWAC	29.1	68.0	N/A	ebb	1.9	2.5	mid
11/02/2019	Winter	SWAC	23.1	22.0	N/A	ebb	0.7	3.4	mid
13/02/2019	Winter	SWAC	20.9	18.0	N/A	N/A	N/A	4.1	spring
15/02/2019	Winter	SWAC	20.1	32.0	N/A	HWS	-0.8	3.7	spring
18/02/2019	Winter	SWAC	24.8	4.0	N/A	flood	0.7	2.8	mid
20/02/2019	Winter	SWAC	29.2	20.0	N/A	flood	1.8	2.4	neap
22/02/2019	Winter	SWAC	29.0	14.0	N/A	LWS	1.8	2.8	mid
25/02/2019	Winter	SWAC	27.3	14.0	N/A	ebb	0.3	4.0	spring
27/02/2019	Winter	SWAC	17.3	24.0	N/A	HWS	-0.5	4.2	spring
01/03/2019	Winter	SWAC	15.5	2.0	N/A	HWS	-0.7	4.1	spring
04/02/2019	Winter	MAY	23.9	12.0	N/A	flood	1.1	1.8	neap
06/02/2019	Winter	MAY	23.4	16.0	N/A	flood	1.2	1.6	neap
08/02/2019	Winter	MAY	27.5	64.0	N/A	LWS	1.9	2.5	mid

Sampling Date	Season	Location	Salinity	SSC (mg/L)	Dredging	Tidal State	Tidal Height at Sampling Time (OD)	Tidal Range	Time in Cycle
11/02/2019	Winter	MAY	27.8	2.0	N/A	ebb	1.0	3.4	mid
13/02/2019	Winter	MAY	19.1	8.0	N/A	N/A	N/A	4.1	spring
15/02/2019	Winter	MAY	25.7	18.0	N/A	HWS	-0.7	3.7	spring
18/02/2019	Winter	MAY	20.3	6.0	N/A	flood	-0.1	2.8	mid
20/02/2019	Winter	MAY	22.6	10.0	N/A	flood	1.7	2.4	neap
22/02/2019	Winter	MAY	28.7	16.0	N/A	flood	1.6	2.8	mid
25/02/2019	Winter	MAY	26.7	30.0	N/A	ebb	0.9	4.0	spring
27/02/2019	Winter	MAY	26.3	28.0	N/A	HWS	-0.4	4.2	spring
01/03/2019	Winter	MAY	27.1	46.0	N/A	HWS	-0.6	4.1	spring
06/05/2019	Spring	SWAC	31.0	124.0	N/A	flood	1.7	3.9	spring
08/05/2019	Spring	SWAC	30.5	12.0	N/A	flood	0.5	3.7	spring
10/05/2019	Spring	SWAC	26.0	26.0	N/A	flood	-0.3	3.3	mid
13/05/2019	Spring	SWAC	23.7	100.0	N/A	LWS	-1.3	2.6	neap
15/05/2019	Spring	SWAC	27.4	42.0	N/A	ebb	0.7	3.3	mid
17/05/2019	Spring	SWAC	29.1	46.0	N/A	HWS	1.7	3.9	spring
20/05/2019	Spring	SWAC	30.8	46.0	N/A	HWS	1.9	4.1	spring

Sampling Date	Season	Location	Salinity	SSC (mg/L)	Dredging	Tidal State	Tidal Height at Sampling Time (OD)	Tidal Range	Time in Cycle
22/05/2019	Spring	SWAC	30.1	22.0	N/A	flood	0.3	3.7	spring
24/05/2019	Spring	SWAC	25.7	22.0	N/A	flood	-0.3	3.0	mid
27/05/2019	Spring	SWAC	20.9	26.0	N/A	flood	-0.5	2.0	neap
29/05/2019	Spring	SWAC	25.2	522.0	N/A	ebb	-0.2	2.2	neap
31/05/2019	Spring	SWAC	27.9	14.0	N/A	ebb	1.0	2.9	mid
06/05/2019	Spring	MAY	30.4	54.0	N/A	HWS	1.8	3.9	spring
08/05/2019	Spring	MAY	22.2	28.0	N/A	flood	1.0	3.7	spring
10/05/2019	Spring	MAY	28.1	30.0	N/A	flood	-0.2	3.3	mid
13/05/2019	Spring	MAY	31.3	66.0	N/A	LWS	-1.3	2.6	neap
15/05/2019	Spring	MAY	29.4	424.0	N/A	ebb	0.2	3.3	mid
17/05/2019	Spring	MAY	30.2	20.0	N/A	HWS	1.7	3.9	spring
20/05/2019	Spring	MAY	30.1	18.0	N/A	HWS	1.8	4.1	spring
22/05/2019	Spring	MAY	30.2	42.0	N/A	flood	0.8	3.7	spring
24/05/2019	Spring	MAY	29.6	36.0	N/A	flood	-0.3	3.0	mid
27/05/2019	Spring	MAY	29.8	36.0	N/A	flood	-0.4	2.0	neap
29/05/2019	Spring	MAY	29.6	108.0	N/A	ebb	-0.6	2.2	neap

Sampling Date	Season	Location	Salinity	SSC (mg/L)	Dredging	Tidal State	Tidal Height at Sampling Time (OD)	Tidal Range	Time in Cycle
31/05/2019	Spring	MAY	26.8	36.0	N/A	ebb	0.8	2.9	mid
29/07/2019	Summer	SWAC	30.5	42.0	N/A	ebb	1.1	2.7	mid
31/07/2019	Summer	SWAC	31.7	32.0	N/A	HWS	1.6	3.5	mid
02/08/2019	Summer	SWAC	31.6	36.0	N/A	HWS	2.0	4.2	spring
05/08/2019	Summer	SWAC	31.8	60.0	N/A	flood	-0.3	4.1	spring
07/08/2019	Summer	SWAC	29.1	40.0	N/A	flood	-0.5	3.3	mid
09/08/2019	Summer	SWAC	27.9	24.0	N/A	LWS	-0.7	2.5	mid
12/08/2019	Summer	SWAC	23.4	16.0	N/A	HWS	1.4	2.6	neap
14/08/2019	Summer	SWAC	32.3	22.0	N/A	HWS	1.8	3.2	mid
16/08/2019	Summer	SWAC	32.4	32.0	N/A	HWS	1.8	3.5	spring
19/08/2019	Summer	SWAC	31.8	40.0	N/A	flood	0.4	3.4	mid
21/08/2019	Summer	SWAC	29.2	28.0	N/A	flood	-0.3	3.1	mid
23/08/2019	Summer	SWAC	27.5	20.0	N/A	flood	-0.4	2.6	neap
29/07/2019	Summer	MAY	31.5	62.0	N/A	ebb	0.8	2.7	mid
31/07/2019	Summer	MAY	31.1	42.0	N/A	HWS	1.7	3.5	mid
02/08/2019	Summer	MAY	32.4	26.0	N/A	HWS	2.0	4.2	spring

Sampling Date	Season	Location	Salinity	SSC (mg/L)	Dredging	Tidal State	Tidal Height at Sampling Time (OD)	Tidal Range	Time in Cycle
05/08/2019	Summer	MAY	30.1	58.0	N/A	flood	-0.1	4.1	spring
07/08/2019	Summer	MAY	31.1	92.0	N/A	flood	-0.4	3.3	mid
09/08/2019	Summer	MAY	32.1	214.0	N/A	flood	-0.5	2.5	neap
12/08/2019	Summer	MAY	27.8	20.0	N/A	ebb	1.3	2.6	mid
14/08/2019	Summer	MAY	32.5	28.0	N/A	HWS	1.8	3.2	mid
16/08/2019	Summer	MAY	31.6	30.0	N/A	HWS	1.9	3.5	spring
19/08/2019	Summer	MAY	30.7	30.0	N/A	flood	0.8	3.4	mid
21/08/2019	Summer	MAY	30.9	28.0	N/A	flood	-0.2	3.1	mid
23/08/2019	Summer	MAY	31.9	24.0	N/A	flood	-0.3	2.6	neap
04/11/2019	Autumn	SWAC	19.0	20.0	N	flood	0.3	1.8	neap
06/11/2019	Autumn	SWAC	21.2	16.0	N	flood	-0.2	1.6	neap
08/11/2019	Autumn	SWAC	23.0	8.0	N	ebb	-0.7	2.5	mid
11/11/2019	Autumn	SWAC	29.1	18.0	N	ebb	1.0	3.4	mid
13/11/2019	Autumn	SWAC	29.8	20.0	N	N/A	N/A	4.1	spring
15/11/2019	Autumn	SWAC	29.2	38.0	N	HWS	1.6	3.7	spring
18/11/2019	Autumn	SWAC	26.1	22.0	Y	flood	N/A	2.8	mid

Sampling Date	Season	Location	Salinity	SSC (mg/L)	Dredging	Tidal State	Tidal Height at Sampling Time (OD)	Tidal Range	Time in Cycle
20/11/2019	Autumn	SWAC	23.6	18.0	N	flood	-0.1	2.4	neap
22/11/2019	Autumn	SWAC	19.1	44.0	Y	LWS	-0.9	2.8	mid
25/11/2019	Autumn	SWAC	26.1	16.0	N	ebb	1.1	4.0	spring
27/11/2019	Autumn	SWAC	27.1	18.0	N	HWS	2.3	4.2	spring
29/11/2019	Autumn	SWAC	28.4	2.0	N	HWS	1.9	4.1	spring
04/11/2019	Autumn	MAY	23.6	6.0	N	flood	0.6	1.8	neap
06/11/2019	Autumn	MAY	30.7	16.0	Y	flood	-0.1	1.6	neap
08/11/2019	Autumn	MAY	30.2	38.0	N	LWS	-1.0	2.5	mid
11/11/2019	Autumn	MAY	29.8	18.0	Y	ebb	0.6	3.4	mid
13/11/2019	Autumn	MAY	28.7	24.0	N	N/A	N/A	4.1	spring
15/11/2019	Autumn	MAY	29.8	32.0	N	HWS	1.6	3.7	spring
18/11/2019	Autumn	MAY	29.3	16.0	Y	flood	1.2	2.8	mid
20/11/2019	Autumn	MAY	30.5	110.0	N	flood	0.1	2.4	neap
22/11/2019	Autumn	MAY	25.5	376.0	Y	flood	-0.7	2.8	mid
25/11/2019	Autumn	MAY	26.8	32.0	N	ebb	0.4	4.0	spring
27/11/2019	Autumn	MAY	22.2	20.0	N	HWS	2.2	4.2	spring

Sampling Date	Season	Location	Salinity	SSC (mg/L)	Dredging	Tidal State	Tidal Height at Sampling Time (OD)	Tidal Range	Time in Cycle
29/11/2019	Autumn	MAY	30.2	14.0	N	HWS	1.9	4.1	spring

Appendix B Intertidal Data

Appendix B Table 1 Intertidal Microplastic Abundance and Suspended Sediment Concentrations

Tide Cycle	Time	Microplastics/m2	Microplastics/L	Suspended Sediment mg/L
Spring	13:00	19.4	184.6	248
Spring	13:15	22.4	234.1	116
Spring	13:30	14.3	151.8	124
Spring	13:45	16.8	168.9	98
Spring	14:00	12.1	117.6	70
Spring	14:15	8.1	69.4	272
Spring	15:30	7.1	67.8	52
Spring	16:30	8.7	92.7	126
Spring	16:45	5.6	52.3	62
Spring	17:00	3.9	36.9	174
Spring	17:15	6.2	72.5	38
Spring	17:30	1.9	29.5	70
Spring	17:45	5.9	64.7	64
Neap	07:00	7.1	45.5	926
Neap	07:15	7.1	80.3	382
Neap	07:30	4	44.5	298
Neap	07:45	7.5	75.6	230
Neap	09:30	2.2	23.3	42
Neap	10:30	1.6	18.6	20

Appendix B

Tide Cycle	Time	Microplastics/m2	Microplastics/L	Suspended Sediment mg/L
Neap	10:45	1.9	26.4	8
Neap	11:00	1.6	14	52
Neap	11:15	0.3	10.9	58

Appendix C Resuspension

C.1 Meta Data

Appendix C Table 1 Meta Data for Resuspension Data

Data title	Data from Annual Flume Experiments to determine the resuspension characteristics of microplastics in clay and sand beds
Dataset abstract	The Core MiniFlume, an annual flume, was used to determine the resuspension characteristics of microplastics (PP fibres, PVA nurdles) as part of two types of sediment bed (clay, sand). Model sediment beds were utilised. A stepwise increasing velocity was applied using the flume. Velocity was measured using a Nortek Vectrino Acoustic Doppler Velocimeter (ADV) and turbidity using a Seapoint Optical Backscatter Sensor (OBS).
Data set DOI	https://doi.org/10.5258/SOTON/D1893
Time-series: resolution of data	Variable: ADV: 25 Hz OBS: 1Hz
Platform name	Core MiniFlume
Sampling protocol	Four sediment beds were prepared. Kaolinite clay (ACROS Organics) was used in the preparation of the clay bed, with a clay slurry formed with salt water (35 PSU, prepared with tap water and sea salt (Fluval Sea Marine Salt)) and left to settle for three days before each experiment was run. Sand (marine sand, unknown origin) was sieved to produce three size categories (150-212 µm; 300-425 µm; 600-800 µm). A sediment bed of approximately 7 cm depth was formed at the base of the Core MiniFlume, and a step-wise increasing velocity

	applied to determine threshold of erosion and to observe plastic behaviour. A Nortek Vectrino ADV and Seapoint OBS measured continuously. 20 mL water samples were taken 1 minute before the end of each velocity step to determine suspended sediment concentration. Filename format: SubstrateName e.g., MediumSand
Analytical protocol:	ADV processed to remove measurements with less than 80% correlation; then averaged over 20 second intervals. OBS data was averaged to 20 second intervals, then correlated with measured SSC values. SSC values were then calculated using OBS values.
Absent data value:	#NA

C.2 Resuspension – Suspended Sediment Calibrations

C.2.1 Fine Sand – Suspended Sediment Calibrations

Appendix C Table 2 Fine Sand Suspended Sediment Values (g/L)

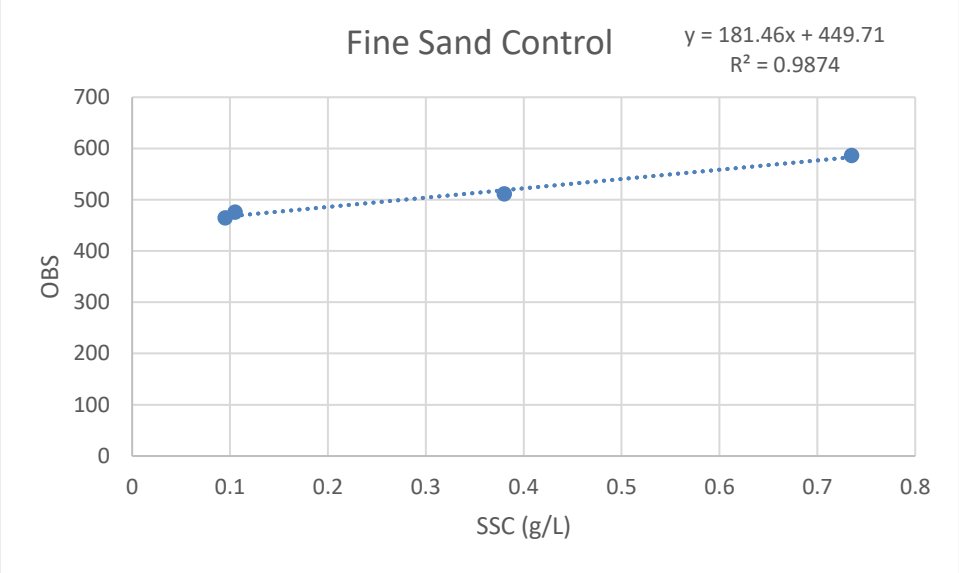
Time (minutes)	**Control**	**Surface Nurdles**	**Buried Nurdles**	**Buried Fibres**
9	0.095	1.31	0.135	0.81
19	0.105	0.105	0.125	0.19
29	0.38	0.325	0.455	0.615
39	0.735	0.31	0.745	2.01
49	3.53	4.29	1.4	1.135
59	3.55	8.51	6.38	8.855
69	12.245	12.665	12.4	18.37
79	16.66	10.605	12.605	20.585

Time (minutes)	Control	Surface Nurdles	Buried Nurdles	Buried Fibres
89	22.18	19.795	13.385	26.405

Appendix C Table 3 Fine Sand Control Calibration Values

Time (minutes)	SSC (g/L)	OBS
9	0.095	464.29
19	0.105	475.52
29	0.38	511.45
39	0.735	586.185

Appendix C Figure 1 Fine Sand Control Calibration



Appendix C Table 4 Fine Sand Surface Nurdles Calibration Values

Time (minutes)	SSC (g/)	OBS
9	1.31	451.27
19	0.105	448.74
29	0.325	488.1

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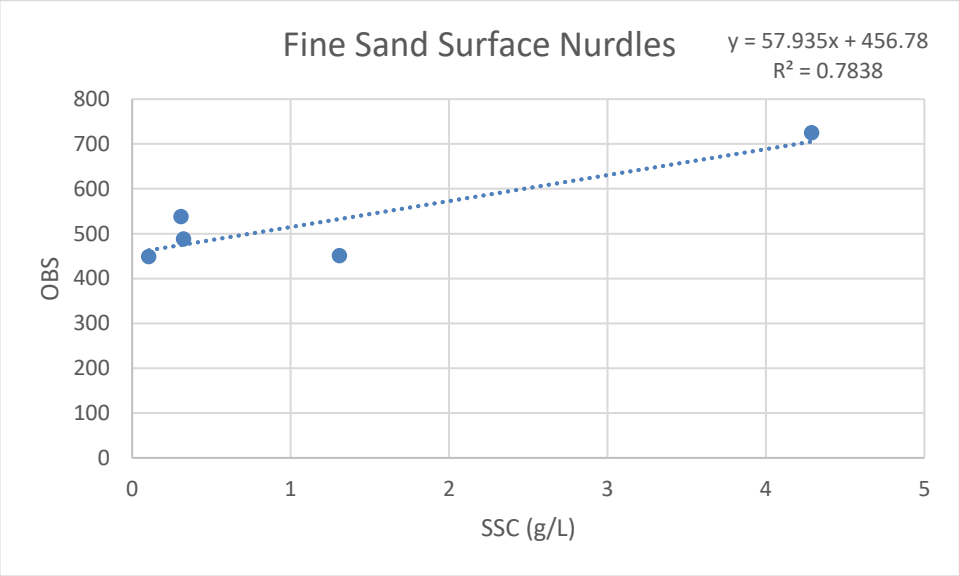
Time (minutes)	SSC (g/)	OBS
39	0.31	538.095
49	4.29	725

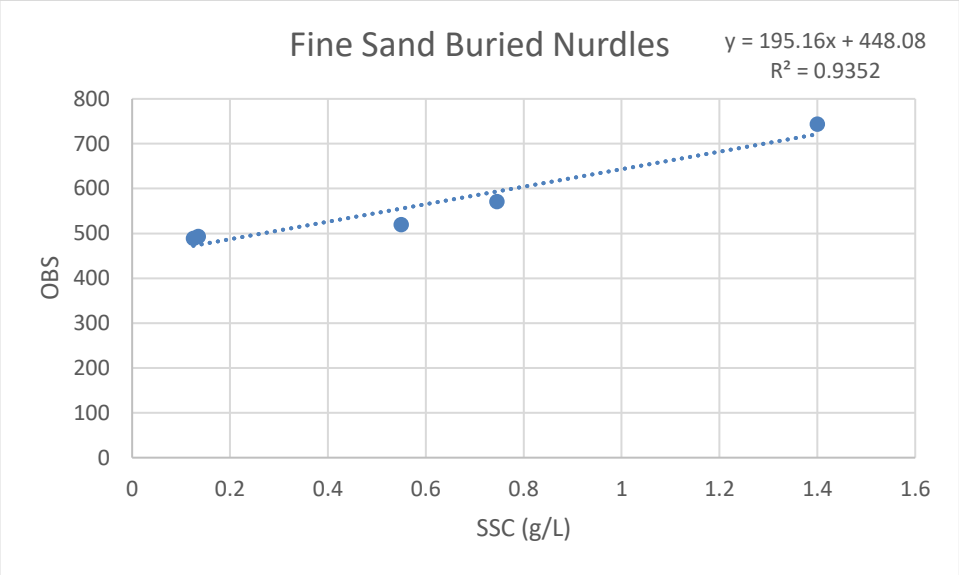
Appendix C Figure 2 Fine Sand Surface Nurdles Calibration



Appendix C Table 5 Fine Sand Buried Nurdles Calibration Values

Time (minutes)	SSC (g/L)	OBS
9	0.135	493.28
19	0.125	489.045
29	0.55	519.485
39	0.745	571.425
49	1.4	743.85

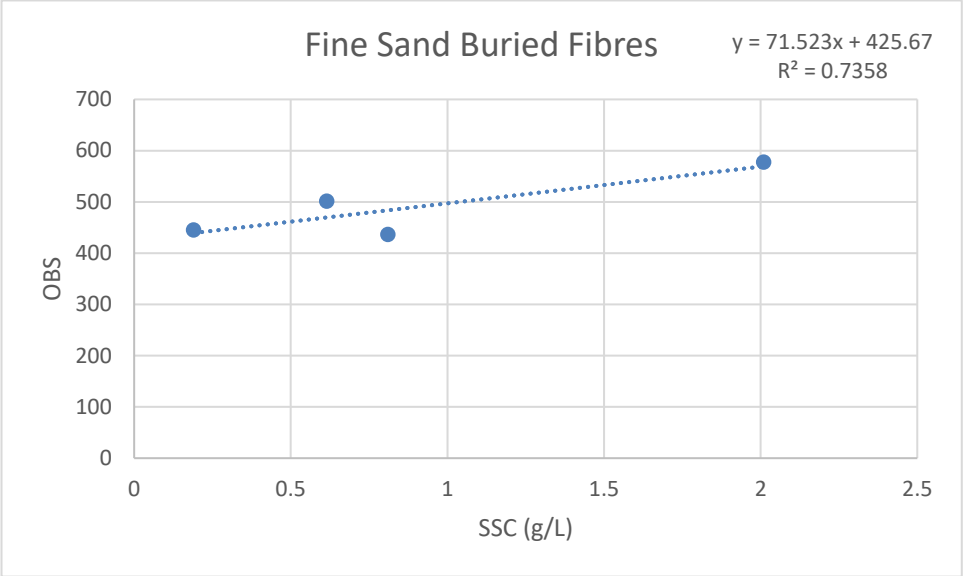
Appendix C Figure 3 Fine Sand Buried Nurdles Calibration



Appendix C Table 6 Fine Sand Buried Fibres Calibration

Time (minutes)	**SSC (g/L)**	**OBS**
9	0.81	436.71
19	0.19	445.39
29	0.615	502
39	2.01	577.855

Appendix C Figure 4 Fine Sand Buried Fibres Calibration



C.2.2 Medium Sand – Suspended Sediment Calibrations

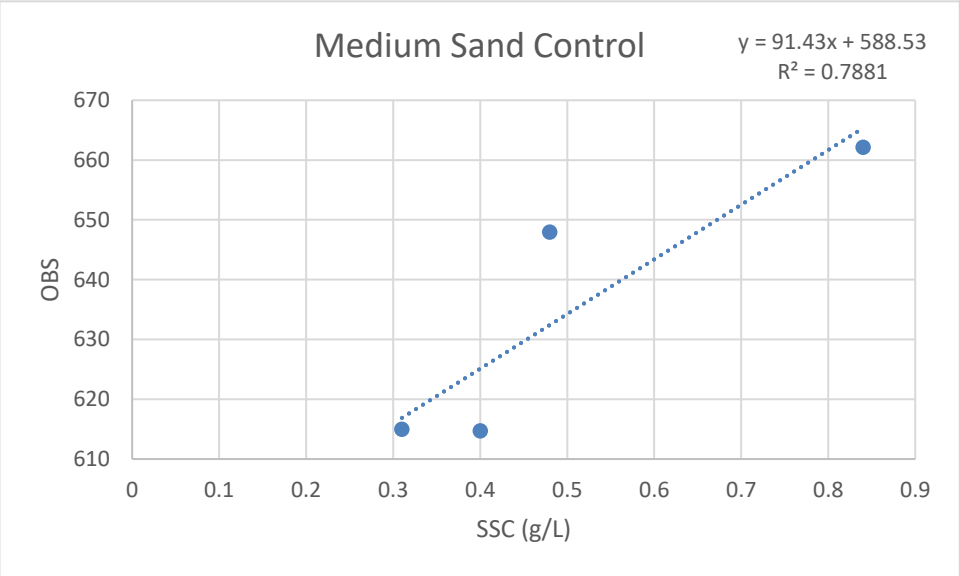
Appendix C Table 7 Medium Sand Suspended Sediment Values (g/L)

Time (minutes)	Control	Surface Nurdles	Buried Nurdles	Buried Fibres
9	2.435	1.925	3.875	0.025
19	0.31	0.06	0.365	0.04
29	0.4	0.545	0.15	0.44
39	0.48	0.66	0.515	0.26
49	0.84	0.675	0.19	1.32
59	1.58	1.115	1.81	2.48
69	6.51	2.685	3.125	2.29
79	9.415	6.885	5.6	7.15
89	11.66	10.72	9.38	16.055

Appendix C Table 8 Medium Sand Control Calibration Values

Time (minutes)	SSC (g/L)	OBS
19	0.31	614.98
29	0.4	614.675
39	0.48	647.95
49	0.84	662.12

Appendix C Figure 5 Medium Sand Control Calibration

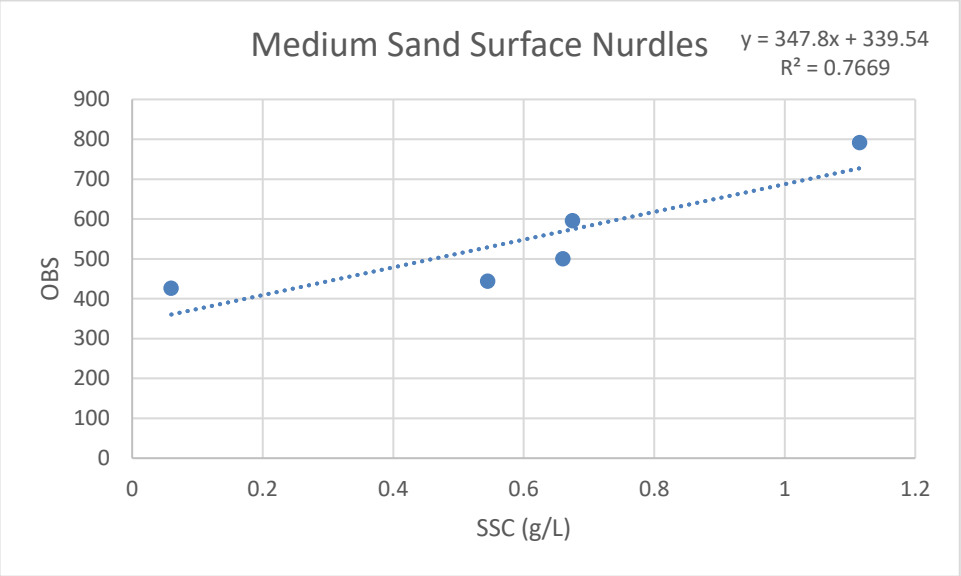


Appendix C Table 9 Medium Sand Surface Nurdles Calibration Values

Time (minutes)	SSC (g/L)	OBS
19	0.06	426.49
29	0.545	444.375
39	0.66	500.86
49	0.675	596.17
59	1.115	792.35

Appendix C

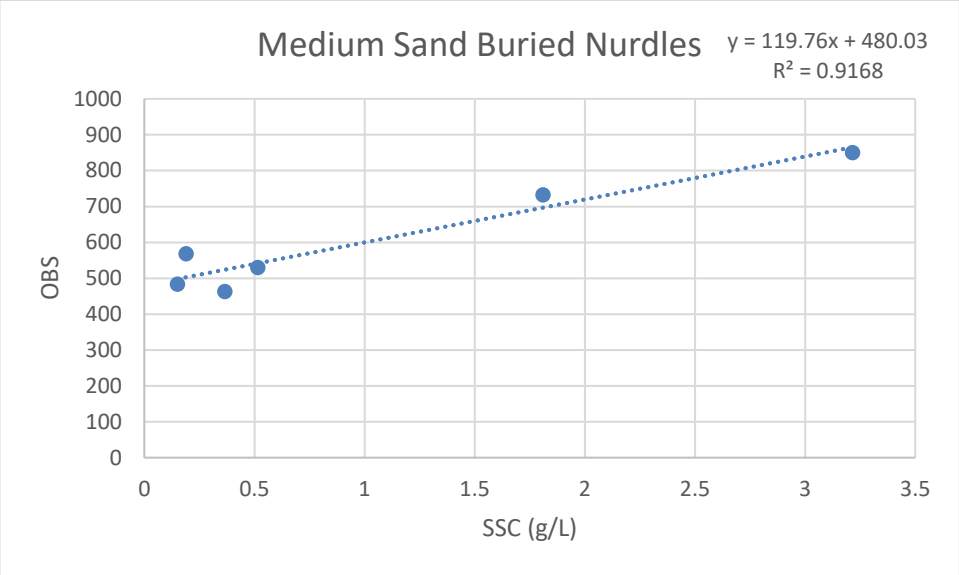
Appendix C Figure 6 Medium Sand Surface Nurdles Calibration



Appendix C Table 10 Medium Sand Buried Nurdles Calibration Values

Time (minutes)	**SSC (g/L)**	**OBS**
19	0.365	462.89
29	0.15	483.93
39	0.515	529.69
49	0.19	568.37
59	1.81	732.8
69	3.215	850.4

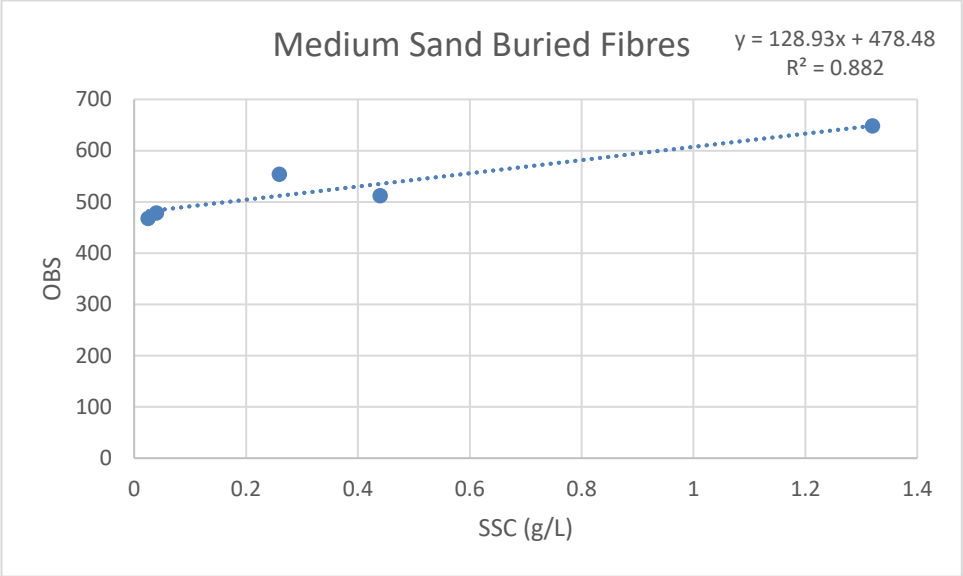
Appendix C Figure 7 Medium Sand Buried Nurdles Calibration



Appendix C Table 11 Medium Sand Buried Fibres Calibration Values

Time (minutes)	**SSC (g/L)**	**OBS**
9	0.025	467.715
19	0.04	478.38
29	0.44	512.48
39	0.26	554.29
49	1.32	648.335

Appendix C Figure 8 Medium Sand Buried Fibres Calibration



C.2.3 Coarse Sand – Suspended Sediment Calibration

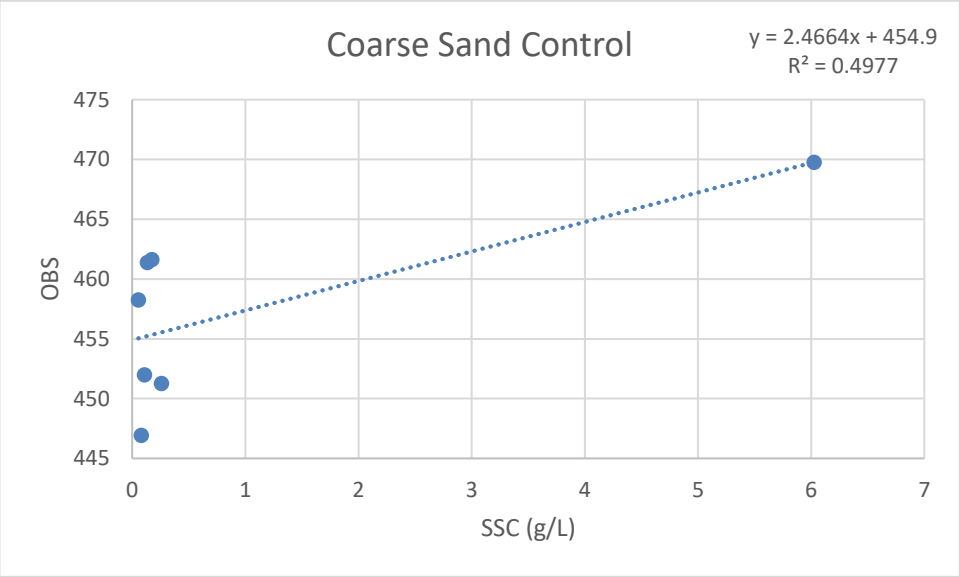
Appendix C Table 12 Coarse Sand Suspended Sediment Values (g/L)

Time (minutes)	Control	Surface Nurdles	Buried Nurdles	Buried Fibres
9	6.025	0.23	0.165	0.07
19	0.135	0.45	0.06	0.005
29	0.26	0.075	0.095	0.05
39	0.08	0.07	0.025	0.105
49	0.055	0.285	0.105	0.19
59	0.175	0.06	0.12	0.085
69	0.11	0.02	0.17	0.125
79	0.29	0.12	0.16	0.12
89	0.295	0.35	0.13	0.225

Appendix C Table 13 Coarse Sand Control Calibration Values

Time (minutes)	SSC (g/L)	OBS
9	6.025	469.765
19	0.135	461.375
29	0.26	451.28
39	0.08	446.925
49	0.055	458.255
59	0.175	461.615
69	0.11	451.98

Appendix C Figure 9 Coarse Sand Control Calibration

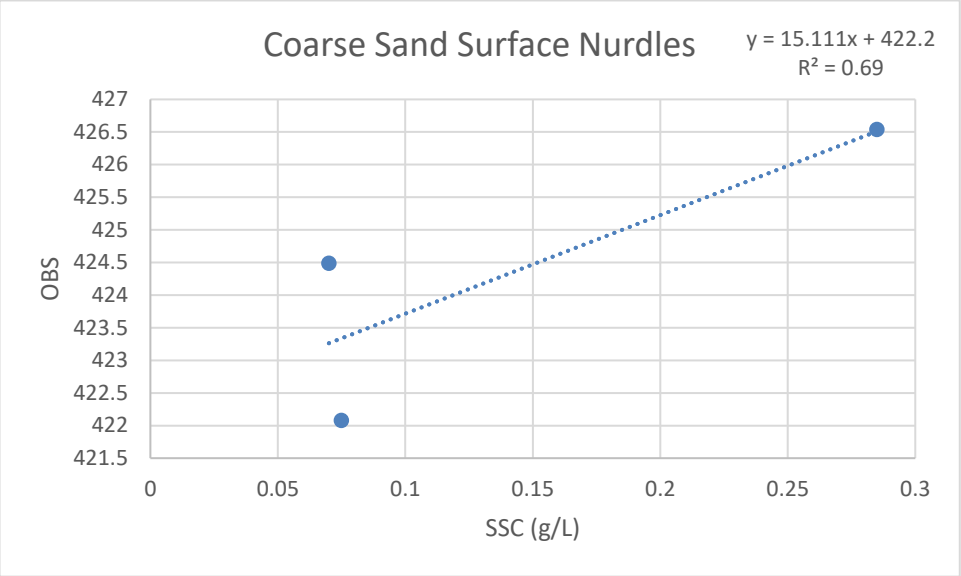


Appendix C Table 14 Coarse Sand Surface Nurdles Calibration Values

Time (minutes)	SSC (g/L)	OBS
29	0.075	422.08
39	0.07	424.49
49	0.285	426.54

Appendix C

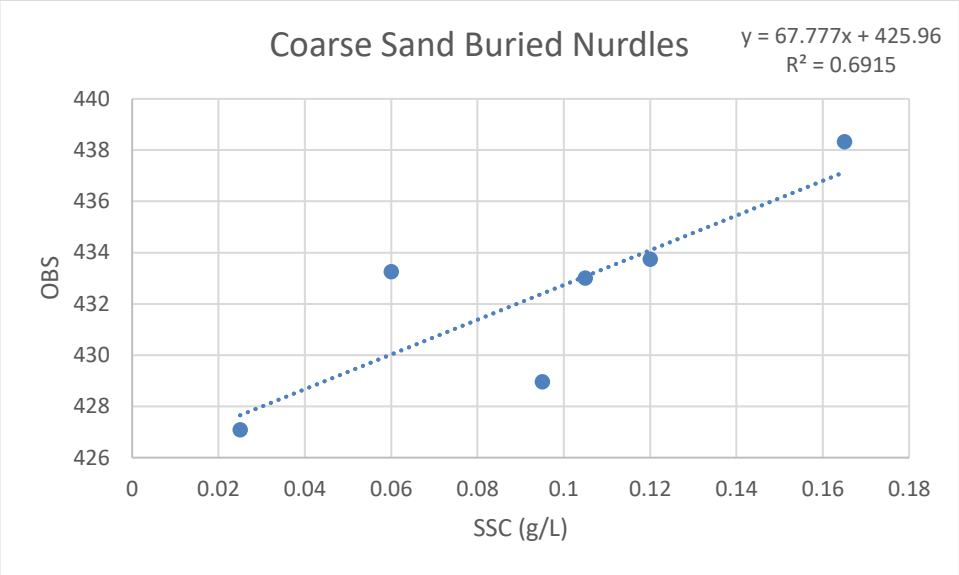
Appendix C Figure 10 Coarse Sand Surface Nurdles Calibration



Appendix C Table 15 Coarse Sand Buried Nurdles Calibration Values

Time (minutes)	**SSC (g/L)**	**OBS**
9	0.165	438.325
19	0.06	433.255
29	0.095	428.96
39	0.025	427.09
49	0.105	433.01
59	0.12	433.75

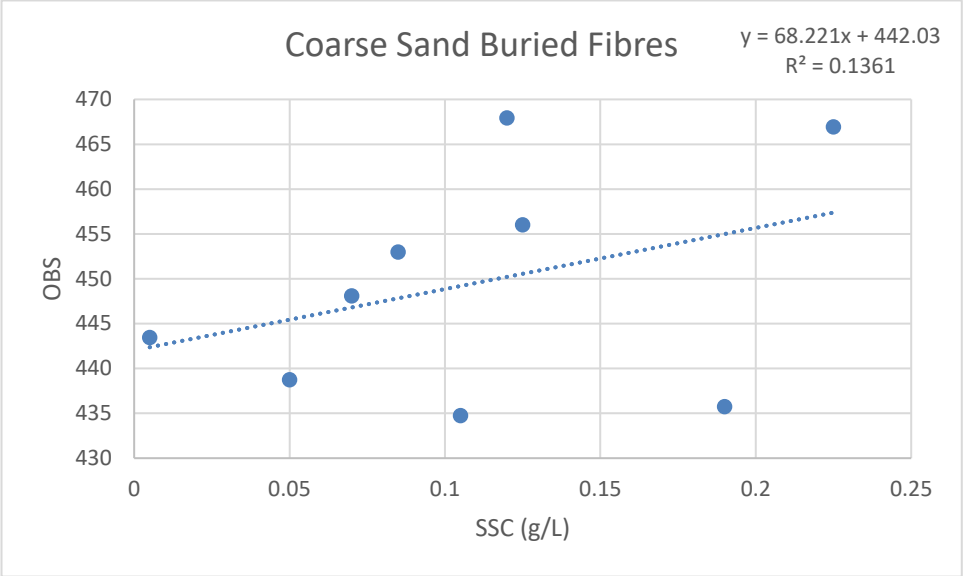
Appendix C Figure 11 Coarse Sand Buried Nurdles Calibration



Appendix C Table 16 Coarse Sand Buried Fibres Calibration Values

Time (minutes)	**SSC (g/L)**	**OBS**
9	0.07	448.09
19	0.005	443.47
29	0.05	438.77
39	0.105	434.765
49	0.19	435.775
59	0.085	452.985
69	0.125	456.04
79	0.12	467.94
89	0.225	466.955

Appendix C Figure 12 Coarse Sand Buried Fibres Calibration



C.2.4 Clay – Suspended Sediment Calibrations

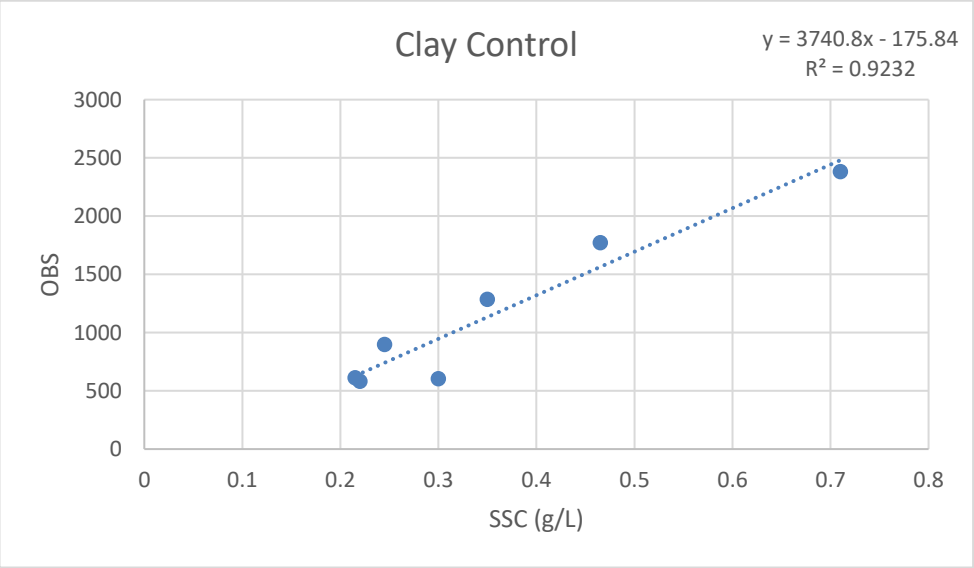
Appendix C Table 17 Clay Suspended Sediment Values (g/L)

Time (minutes)	Control	Surface Fibres	Buried Fibres
14	0.215	0.32	0.15
29	0.22	0.175	0.15
44	0.3	0.195	0.1
59	0.245	0.2	0.135
74	0.35	0.29	0.2
89	0.465	0.285	0.28
104	0.71	0.495	0.425
119	0.695	0.71	0.35
134	1.245	0.645	1.105

Appendix C Table 18 Clay Control Calibration Values

Time (minutes)	SSC (g/L)	OBS
14	0.215	612.375
29	0.22	582.8
44	0.3	604.55
59	0.245	898.95
74	0.35	1286.15
89	0.465	1772
104	0.71	2383

Appendix C Figure 13 Clay Control Calibration



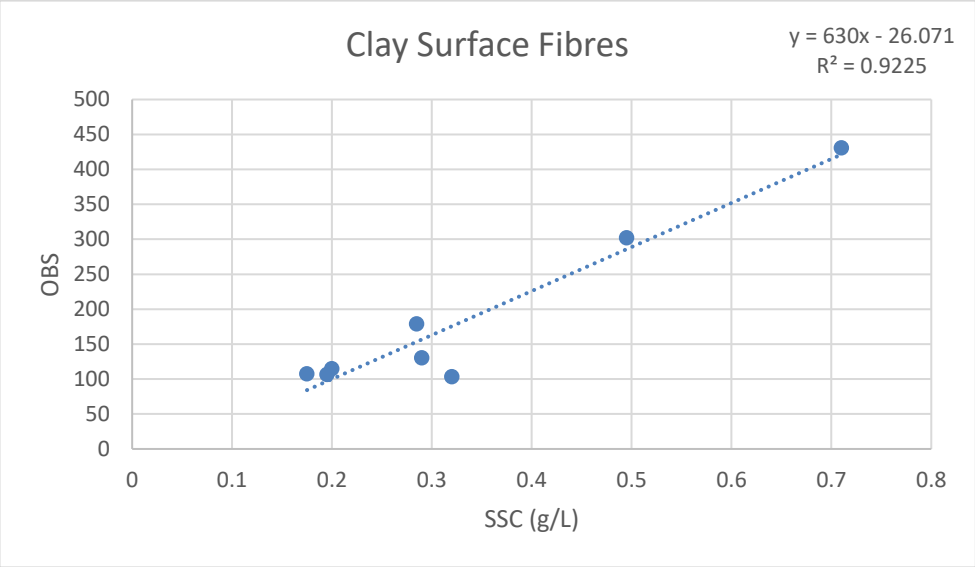
Appendix C Table 19 Clay Surface Fibres Calibration Values

Time (minutes)	SSC (g/L)	OBS
14	0.32	103.05
29	0.175	107.54
44	0.195	106.65

Appendix C

Time (minutes)	SSC (g/L)	OBS
59	0.2	114.71
74	0.29	130.07
89	0.285	178.85
104	0.495	302.15
119	0.71	430.515

Appendix C Figure 14 Clay Surface Fibres Calibration

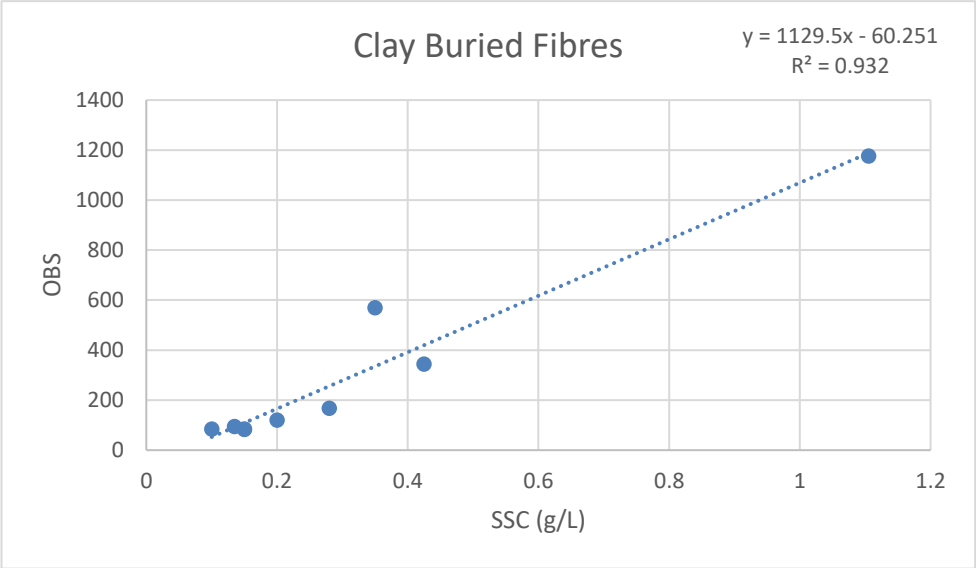


Appendix C Table 20 Clay Buried Fibres Calibration Values

Time (minutes)	SSC (g/L)	OBS
14	0.15	83.59
29	0.15	84.28
44	0.1	85.24
59	0.135	95.255
74	0.2	120.73
89	0.28	167.56

Time (minutes)	SSC (g/L)	OBS
104	0.425	344.83
119	0.35	569.765
134	1.105	1176.45

Appendix C Figure 15 Clay Buried Fibres Calibration



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