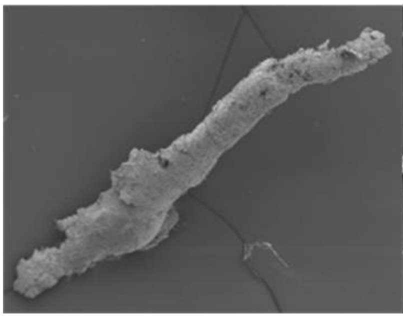
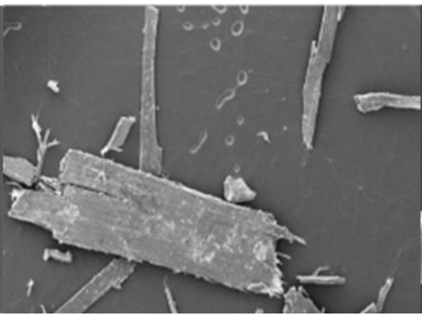
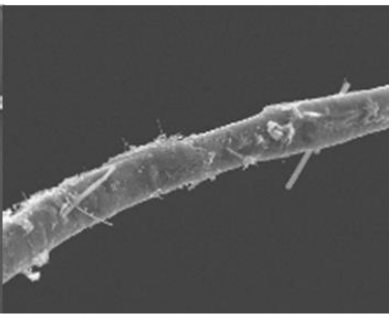
Investigating the sources and pathways of synthetic fibre and vehicle tyre wear contamination into the marine environment


Tyre wear particle


Fragments of abraded rope


Synthetic fibre

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We wish to acknowledge the landowners and water service companies who enabled sampling to take place. We would also like to thank the technicians at the University of Plymouth's Marine Biology and Ecology Research Centre. Particular thanks also go to Paul Donohue (UoN), Aaron Barrett (UoP), and Luka Wright (UoP). Lastly, we also wish to gratefully acknowledge the University of Plymouth's Electron Microscopy Centre for their support and assistance in this work.

Picture credits. Tyre wear particle collected from roadside drain material, Plymouth, UK, fragments of abraded rope, and synthetic fibres collected from atmospheric deposition beside an urban roadway, Plymouth UK. Plymouth Electron Microscopy Centre, University of Plymouth., 2019.

Executive summary

Microplastics are small pieces of plastic debris (<5 mm) that have accumulated either because of the fragmentation of larger items of plastic in the environment or have entered the environment directly as particles of less than 5 mm. It is widely accepted that microplastic contamination is widespread and increasing. Recent reports indicate that associated negative consequences could become widespread within the next 50 – 100 years unless current rates of contamination are reduced. It has been suggested that microplastics generated during use, for example from the wear of textiles and tyre tread are potentially the major sources of microplastic, yet empirical evidence on their pathways to the environment are lacking. The principal aims of this study were therefore to investigate the sources and pathways of synthetic fibre and tyre wear contamination to the marine environment. Some data exist on the sources of synthetic fibres, and it is clear they are widely distributed in the marine environment. However, data on the pathways for tyre wear particles from roads to the marine environment is sparse, and for that reason much of our environmental sampling was focused around roadways.

Once in the marine environment, tracing microplastics back to their source presents many difficulties. Therefore, our approach was to quantify both tyre particles and synthetic fibres as they enter the marine environment. Three points of entry were considered; release from treated wastewater effluent, direct release from storm water drains adjacent to roads, and deposition from the air within 50 m of roadsides. Samples were collected from replicate sites in the South West of England.

Tyre particles and synthetic fibres were detected entering the environment via all three pathways examined. Based on the sampling sites examined here, the presence of tyre particles reaching the environment, via all three pathways, appears to be substantially greater than the presence of fibres. Based on the locations sampled it would appear that storm water discharges, which pass directly from roads to aquatic environments, probably represent the most important pathway for tyre particles, whereas deposition from the atmosphere is likely to be the key pathway for fibres. Relatively low quantities of fibres and tyre particles were found in wastewater effluent.

Several intrinsic confounding factors limit the potential to make formal comparisons between pathways. For instance, while the volumes of effluent passing via wastewater treatment are documented, no such data exists for volumes of surface water runoff. Care should also be taken in extrapolating data on deposition form the air to distances greater than 50 m from roadways. It was clear, for example, that while tyre particles were abundant near to motorways and that fibres were not. This was probably because of the low number of pedestrians; it would therefore be important in

future sampling to consider locations a wider range of locations including those with high pedestrian footfall, but low traffic volumes. By contrast, it is also important to gain a better understanding of longer distance transport in the atmosphere; since fibres have recently been detected in samples from the Alps. Hence, pathways to the marine environment are likely to be more complex than the three pathways examined here.

Textile fibres are known to be widely distributed in the environment including remote locations such as the deep sea and the Arctic. Our findings indicated that tyre particles were typically denser and more heterogeneous in shape and size than textile fibres. From the perspective of transport in the marine environment, settlement velocity indicated that while a greater proportion of tyre wear particles, than fibres, were likely to settle close to their source, that some tyre wear particles had the potential to travel considerable distances. In addition, even for tyre particles that settled to the seabed the potential for resuspension was relatively high. Hence, we consider that the lack of tyre wear particles reported in previous studies, sampling the water column, sediment and biota, is likely to be caused by inadequate analytical methods rather than by an absence of tyre particles themselves.

In the case of fibre release to the marine environment we also considered, as a supplementary objective, fragmentation of rope and netting from maritime activities. This was examined by hauling new and old ropes over a pulley, both on the deck of a vessel and in a laboratory setting. This demonstrated that substantial numbers of microplastic pieces, as opposed to fibres, are likely to be generated by activities such as hauling of fishing nets and pots. We estimate that even under very modest loading a new rope could release roughly 40 microplastic pieces per meter hauled; whereas an older rope could release over 700 pieces per meter hauled.

From the perspective of intervention, these data indicate for example, that fitting filters to washing machines could be less effective than strategies to reduce fibre emission more directly via fabric design. This is because filters will only intercept fibres entering wastewater, but will not influence release to the air which, in light of these findings and other recent work, could be a more substantial pathway. Further research to examine the efficacy of drainage sumps to collect particulates prior to their passing to water courses may also be beneficial. More research is also needed to consider a mass balance approach to evaluate a wider range of sources and transport pathways. This should consider quantifying tyre particles and fragments along their entire transport pathways and at greater distances, 1, 10 and 100 km from roads and urban areas with sampling in seawater and air. It is also important to establish the fate of fibres and tyre particles that are intercepted either in roadside drains or wastewater treatment as it seems likely that current practices allow captured material, together with any microplastics, to be returned to the environment.

In conclusion, the findings of this report support the predictions of previous desk based studies that tyre wear particles are a major direct source of microplastics to the environment. It is important to note therefore that inadequate sampling of tyre particles in previous microplastic sampling is likely to have resulted in a considerable underestimate of the total microplastic burden that has accumulated in the environment. That is to say, tyre particles represent a substantial source of microplastics that is in addition to previously reported quantities of micropalstics from other sources (fibres, fragmentation, microbeads from cosmetics).

Contents

1.0 Background

Plastics are durable, inexpensive lightweight, highly versatile materials with a wide range of applications (Thompson *et al*., 2009; Cole *et al*., 2011). Consequently, plastic products have penetrated virtually all aspects of everyday life (Verschoor *et al*., 2016). However, it is recognised that microplastic contamination is widespread in the marine environment and may have a range of negative consequences (Wright *et al.,* 2013; Law and Thompson, 2014).

Microplastics are small pieces of plastic debris (<5 mm) that have accumulated either because of the fragmentation of larger items of plastics in the environment (secondary microplastics), or having entered the environment directly as particles of less than 5 mm (primary microplastics). The latter can occur as a consequence of the release small particles such as microbeads in cosmetics (Napper *et al.,* 2015), or the abrasion during use of larger items such as tyres or textiles which can result in the emission of small particulates (Napper and Thompson, 2016; Kole *et al*., 2017).

Verschoor *et al.* (2016) reviewed existing definitions and concluded there to be five major specific criteria in order to classify an item as microplastics; composition (synthetic polymer based), physical state (solid), size (<5 mm), solubility (insoluble in water), and degradation rate - low.

Some categories of microplastics, such as microbeads, are already under regulation in some locations and are not within the scope of this project. Microplastics generated during use, for example from the wear of textiles and tyre tread are potentially major contributors to microplastic emissions, yet empirical evidence on their pathways to the environment are lacking. The principal aims of this study were therefore to investigate the sources and pathways of synthetic fibre and tyre wear contamination to the marine environment.

This report will first review current understanding on the characteristics, and fate of tyre particles and synthetic fibres in the environment.

1.1 Tyre wear particles

The accumulation of tyre wear particles in the environment was described as early as the 1970's (Dannis, 1974; Pierson and Brachaczek, 1974; Cadle and Williams, 1978), however the potential for these particles to constitute a major proportion of microplastic contamination is a relatively new concept. The vast majority of articles referring tyre particles as a major component of microplastic litter stem from recent reports from Scandinavia and Germany (Sundt *et al*., 2014; Lassen *et al*., 2015; Essel *et al*., 2015; Magnusson *et al*., 2016), which identify releases of tyre wear to account for around half of all microplastic emissions in their respective countries (Germany, Norway, Sweden, and Denmark). These studies have taken a desk-based approach, synthesizing existing particle emission information as far as possible since empirical data from the environment is lacking. That said, they acknowledge these limitations and recognise the potential for substantial uncertainty in their findings. These reports have also provided a basis for extrapolative estimates produced by the IUCN and Eunomia (Eunomia, 2018; Boucher and Friot, 2017). The IUCN estimate tyre wear to contribute 28 % to emissions of primary microplastics (pieces that enter the environment within the microplastic size range <5 mm) to global ocean (420,000 tonnes yr^{-1}) (Boucher and Friot, 2017). In Europe, Eunomia (2018) estimate annual emissions of tyre wear to surface waters to be in the range of 52,000 to 136,000 tonnes yr^{-1}, making it the largest primary microplastic emitter to aquatic environments. However, these estimates are in stark contrast with the frequency with which tyre wear particles are actually reported from environmental samples (Figure 1).

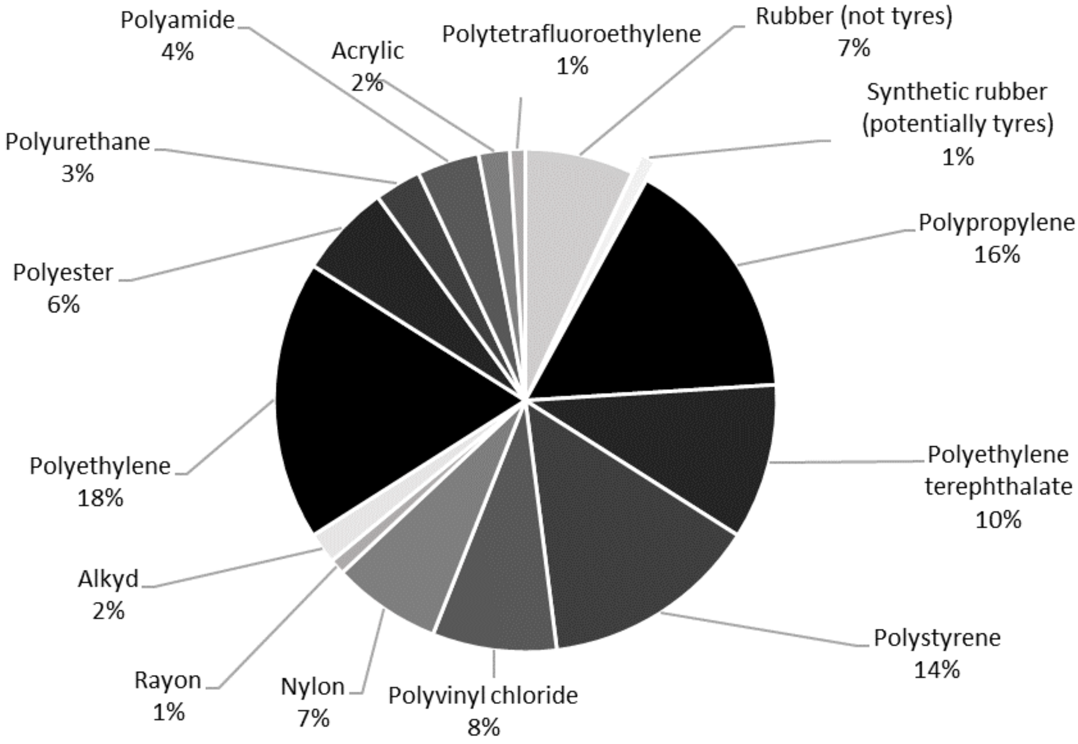

Fig. 1 The number of times different types of microplastic particles have been identified across 33 microplastic research papers retrieved from the search "microplastics" between 2000-2018 (Web of Science).

Tyre particles do not respond well to the conventional methods used for microplastic isolation from environmental samples and subsequent identification, making their quantification in environmental mediums challenging. Therefore, it is not clear whether the relatively low levels of detection in marine samples (Figure 1) are a consequence of a low environmental concentrations, or methodological limitations (Kole *et al.*, 2017). Publications regarding tyre wear reach a general consensus that their importance relative to other emissions is not certain, with little reliable quantitative data on their pathways to, or fate in the environment (Councell *et al*., 2004; Kreider *et al*., 2010; Magnusson *et al*., 2016; Siegfired *et al*., 2017). For tyre particles that do enter the environment, potential for transfer away from their point of entry is not certain (Essel *et al*., 2015).

Tyre wear particles can be generated from frictional energy between a tyre tread and the road surface, creating shear forces and heat leading to the generation of micro particles, sometimes referred to as TRWP's (tyre-road wear particles) (Dall'Osto *et al*., 2014). The stress and stretching of the tyre tread during this interaction, creates particles that are typically elongated in shape (Wu, 2016), see Figure 2A, though tyre wear particles have also been described as jagged and near-spherical (Dahl *et al*., 2006; Gustaffon *et al*., 2008; Want *et al*., 2017; Wagner *et al*., 2018). The rough exterior and large surface area, combined with the flexible properties of the rubber material, allows for adhesion and attachment of road dust, further increased by the rolling of the particles against the road by subsequent vehicles (Schramm, 2002; Sommer *et al*., 2018).

The interaction of these two surfaces, tyre and road surface, is so substantial that it can alter the chemical composition of the tread rubber material. Components of the road surface material (Fe and Ca), and tyre tread (Zn) have been reported in these particles, indicating the formation of aggregates (Kwak *et al*., 2013; Panko *et al*., 2019) (Figure 2B). Furthermore, these aggregates are not uniform, Sommer *et al.* (2018) reported the relative proportion of tyre to road material to vary considerably with up to 50 % encrustment of road material. These aggregates are likely to differ considerably from material abraded directly from tyre tread, or from particles artificially generated on a laboratory road simulator, and are therefore relatively poor proxies for those found in the environment (Kreider *et al.,* 2010). This further adds to the complexity of tracking and enumerating tyre particles in the environment (Cadle and Williams, 1978; Padovan *et al*., 1999; Adachi and Tainosho, 2004; Kreider *et al*., 2010; Panko *et al*., 2013; Wagner *et al*., 2018).

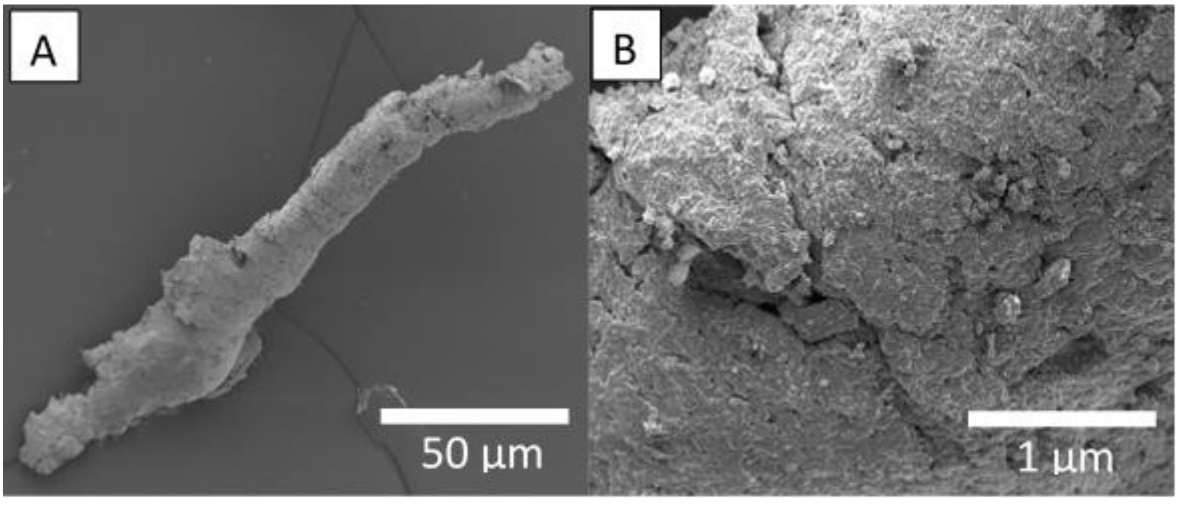

Fig. 2 (A) Tyre wear collected from roadside drain material, Plymouth, UK, (B) at greater magnification to highlight the incorporation of other material to the rubber matrix. Plymouth Electron Microscopy Centre., 2017.

Tyre tread is composed of a complex blend of compounds (Wagner *et al*., 2018). The major contributors (40 - 60 %) are a combination of rubbers, SBR (Styrene butadiene), NR (natural rubber), and PBR (Polybutadiene rubber). The remainder is comprised of a mixture of plasticizers and oils for elasticity, as well as minerals and vulcanization accelerators (added to improve durability), and fillers such as carbon black and silica, for increased resistance and strength (Kreider *et al*., 2010; Grigoratos and Martini, 2014; Kole *et al*., 2017; Vogeslang *et al*., 2018). The formation of aggregates of tyre tread and non-exhaust traffic emissions can potentially provide further polymer emissions to the environment. Road surfaces are typically comprised of aggregates, modifiers (including fillers and adhesives), as well as bitumen. The latter being added to improve strength, stability, adhesion, and elasticity as well as acting as a binder for the gravel (Zhang and Hu., 2013), and is itself a source of polymers, typically modified with SBR (styrene-butadiene rubber) and SBS (styrene-butadiene-styrene). Road surface markings, which can form aggregates with tyre tread wear, are also a source of polymers since road paint contains thermoplastic elastomers, typically EVA (ethylene vinyl acetate), SIS (styrene isoprene styrene), PA (polyamide), and polyacrylate.

Brake pad wear can also contribute to polymer emissions. For example, organic brake pads, the common the choice for passenger cars, use phenolic resin as a binder which incorporates rubber (typically SBR) to improve flexibility and damping (Saffar and Shojaei, 2012). While organic brake pads are both inexpensive to manufacture, and suitable for driving across many environments, they are not durable compared to alternatives, generating considerable particle wear.

The life expectancy of a passenger car tyre is around 40,000 km to 50,000 km, during which it will shed roughly 10 - 30 % of its total weight, and 30 - 50 % of its tread weight to the environment (Dannis, 1974; Grigoratos and Martini, 2014; Milani *et al*., 2004). The rate of production, size, and composition of tyre wear particles are highly complex, and influenced by a number of factors including, but not exclusive to; tyre type (radius, width, and depth), road characteristics (material, texture, porosity, and condition), contact area, vehicle maintenance, accumulated mileage, vehicle operation, and weather conditions. Under or over inflation of tyres, vehicle weight and load, deviations in wheel alignment, vehicle type, exposure to UV, road angle, and high traffic densities, are all expected to further increase tread wear (Albert and Walker, 1965; Councell *et al*., 2004; Gillies *et al*., 2005; Carslaw *et al*., 2006; Thorpe and Harrison, 2008; Verschoor *et al*., 2016; Kole *et al*., 2017; Wagner *et al*., 2018; Vogeslang *et al*., 2018).

Dahl *et al.* (2006) explored the effects of speed, tyre type, and road surface on tyre wear generation, using particles generated on a laboratory road simulator. Speed, which determines mechanical stress and consequently tread temperature, was consistently identified as the dominant factor in particle generation, where particle diameter decreased linearly with increased temperatures.

The rate of generation of tyre wear particles should be considered alongside the exponential surge in the global production of thermoplastics. In 2015 production of plastics reached 322 million tonnes yr^{-1} (Plastics Europe, 2015; Kole *et al*., 2017), and is likely to increase further. Alongside which, the number of cars on the roads, is anticipated to increase by 40 % from 2000 to 2025 (in the UK), and globally three fold by 2025 (POLMIT, 2002; ETRma, 2011).

Despite accounting for a smaller portion of overall mileage, the dynamic network of urban environments are subject to amplified braking, accelerating, and cornering, generating greater wear emissions (ten Broeke *et al*., 2008; Kwak *et al*., 2013) compared to motorway and rural driving (Dannis *et al*., 1974; Councell *et al*., 2004). These greater emission environments typically coincide with impervious urban surfaces (Sörme and Lagerkvist, 2002) which facilitate runoff. However, previous work has not found significant trends in tyre concentrations between dense populations and traffic loads (Panko *et al*., 2013).

Particle density is an important factor influencing the transport and fate of tyre wear particles in the environment. However, the density of tyre wear is variable due to their complex chemical make-up, numerous tread formulations, size, shape, porous nature, and ability to form aggregates (Milani *et al*., 2004; Wagner *et al*., 2018). The density of SBR, the chief component of tread material, varies according to the proportion of styrene, but is reported in the range of 0.94 – 1.04 g cm^{-3} (Sigma Aldrich, 2012a; Sigma-Aldrich, 2012b; Wagner *et al*., 2018). Carbon black, another principal component has a reported density of 1.8 - 2.1 g cm^{-3} (Simga-Aldrich, 2013; Chemical Book, 2017). Density calculations from directly abraded tread material have been reported between 1.13 to 1.16 g cm^{-3} (Rhodes *et al*., 2012). Density values for tyre wear found in the environment itself are limited and more variable, see Figure 3. Verschoor *et al.* (2016), reports 1.2-1.3 g cm^{-3}, while Vogeslang *et al.* (2018), reports 1.7 - 2.1 g cm^{-3}, with some particles reaching highs of 2.5 g cm^{-3}. Sommer *et al.* (2018) reports an estimate of 1.26 g cm^{-3} based upon the ratio of tread (1 g cm^{-3}) to incrustations (minerals 2.6 g cm^{-3}, brake materials 8 g cm^{-3}) of 1:1. Unice *et al.* (2019a) suggests a central density estimate of 1.8 g cm^{-3} (0.94- 2.4 g cm^{-3}).

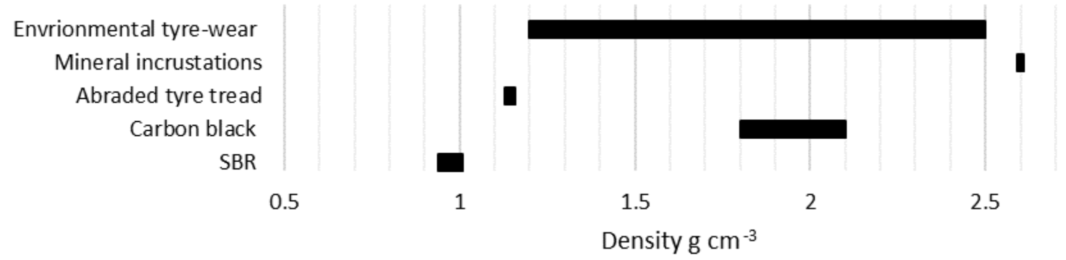

Fig. 3 Reported density ranges of major tyre wear components and environmental tyre wear particles. Sources: Rhodes *et al*., 2012; Sigma Aldrich, 2012a; Sigma-Aldrich, 2012b; Verschoor *et al*., 2016; Sommer *et al*., 2018; Unice *et al*., 2019a.

It is well documented that particle density will influence transport potential of plastics (Andrady, 2011). Density estimates for tyre wear suggest that most particles are likely to sink, but could be re-suspended at greater flow velocities or turbulence (Verschoor *et al*., 2016). It is probable that coarser particles are more likely to be retained in sediments than finer ones, but clear information on how properties vary between each fraction is lacking (Wagner *et al*., 2018).

Biofouling may also act as a mechanism increasing sedimentation (Andrady, 2011; Enger, 2012; Van Cauwenberghe *et al*., 2013). With even low density polymers, such as polyethylene, sinking as a consequence of fouling (Engler, 2012).

Previous research on the size distribution data of tyre particles have focused on specific types of particulate, such as fine airborne particles, and typically do not encompass the entire size range. However, when these studies are pooled (Figure 4), it is clear tyre wear particle size distribution can be highly variable ranging between 0.01– 350 µm.

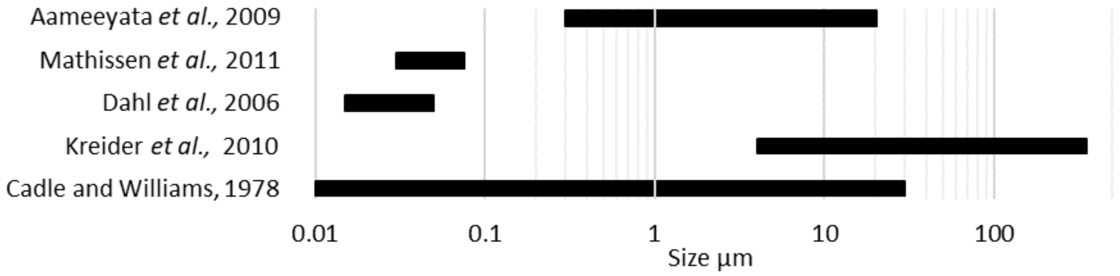

Fig. 4 Reported size distributions of tyre wear particles. Sources: Cadle and Williams, 1978; Dahl *et al*., 2006; Aatmeeyata *et al*., 2009; Kreider *et al*., 2010; Mathissen *et al*., 2011. Adapted from Kole *et al*., 2017. Note a log scale.

Irrespective of road type, it has been estimated that 1 - 10 % of tyre wear particles may become airborne (ten Broeke *et al*., 2008). The remaining, coarser particles, being deposited close to the point of emission (Pierson and Brachaczek, 1974; Wagner *et al*., 2018), with potential for re-suspension by wind or precipitation. The relative spatial distribution of tyre particles has been estimated in several studies (Figure 5). A combined average of these existing estimations suggests the majority of tyre wear particles reach soils, sewers, or are depositied on the road surface (Figure 5 'combined average'). However, while soils could potentially act as a sink, the others could provide pathways, potentially to marine environments.

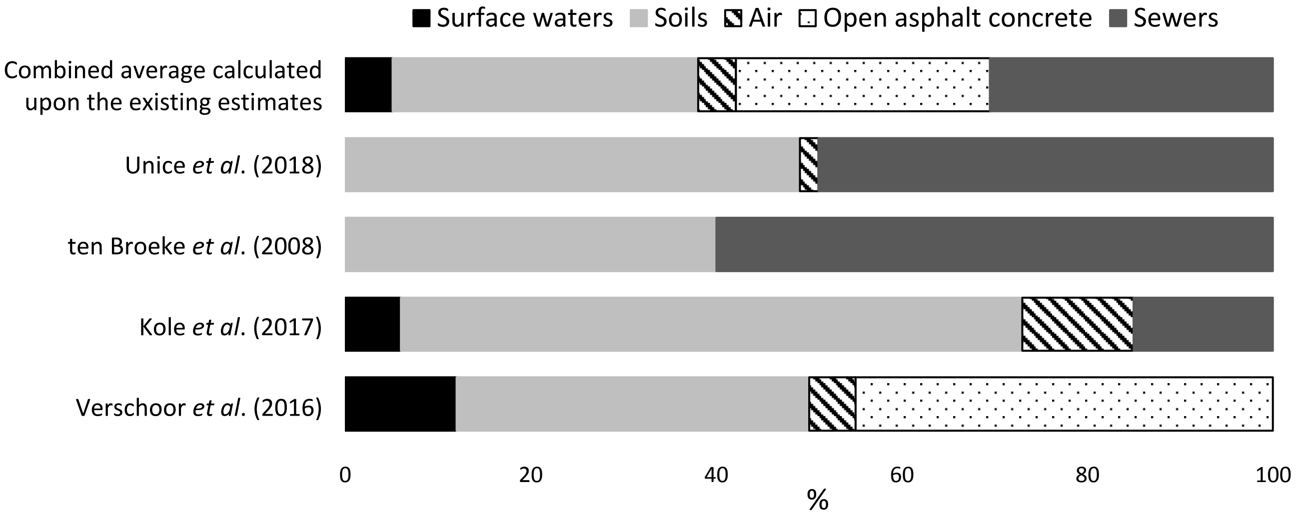

Fig. 5 Estimated relative transmission pathways of tyre wear particles, alongside a combined average of ten Broeke *et al*., 2008; Verschoor *et al*., 2016; Kole *et al*., 2017; Unice *et al*., 2019a.

Furthermore, these figures are generally applicable to urban areas that are well connected to sewer systems. In rural environments, which are not so well served by drainage, coarse tyre wear particles are expected to be more abundant adjacent to roads (Verschoor *et al*., 2016; Wagner *et al*., 2018; Unice *et al*., 2019a).

Various sewerage systems exist in the UK, the most common being combined sewers, or surface water drainage. The former receives waste from commercial, industrial, and residential discharges, in addition to surface run off. These waters undergo various methods of treatment prior to discharge to recipient waters (Fuchs *et al*., 2010). During extended periods of heavy rainfall, the combined system may exceed capacity, in the event of which excess flow is diverted to surface waters following only primary treatment (e.g. settling and screening) (Fuchs *et al.*, 2010). By contrast, surface drains generally only receive surface run-off and are not subject to treatment. Surface drains reduce loads reaching treatment plants, lessening the likelihood of an overflow event. The release of tyre wear from storm water runoff will depend on the retention capacity of the roadside sumps. When the sump is at capacity, flow containing suspended material may pass directly through the outlet (Pitt, 1958).

1.2 Synthetic fibres

In contrast to tyre wear, substantial quantities of fibres have been reported in the marine environment (Buchanan, 1971; Thompson *et al*., 2004; Browne *et al*., 2011; Lusher *et al*., 2013; Obbard *et al*., 2014; Woodall *et al*., 2014; Neves *et al*., 2015; Courtene-Jones *et al*., 2017; Peng *et al*., 2017).

Synthetic fibres currently account for 60 % of all fibre production globally, with polyester, polyamide, acrylic, and polyolefin being the most common (FAO-ICAC, 2013; The Fibre Year Consulting, 2018; Environmental Audit Committee (U.K.), 2019). Microplastic fibres can originate from a variety of sources; such as the disintegration of ropes, fabrics, packaging materials, and washing of synthetic clothing (Browne *et al*., 2011; Napper and Thompson, 2016; Niaounakis, 2017). Microfibres can enter the environment as both primary sources (fibres <5 mm in size released during production and use of textiles) and secondary sources (fragmentation of clothing during the washing cycle).

Synthetic fibres are frequently reported as the predominant microplastic in the environment, detected in; intertidal sediments (Browne *et al*., 2011; Mohamed Nor and Obbard, 2014; Nel and Froneman, 2015), subtidal sediments (Thompson *et al*., 2004; Frias *et al*., 2016), surface and sub-surface waters (Buchanan, 1971; Thompson *et al*., 2004; Cole *et al*., 2014; Desforges *et al*., 2014; Dubaish and Liebezeit, 2013; Zhao *et al*., 2014) and sedimentary deep-sea habitats (Fischer *et al*., 2015; Woodall *et al*., 2014). They are also ingested by biota; and have been reported in fish (Cartes *et al*., 2016; Lusher *et al*., 2013; Rochman *et al*., 2015), and invertebrates (De Witte *et al*., 2014; Mathalon and Hill, 2014; Devriese *et al*., 2015; Welden and Cowie, 2017).

The most prevalent use of fibres is for textiles, where more than 60 million tons are produced annually (The Fiber Year Consulting, 2018). As much as 0.19 million tonnes of microfibres from synthetic textiles, particularly domestic laundry of clothing, have been estimated to enter the marine environment annually (Eunomia, 2018), and as consumption grows that figure seems set to rise further. The first study highlighting domestic textile washings as a potential key source of microplastics was published by Browne *et al.* (2011). Since then, it has been predicted that over 700,000 can be released from a single wash load into the effluent (Napper and Thompson, 2016).

In countries with sewage infrastructure, the effluent from washing machines is discharged into the local sewer system and treated before being discharged as treated effluent to surface waters. Leslie *et al.* (2013) found concentrations from treated wastewater effluent ranged from 9 to 91 microplastic particles L^{-1}. Murphy *et al.* (2016) assessed the removal efficiency, reporting a 98.41 % decline in microplastics between influent and treated effluent (15.70 L^{-1} ± 5.23 to 0.25 L^{-1} ± 0.04). Despite high removal rates, due to the continual discharge of large volumes of effluent, microplastic emissions to the environment may still be substantial. It is estimated that a wastewater treatment plant in the United Kingdom could release up to 65 million microplastics into the receiving water every day (23,725 yr^{-1}) (Murphy *et al*., 2016). Consequently, wastewater treatment plants play a potentially critical role in the fate and transport of microfibres into the environment.

Microfibres are also reported within terrestrial habitats. For example, microplastics that are retained during wastewater treatment may enter the natural environment if the resultant sewage sludge, a by-product of the process, is returned to the land as soil fertiliser (Habib *et al*., 1998; Zubris and Richards, 2005). Mintenig *et al.* (2017) reported concentrations of synthetic particles in sewage sludge from German wastewater treatment plants reaching up to 24 particles g^{-1} of dry weight. There is also potential for the transfer of fibres from the sludge to aquatic environments as a result of runoff. Habib *et al*. (1998) collected sediments from a bay downstream of a sewage treatment plant and found as distance from the sewage treatment plant increased, the size and abundance of fibres decreased (Habib *et al*., 1998).

Microfibres may also be transported through the atmosphere. Dris *et al.* (2016) evaluated the presence of fibrous microplastics in atmospheric fallout. The study sampled an urban site and a suburban site in Paris and found fibrous material accounted for the majority of material collected over a 1-year period (between 2 and 355 fibres m^2 d^{-1}). Total atmospheric fallout fluxes were systematically higher at the urban site than at the suburban one, probably linked to the density of the surrounding population. Stanton *et al.* (2019) also examined atmospheric fallout, and found that natural textile fibres constituted a greater proportion of environmental textile fibre than synthetic fibres. Fibres have even been reported in remote and pristine environments as a result of aerial pollution (Bergman *et al.,* 2019; Allen *et al*., 2019).

A further, but yet unquantified source of microfibers is from the wear of rope and netting used in maritime activities (Buchanan, 1971). Here any microfibers generated as a consequences of abrasion during use likely enter the water directly. A further source of fibres is the disintegration of rope and netting that has been lost of abandoned in the marine environment.

1.3 Project objectives

This project addresses six main objectives requested by Defra.

Objective 1) Assess whether tyre particles are entering the marine environment and by what pathway

Objective 2) Determine whether the amount of tyre particles entering the marine environment can be quantified, validate and compare to existing modelled results

Objective 3) Determine the key sources of synthetic fibres entering the marine environment

Objective 4) Identify the key pathways for synthetic fibres entering the marine environment, investigating a range of fibre types including textiles, and maritime gear

Objective 5) Identify the distribution of tyre particles within the marine environment, considering distribution both geographically from sources and within the water column, investigating whether particles sink or float, and accumulate within the sediment or the water column

Objective 6) Identify the distribution of synthetic fibres within the marine environment, considering both geographic and spatial dispersal

In this report we consider objectives 1 and 2, 3 and 4 and finally 5 and 6 are alongside one another. Emissions of microplastics from maritime activities are then considered separately as a final topic.

2.0 Methodological approach

2.1 Environmental sampling

Once in the marine environment, tracking microplastics back to their source presents many difficulties. Therefore, our approach was to quantify both tyre particles and synthetic fibres at their point of entry to the marine environment. Three points of entry were considered; release from treated wastewater effluent, direct release from storm water drains, and deposition from the air. For fibre release we also consider fragmentation of rope and netting from maritime activities, see Section 3.6.

Sampling of tyre particles and synthetic fibres was conducted within a 60 x 60 km radius of two cities in the South-West of England, these locations are broadly described as Bristol and Plymouth. There were no specific hypotheses relating to the two locations; they were selected to help give generality to the findings and so broaden its applicability. As a consequence, we do not present the results according to location. Some data exist on the sources of synthetic fibres, and it is clear they are widely distributed in the marine environment. However, empirical data on the source and distribution of tyre wear particles is scarce, and for that reason much of our environmental sampling was focused around roadways. It should be noted that this could result in a sampling bias skewed toward tyre particles rather than fibres.

Final effluent was collected from wastewater immediately prior to its passing into surface waters (fresh, estuarine, or marine) from wastewater treatment plants serving catchments areas ranging from 1 to 22 km^2, and populations between 3,000 and 65,000. The WWT plants sampled received both foul water and surface drain runoff. To achieve replication, two treatment plants were sampled in each region, on two occasions, and on each occasion three replicate 10 L samples were collected from each plant.

Storm water effluent was collected within the first hour of a rainfall event at locations where surface runoff drains from roads flowed directly into marine or estuarine waters. Two such drains were sampled on two occasions in Plymouth only. On each occasion three replicates of 5 L samples were collected.

In both Bristol and Plymouth atmospheric deposition was collected on each of two occasions at a distance of 20 m from three different road types, urban, rural, and motorway (irrespective of distance from a watercourse, and categorised based upon the Eurostat Transport Glossary, where roads outside of built up areas, which were not major trunk roads, motorways, or A-roads we considered rural). There were two replicates of each road type for each city. Sites were selected on the basis of access, and the relative isolation from other roads. The effect of distance from road was considered as an additional factor. This was done in Plymouth only, by collecting additional samples on each occasion at a distance of 50 m of road. These distances were selected as being relevant in terms of the potential for settlement of particles from roads into neighbouring waterways. Since our assessment was of the settlement of particles in relation to road type and distance the actual proximity of the roads to waterways was not a key selection criteria. Instead, we subsequently quantified the proportion of roads within 50 m of a waterway in order to estimate the potential for transport to waterways. On each sampling occasion air temperature, wind speed and direction was recorded at one minute intervals for the same 24 h period using a Kestrel 4500 Weather Meter.

On each sampling occasion three replicate straight sided glass dishes (surface area 0.0177 m^2) containing ion exchanged deionised water were deployed for 24 hours, capturing fallout on the meniscus. After which the deionised water was poured through a glass funnel into 1 L glass Duran bottles. The dishes were rinsed three times with ion exchanged deionised water, and water from the rinses added to the sample. The data obtained were then used in conjunction with a desk based study to establish the potential surface area on which particles might settle.

2.2 Laboratory analyses

2.2.1 Particle isolation

Samples were vacuum pumped through Whatman cellulose nitrate membrane filter papers. Samples collected from atmospheric fallout were filtered through a pore size of 0.45 µm. Due to the large volumes and high content of suspended solids, storm water and wastewater samples were first passed through 30 µm (stainless steel) and 12 µm (nylon) meshes. Both meshes were back washed into a beaker with ion exchanged deionised water, reducing the volume of the sample. Finally, the sample was vacuum pumped through a 12 µm Whatman cellulose nitrate membrane filter paper. This difference in approach did not affect quantification of fibres as it is not possible to identify fibres of less than 20 µm (see below), however it could have resulted underestimate of the smaller size fraction of tyre particles when compared to the atmospheric samples. All filter papers were dried until at a constant weight.

2.2.2 Quantification of synthetic fibres

All filter papers were examined using an LED Microtec light microscope and potential synthetic fibres removed onto a blank Whatman glass microfiber 1.6 µm filter paper. Where the abundance of fibres was very dense, sub-sampling was employed; 50 % of the filter paper surface was analysed. Images of the isolated fibres were taken by using LEICA M205C light microscope and used to approximately measure length and diameter using Image J. Colour was also recorded. Previously used criteria were employed in order to identify any suspected synthetic fibres (Dris *et al*., 2015; Hidalgo-Ruz *et al*., 2012). Identification was via FTIR spectroscopy in transmission mode with a Hyperion 1000 microscope coupled to a Vertex 70 spectrometer (Bruker). For each sample, the spectra were recorded with 32 scans in the region of 4000 to 600 cm. Spectra obtained were compared against a spectral database of synthetic polymers (BPAD polymer & synthetic fibres ATR). If any sample contained >10 fibres, a sub-sample of 10 random fibres were selected to be analysed by FTIR. Relative proportions of different polymer types were then adjusted to give an approximation for the whole sample.

A number of procedures to minimise contamination were put in place during analysis. All glassware was washed with detergent, rinsed in ion exchanged deionised water (x 3), soaked in 2 % HNO_3 for a minimum of 6 hours, rinse in ion exchanged deionised water (x 3), dried, covered and stored in a designated clean laboratory. Samples were always covered to avoid air exposure. Laboratory blanks were performed to verify that no microplastics were added to the samples during the laboratory procedures. The blank results did not reveal any significant contamination (only 3 blanks samples had a total of 1 fibre each). A fresh blank was performed every 30 minutes of analysing in the laboratory.

2.2.3 Quantification of tyre particles

We explored several methods to quantify tyre particles including FTIR and Raman spectroscopy (Appendix 1). However, pyrolysis gas chromatography – mass spectrometry (Py-GC-MS) proved to be the most effective and was used as the primary method for quantification of tyre wear particles. After removal of fibres, filter papers were subject to chemical analysis using Pyrolysis GC-MS to assess the concentration of benzothiazole (vulcanisation accelerator). Despite being utilized within a number of products, including biocides, antimicrobial anti-algal agents, and antifreeze (Brownlee *et al*., 1992; Wik and Dave., 2009; He *et al*., 2011) according to Kumata *et al.* (2000) no other sources are able to produce such large or continual emissions of benzothiazole to the environment, serving as an effective marker for tyre wear in the environment.

Sample analysis was performed with a CDS Pyroprobe via a CDS1500 valved interface (320 °C) linked to a Hewlett-Packard 6890GC split injector (320 °C) linked to a Hewlett-Packard 5973MSD (electron voltage 70eV, emission current 35uA, source temperature 230 °C, quadrupole temperature 150°C, multiplier voltage 2200V, interface temperature 320 °C). The acquisition was controlled by a HP kayak xa chemstation computer in full scan mode (50 - 650 amu). From the centre of region of each filter paper, three 1 x 10 mm strips were cut with a clean scalpel blade and placed in a quartz pyrolysis tube. The tube was then placed into a pyroprobe platinum heating coil and then sealed into the valved interface. The samples were then pyrolysed at 610 °C for 10 seconds on an open split 40 ml PY-GC-MS system which took an hour for all the peaks to elute. The TIC and m/z 135 Ion chromatogram were integrated between 18 and 24 minutes (elution time of Benzothiazole) and the areas recorded. Separation was performed on a fused silica capillary column (60 m x 0.25 mm i.d) coated with 0.25 um 5 % phenyl methyl silicone (ZB-5MS). Initially the GC was held at 50 °C for 5 minutes and then temperature programmed from 50 - 320 °C at 5 °C minute and held at final temperature for 15 minutes, with Helium as the carrier gas (constant flow 1ml/min, initial pressure of 120 kPa, split at 30 mls/min). Each acquired data run was stored on DVD for later data processing, integration and printing. For each set of three replicates, two samples were analysed by py-GC-MS, and the third was retained for potential future analysis.

In order to relate mass spectrometry data back to tyre emissions, the quantity of benzothiazole in tyres was quantified from pyrolysates of using fragments of known tyre tread (0.26 mg), pyrolysed in the same manner as described above. The instrument response was measured using a calibration curve of peak intensity versus the weight of an authentic standard of benzothiazole averaged over three pyrolysis runs (R^2= 0.9905) again using the same method described above. Data were then converted to give a mass of tyre particles per sample.

Blank cellulose nitrate filter papers yielded some peaks similar to that of tyre fragments, but in much smaller quantities, and did not yield any traces of benzothiazole. Procedural blanks were also analysed in the same manner.

2.2.4 Visual characterisation of tyre wear particles

After removal of fibres, filter papers were photographed on a Lecia M205C light microscope, and processed using Image J. It was possible to make a qualitative assessment of tyre particles based upon their morphological and physical characteristics; colour, shape, and texture. Particles that did not fit these criteria were removed, see Figure 6. Particle size was determined by measuring Feret diameter (longest length Fh, and widest width, Fv, Figure 6). Tyre particles were confidently identified by this method down to 15 µm, those measuring less than 15 µm by their longest length were removed from analysis.

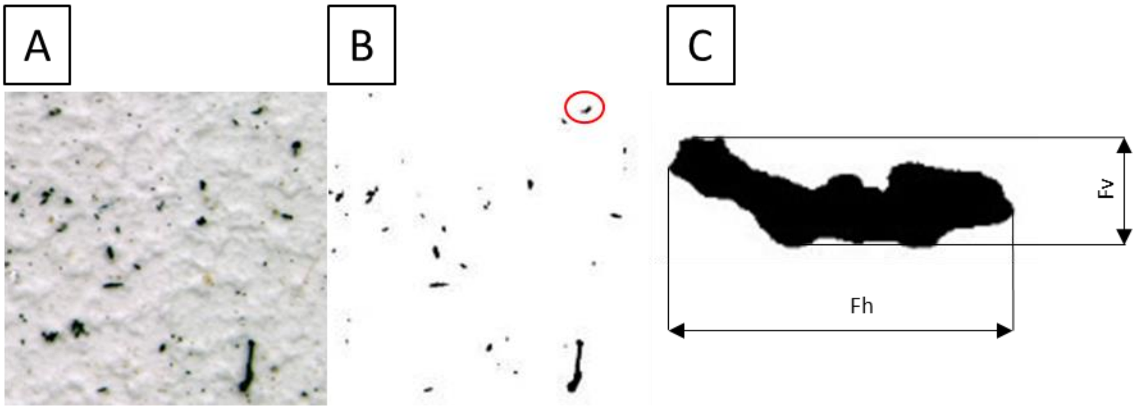

Fig. 6 (A) Image showing a section of a sample containing tyre wear particles collected from atmospheric deposition, (B) suspected tyre particles isolated from original image by visual analysis, (C) example of calculation of Feret diameter of an individual tyre wear particle (C).

3.0 Results

3.1 Objective 1) Assess whether tyre particles are entering the marine environment and by what pathway

Tyre particles were detected by pyrolysis-GC-MS passing into the marine environment by each of the pathways sampled (Figures 12A, 13A, 14A & 15A). Neither the blank filter papers or the procedural blanks yielded any traces of benzothiazole. Samples which recorded concentrations at the detection limit of 1 ng or less were not included in the analysis. Half of all the samples collected from wastewater effluent recorded concentrations at or below the detection limit of 1 ng benzothiazole. Whereas only 2.5 % of samples collected from atmospheric fallout (50 m from rural roadsides), and 12 % of samples from storm water run-off had recorded concentrations at or below the limit of detection. Since it was sufficiently clear at an early stage in our work that tyre particles were indeed entering the marine environment via all pathways, much of our focus was on Objective 2.

3.2 Objective 2) Determine whether the amount of tyre particles entering the marine environment can be quantified, and compare to existing modelled results

Visual analyses (see Section 2.2.4) also showed presence of particles likely to be tyre wear in every pathway sampled. However, with this method, the potential for errors due to incorrect identification of tyre wear particles increased with decreasing particle size. Tyre wear was confidently identified down to 15 µm in length, below which particles were not included in the analysis. The dimensions of 977 tyre particles were obtained; on average particles measured 43 µm in length, with a mode centred around 20 µm. The largest recorded particle was 415 µm, the smallest were limited by the methods detection, at 15 µm. The aspect ratio was 0.4:1.

There were some qualitative differences of tyre wear particles between pathways (see Figure 7A). Tyre wear transported via atmospheric deposition had an average particle length of 36 ± 0.9 µm ($\bar{x}$ ± SE) (largest 164 µm). Particles present in treated wastewater effluent had a very narrow size range, recording an average length of 21 ± 0.8 µm ($\bar{x}$ ± SE), the largest particle measuring 42 µm. Storm water run-off had larger particles on average (62 ± 2.8 µm, $\bar{x}$ ± SE), reaching lengths of up to 415 µm. Tyre wear within wastewater effluent and atmospheric fallout had average aspect ratios of 0.49:1, compared to a larger length to width ratio in storm water of 0.4:1.

Differences in the dimensions of tyre wear collected from atmospheric fallout beside different road types was observed (Figure 7B). The largest particles from urban and rural roadsides with lengths of 164 and 139 µm respectively, compared to 81 µm beside motorways.

Size distribution profiles generated from particles collected at 20 m and 50 m from roadsides displayed similar profiles, however their modes were 27 and 20 µm respectively (Figure 7C).

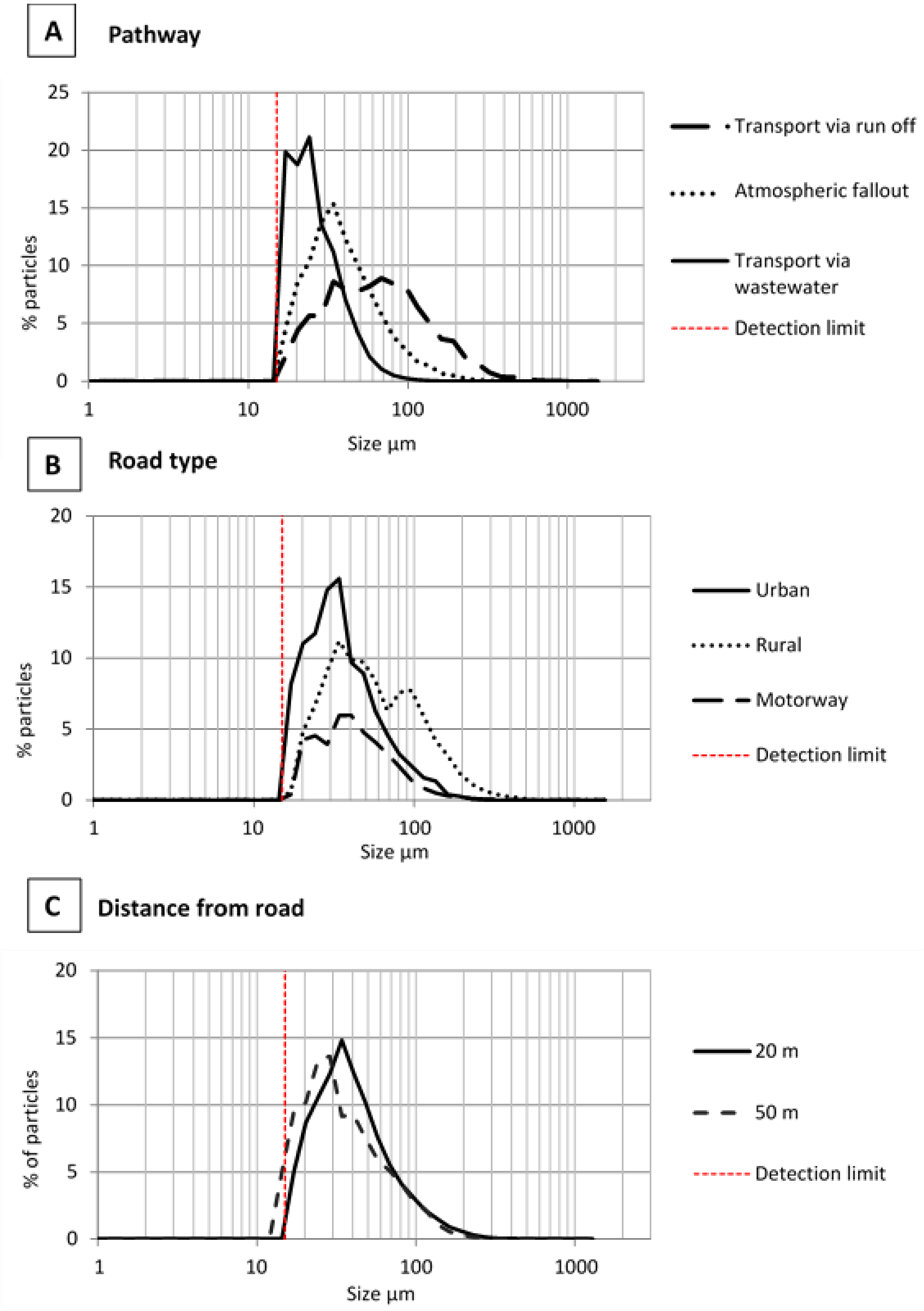

Fig. 7 Tyre particle size distribution profiles (by the percentage contributed by individual particles to total abundance), determined by visual identification. (A) Collected from atmospheric fallout, storm water runoff, and treated wastewater effluent, (B) beside urban, rural and motorways, and (C) 20 m and 50 m from roadsides. The dashed red line indicates the identification detection limit (15 µm).

Using py-GC-MS, tyre wear in wastewater effluent was detected at average concentrations of 0.02 ± 0.01 mg L^{-1} ($\bar{x}$ ± SE). Concentrations recorded at plant 2 were significantly greater than the other WWT plants (ANOVA; df= 3, p <0.05). When the concentrations of tyre wear detected at each plant are normalised by population density (see Section 3.4, Figure 12A), WWT plant 2 still records the highest emissions, but emissions from plant 4 are also high, and no significant effect is observed (ANOVA df=3, p> 0.05). The same pattern was observed for population when the concentrations of tyre particles are normalised by catchment (ANOVA df=3, p> 0.05).

Concentrations of tyre wear within storm water runoff were on average 2.5 ± 1 mg L^{-1} ($\bar{x}$ ± SE). There was considerable variability between discharge points, but an analysis of variance found no significant effects (df= 1, p> 0.05), see Figure 13A. It is difficult to normalise concentrations of tyre particles within storm water to a catchment as the surface area that each drain serves in unknown and will vary with factors such as gradient.

Tyre wear was recorded in atmospheric fallout at concentrations of 6.2 ± 0.66 mg 0.25 m^2 d^{-1}($\bar{x}$ ± SE). Concentrations of tyre wear appeared to decrease with increased distance from the roadside (Figure 14A), but ANOVA showed no significant effects at the distances evaluated here (Satterthwaite's method, df= 18, p> 0.05).

Deposition of tyre wear differed significantly between road types (Figure 15A, ANOVA, Satterthawiate's method df=18, p < 0.05). Concentrations were typically greatest beside motorways, 30 % and 70 % more than urban and rural (planned contrasts, df= 18, both p< 0.05). Urban concentrations were typically more than two-fold that of rural, but this had no significant effect (planned contrasts, df= 18, p> 0.05).

3.2.1 Discussion

Larger particles were recorded in storm water compared to wastewater. This could indicate that bigger particles are more effectively retained during the water treatment processes, where particles in storm water are not subject to treatment; therefore, giving rise to a greater distribution of particle sizes. In atmospheric fallout, smaller particles were recorded at greater distances from the road source. This possibly indicated that smaller airborne tyre wear had a greater transport potential, where the larger particles were deposited closer to the point of emission.

Size distribution data provided by Kreider *et al.* (2010) produced from tyre wear particles generated on a laboratory road simulator indicated that the tyre wear ranges between 4 and 350 µm with greatest abundance of particles < 25 µm (Figure 8 % particles), but the greatest proportion of mass was within particles > 50 µm (Figure 8, % volume). The size distribution profiles recorded between Kreider *et al*. (2010) and this study (% particle, this study) display similarities in tyre particles larger than >15 µm, but highlights that visual identification of tyre particles fails to quantify a large proportion of the particles likely present in the environment (< 15 µm).

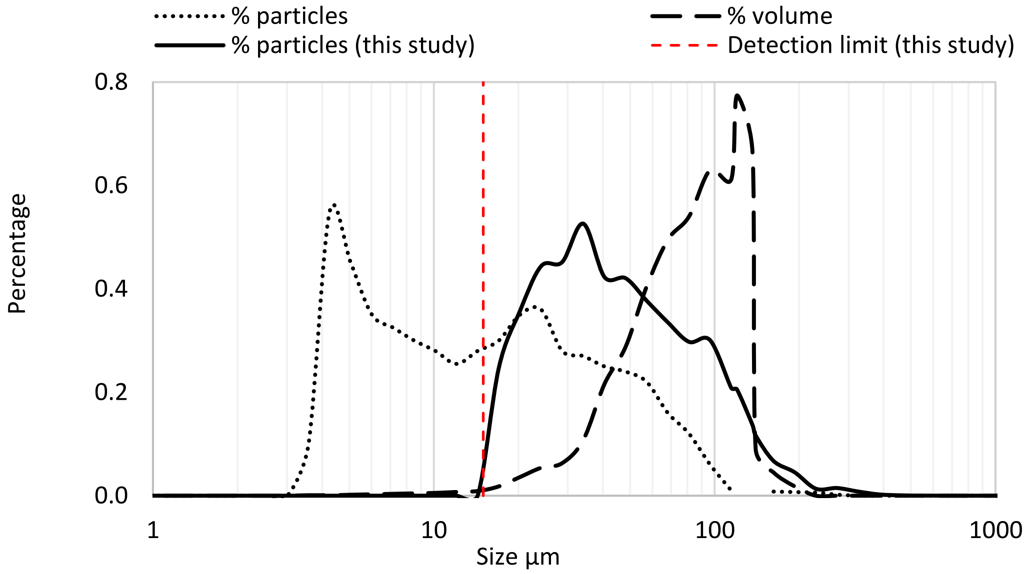

Fig. 8 Size distribution profiles of tyre wear particles % particles (the percentage contributed by individual particles to total abundance) and % volume (the percentage contributed by individual particles to the total volume) adapted from Kreider *et al.* (2010) vs % particles recorded in this study, highlighting a large portion of the particle population missed by visual identification. The dashed red line indicates the identification detection limit (15µm). The data is smoothed and displays probability distribution.

Since differences in particle release between wastewater treatment plants were no longer evident when concentrations were normalised by population density and catchment, it would appear these factors are potentially good indicators of the potential drivers for tyre pollution. The highest recorded concentration at a WWT plant coincided with a heavy rainfall event where the plant exceeded its treatment capacity, and excess water was released that had been treated by screening and storm settlement only. Sampling was stratified across two sampling dates but this was solely to achieve replication and it was therefore not possible to draw statistical comparisons between sampling dates, greater replication in future work is advised to help recognise temporal trends. Concentrations of tyre wear recorded within treated wastewater effluent were lower than previous in reports, 1 mg L^{-1} (Zeng *et al*., 2004).

Concentrations within storm water run-off were also lower than reported in previous studies (12–179 mg L^{-1} (Reddy and Quinn, 1997; Kuamta *et al*., 1997; Baumann and Ismeier, 1998; Kumata *et al*., 2000; Kumata *et al*., 2002; Zeng *et al*., 2004; Wik and Dave, 2009).

In contrast to earlier reports, (ten Broeke *et al*., 2008; Kwak *et al*., 2013) the presence of tyre wear in our study (based on py GC-MS) was highest besides motorways, rather than urban roads. This is likely attributable to the volume of traffic, and the speed of motorway driving. Speed is a major influence on tyre wear generation, increasing its generation of smaller particles (Dahl *et al*., 2006).

Concentrations at urban roads are likely to also be associated with traffic loads, but are further influenced by driving behaviour. As anticipated, rural roads had the lowest average concentrations, probably because of the lower traffic density. Differences in particle size between 20 m (mode, 27 µm) and 50 m (mode, 20 µm) could indicate the smaller fraction has greater ability to travel further from their point of generation, and suggests a sizable portion of tyre wear is subject to atmospheric fall out close to its source. This finding is in agreement with a previous study which reported a decline in tyre particles with distance from the roadside within road dust (Satio, 1989), as well as with depth in roadside soils (POLMIT, 2002) and height in ambient air (Kim *et al*., 1990). In summary, this indicates atmospheric fall out is likely to be a prominent pathway of tyre particles to surface waters (and other habitats) that are relatively close to roadsides.

We have included a discussion on the extent to which our findings compare to existing modelled results for both tyre particles and synthetic fibres in section 4.0.

3.3 Objective 3) Determine the key sources of synthetic fibres entering the marine environment and whether direct evidence can provide quantification from different sources, including textiles, synthetics and fishing gear

Synthetic fibres were detected passing to the marine environment via treated waste water effluent, storm water runoff, and atmospheric fallout, and were detected in 41 % of the samples examined (46 % of the samples from atmospheric deposition, 17 % of the samples from storm water runoff, and 38 % of wastewater effluent samples). Fibres were on average 420 µm in length, and 13 µm in diameter.

3.4 Objective 4) Identify the key pathways for synthetic fibres entering the marine environment

Fibres of eight synthetic materials were identified by FTIR. Acrylic, polyester, and nylon were the most dominant materials, contributing 53, 40, and 14 % respectively to the total. The remaining four materials comprised of polyester-cotton blend, polyurethane, polypropylene, and polyethylene, each contributing <5 % (Figure 9). FTIR spectroscopy cannot reliably be used to distinguish semi-synthetic cellulosic based fibres, such as Rayon, from some natural cellulosic material. Therefore, these fibres were not included in the analysis (see Figure 11). Atmospheric samples had the greatest diversity of fibres (acrylic, polyester, nylon, polyester-cotton, polyurethane, polyethylene, and polypropylene), while samples from wastewater recorded two fibre types (acrylic and polyester), and storm water only one (polyester). This pattern matches the trend in the relative abundance of fibres in samples from each pathway, where waste water effluent and storm water run-off had a fraction of the abundance of fibres that were found with atmospheric fallout samples, therefore the greater diversity may in part be a reflection of greater number of fibres examined.

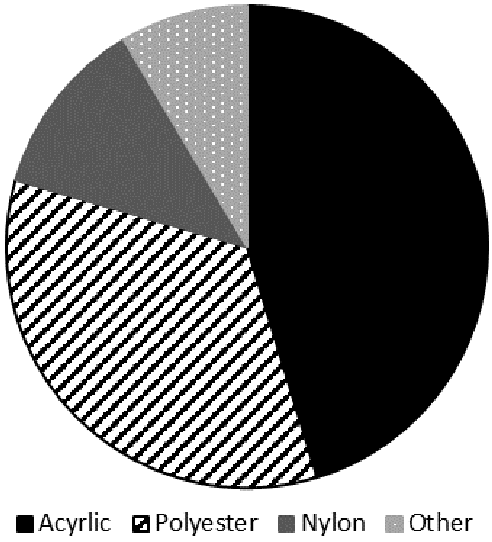

Fig. 9 Relative proportions of polymers detected within atmospheric fallout, treated wastewater effluent, and storm water runoff.

The majority of the fibres were either blue or black. Red or green; and clear fibres were less abundant, accounting for around 10 % of the total, while brown, grey, yellow, white, orange and purple contributed less than 5 % (Figure 10).

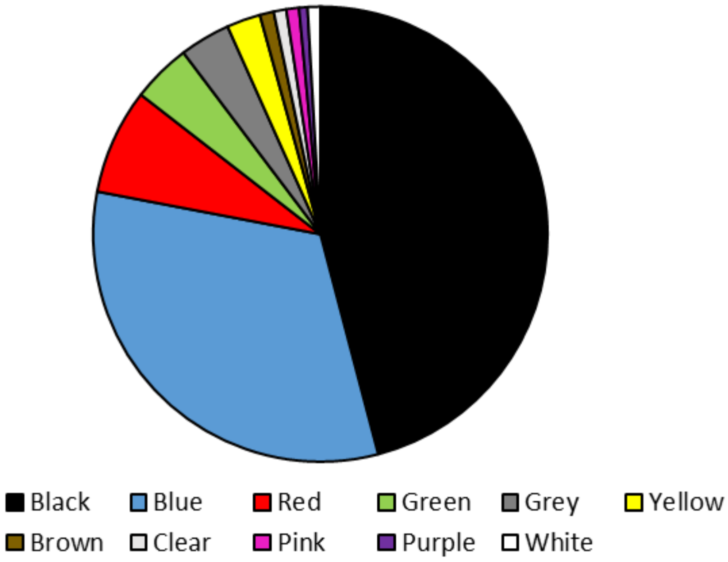

Fig. 10 Relative proportion of the colours of synthetic fibres collected from atmospheric fallout, treated wastewater effluent, and storm water runoff.

Fibre size and fibre material were very similar in atmospheric samples collected 20 and 50 m from roadsides. There were qualitative differences in fibre sizes between rural and urban roads compared to motorways. The smallest fibre collected beside a motorway measured 233 µm in length, where fibres beside urban and rural roadsides recorded lengths down to 43 and 34 µm respectively. The variety of materials found beside each road type was relatively uniform.

Fibres that were identified as ‘rayon’ dominated both the storm water and atmospheric fallout (90 %) (Figure 11 ‘other’), whereas fibres found in wastewater effluent were relatively evenly distributed. Given the dominance of black, blue and red fibres and the apparent twisted nature of many of the fibres examined it seems highly likely that the majority were indeed textile fibres including Rayon, but this could not be established with certainty. As a consequence, we have not included Rayon in the data presented here; this will result in lower numbers of microplastics compared to studies that have chosen to include semi-synthetic fibres such as Rayon.

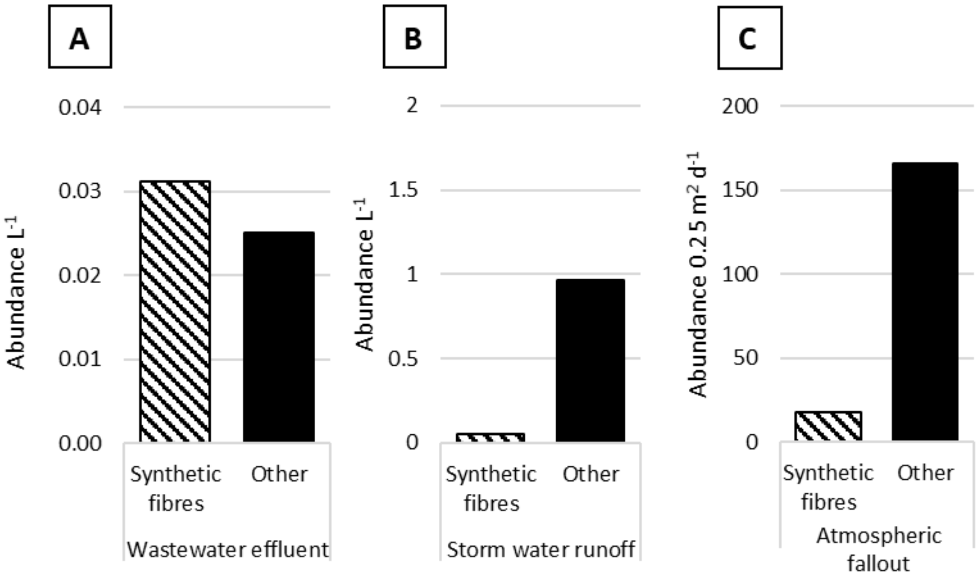

Fig. 11 Abundance of synthetic fibres and natural or regenerated cellulosic fibres (other), collected from (A) treated wastewater effluent (abundance L^{-1}). (B), storm water runoff (abundance L^{-1}), and (C) atmospheric fallout (abundance 0.25 m^2 d^{-1}). Note the difference in the scale along the y-axis.

Synthetic fibres were recorded on average in concentrations of 0.03 L^{-1} ± 0.01 L^{-1} ($\overline{x}$ ± SE) within wastewater effluent. There was no difference in fibre concentrations between WWT treatment plants (ANOVA, df = 3, $p > 0.05$). However, when fibre concentrations were normalised by the serving population (and scaled to 10,000 people), plant 3 had a significantly greater concentration of fibres than plant 1, 2 or 4 (Figure 12B, ANOVA, df = 3 $p = < 0.01$). The same pattern was observed when the data was normalised by catchment area served (km^2) that each plant served, plant 3 having significantly higher fibre emissions than plants 1, 2 and 4 (ANOVA, df = 3, $p = < 0.01$). Because Cochran's test was significant (after applying a log+1 transform), a conservative approach was taken and only p-values >0.01 were considered significant.

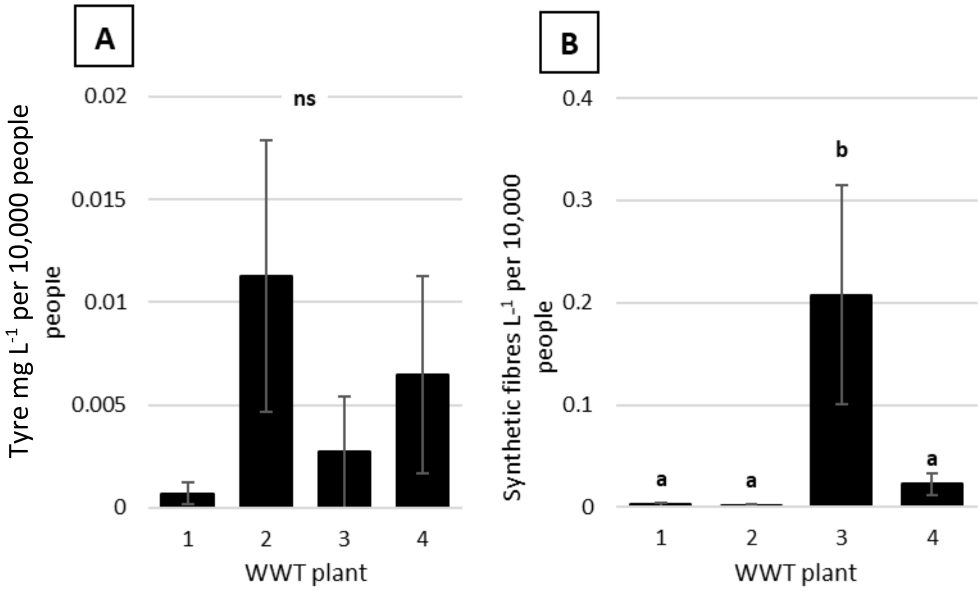

Fig. 12 Concentrations of (A) tyre wear mg L^{-1} from four wastewater treatment plants (B) and concentrations of synthetic fibres (abundance L^{-1}), averaged over two sampling dates and normalised by population (scaled to 10,000 people). Error bars represent standard error. Within each plot letters a, and b denote categories that are statistically different.

Within storm water run-off, synthetic fibres were recorded at average in concentrations of 0.017 L^{-1} ± 0.01 L^{-1} ($\overline{x}$ ± SE). Synthetic fibres were only recorded at one of the two outfall sites (Figure 13B).

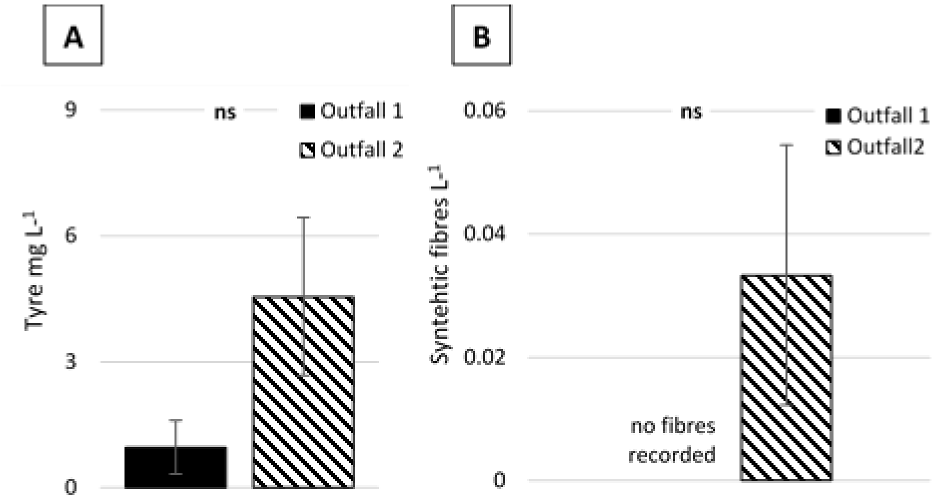

Fig. 13 Average concentrations of (A) tyre wear mg L^{-1} within storm water runoff, and (B) abundance of synthetic fibre L^{-1} within storm water runoff, from two surface runoff outfalls, averaged over two sampling dates. Bars represent standard error.

Synthetic fibres were present at average concentrations of 16 ± 2.2 fibres 0.25 m^2 d^{-1} ($\overline{x}$ ± SE) from atmospheric fallout (0 - 108 fibres 0.25 m^2 d^{-1}). There was a trend of decreasing fibre concentrations between 20 m and 50 m from the roadside. However, like tyre particle concentrations (see Section 3.2), synthetic fibre concentrations did not show a significant difference between concentrations recorded at the 20 m and 50 m from the roadside (ANOVA, Satterthawiate's method, df =28, *p* >0.05), see Figure 14B.

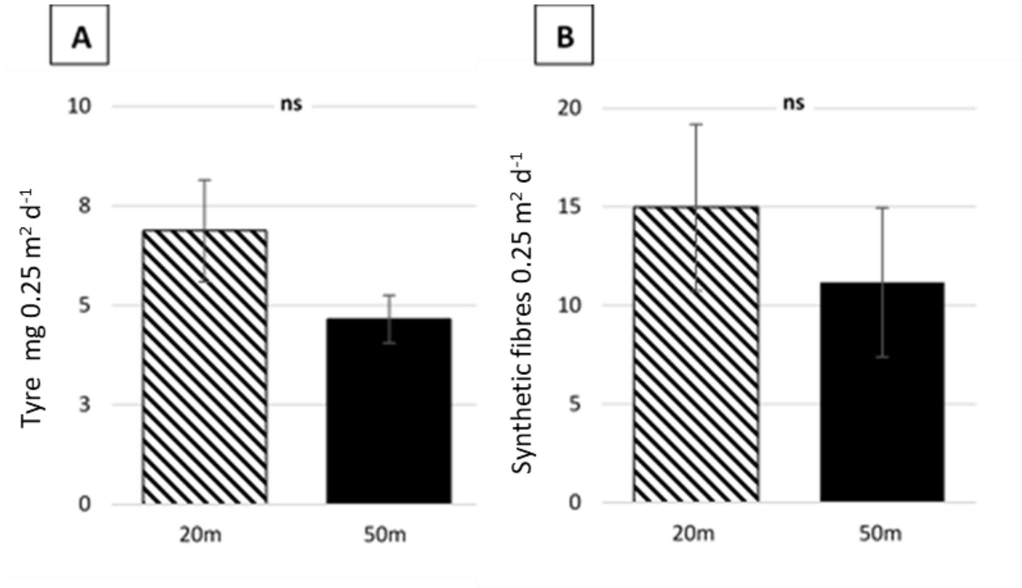

Fig. 14 Average concentrations of (A) tyre wear mg 0.25 m^2 d^{-1} (B) and abundance of synthetic fibres 0.25 m^2 d^{-1}, collected from atmospheric fallout 20 m and 50 m from roadsides (averaged over urban, rural, and motorway). Error bars represent standard error.

Similar to tyre particle concentrations (see Section 3.2), synthetic fibre concentrations differed significantly between road types, see Figure 15B (ANOVA, Satterthawiate's method, df = 22 $p <$ 0.01). Concentrations of fibres were significantly different between urban and rural and urban and motorway roadsides (planned contrasts, both $p <0.05$), concentrations of fibres between rural and motorway roadsides were not significant ($p >0.05$). On average, urban environments had the largest concentrations of synthetic fibres from atmospheric fallout (39 fibres 0.25 m^2 d^{-1}), followed by rural (11 fibres 0.25 m^2 d^{-1}) and motorway (6 fibres 0.25 m^2 d^{-1}).

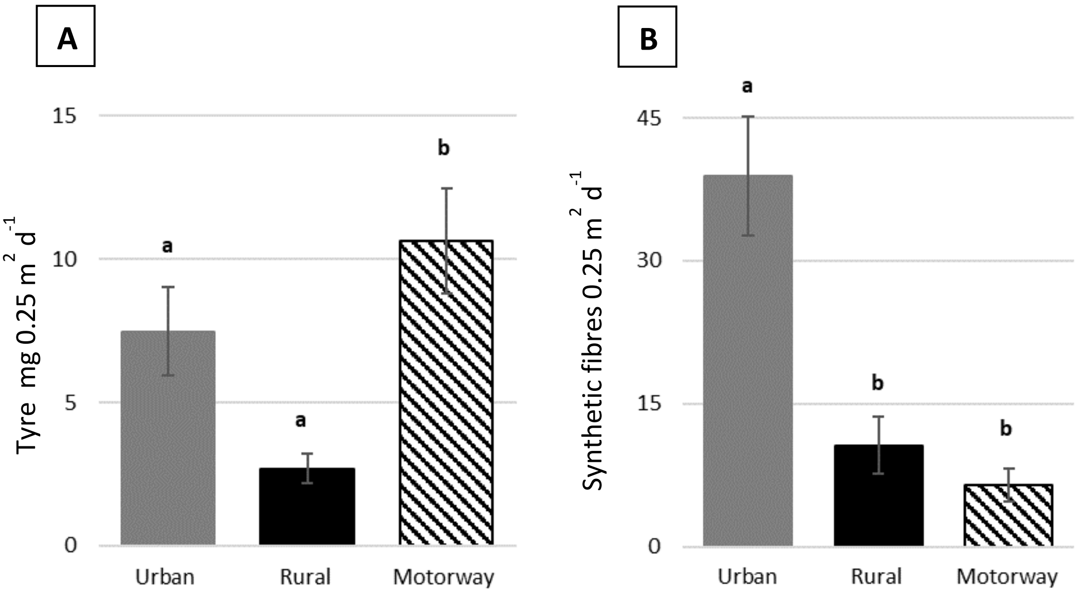

Fig. 15 Average concentrations of (A) tyre wear expressed as mass mg 0.25 m^2 d^{-1} and (B) synthetic fibres expressed as numerical abundance 0.25 m^2 d^{-1} collected from atmospheric fallout beside urban, rural and motorways. Error bars represent standard error. Letters a, and b denote categories that are statistically different.

3.4.1 Discussion

Synthetic fibres. Previous reports of microplastic concentrations in treated wastewater effluent (Leslie *et al*., 2013; Murphy *et al*., 2016) are generally higher than detected in this study. However, these studies reported concentrations of all microplastics, not specifically fibre concentrations, some previous studies also include cellulosic fibres such as rayon. To the best our knowledge, while road run-off via storm water is frequently considered a pathway for microplastic particles of tyre wear and paint markings to the aquatic environment (Sutton *et al*., 2016; Boucher and Friot, 2017; Eunomia, 2018), no empirical data exits on emission rates of fibres from this source.

The high concentrations of fibres recorded within atmospheric fallout in urban samples is likely associated with the higher population density and wider range of textile uses (clothing, carpets as well as activities such as laundering). A similar logic can be applied to rural roads which have considerably fewer pedestrians, and motorways where is it unlikely there will be any pedestrians, and consequently they have much lower fibre concentrations. This pattern between footfall and fibre concentrations has also been observed in previous studies (Dris *et al*., 2016; Stanton *et al*., 2019). Fibre pollution in the rural areas sampled, removed from infrastructure and populations could possibly indicate long-range transport of fibres. Synthetic fibres have been reported in environments as remote as the Alps, having been transported in the atmosphere up to an estimated 95 km (Allen *et al*., 2019), and within Arctic snow (Bergman *et al*., 2019). If fibres are transported long distances in ambient air, the exposed nature of rural sites may lend themselves to fibre accumulation.

Fibres determined by FTIR as ‘rayon’ were found to contribute 90 % to the total fibres analysed in this study. Of the remaining 10 %, concentrations of synthetic fibres detected in this study were in the range of 0 - 432 m^2 d^{-1}, averaging 64 ± 9 m^2 d^{-1} ($\bar{x}$ ± SE). Dris *et al.* (2016) reported by fibre concentrations in the range of 2 – 355 m^2 d^{-1}, averaging 53 ± 38 ($\bar{x}$ ± SD). 29 % of fibres recovered by Dris *et al.* (2016) contained petrochemicals (synthetic and semi-synthetic), while the remainder were identified as natural materials such as cotton and wool. Likewise, Stanton *et al.* (2019), reported synthetic fibre concentrations lower than found in this study, with maximum concentrations of extruded fibres (synthetic and regenerated such as rayon) reaching 2.9 m^2 d^{-1}. The differences in the concentrations recorded in this study may be explained by the sampling method employed. Both Dris *et al.* (2016) and Stanton *et al.* (2019) collected samples on roof tops with the use of a funnel, while this study collected atmospheric fallout of fibres at ground level capturing fibres on the meniscus of a water surface. Among other variables, this might suggest that fibre pollution from atmospheric fallout may be greater at ground level, or more effectively captured by water than a funnel. Fibre abundance is also correlated to population density (and consequently varying levels of textiles, carets, etc. upholstery) which varies between the sampling location of these studies. The occurrence of synthetic or extruded fibres at rural sites noted both in this study and by Stanton *et al.* (2019) highlights the importance of aeolian transport in fibre pollution.

3.5 Objective 5) Identify the distribution of tyre particles within the marine environment, Objective 6) Identify the distribution of synthetic fibres within the marine environment

Environmental data was complimented by laboratory experiments examining the transport potential for tyre wear particles and synthetic fibres to enter the marine environment.

Synthetic fibres in the global ocean are widely reported to have penetrated the marine environment, spatially and geographically. Conversely, reports of tyre wear in the marine environment are seldom. To aid our understating of the fate of these particles, reports of tyre wear in environmental mediums are summarized.

The predicted residence time of tyre wear in the atmosphere varies by particle size. Those in the range of 1 - 10 µm are expected to stay airborne for minutes to hours, whilst particles measuring smaller than 1 µm could be considered comparable to $PM_{2.5}$, which can stay in the atmosphere up to weeks with a mich longer range transport potential (Kole *et al*., 2017). Aside from gravitational settling, tyre wear may be removed from the air by wet deposition or scavenging, where particles become incorporated into rain droplets and returned to sea level, or incorporated into clouds and carried by convection (POLMIT, 2002). The potential for airborne tyre wear particles to reach the marine environment has not yet been studied (Kole *et al*., 2017).

Particles that do not become airborne are likely to be deposited on, or close to the road surface (Wik and Dave, 2009), forming part of the road dust (previously reported in concentrations of 0.7 and 210 g kg^{-1}) (Hopke *et al*., 1980; Satio, 1989; Rogge *et al*., 1993; Reddy and Quinn, 1997; Fauser *et al*., 1999; Kumata *et al*., 2000; Kumata *et al*., 2002). During intense precipitation events, tyre particles on the road surface can become mobilised within runoff. Brodie (2007) reported tyre wear to accumulate on road surfaces until threshold intensity is reached, subsequent to which tyre wear can get flushed from the road. Unice *et al.* (2019a) estimates some mobilisation once an intensity of 2 mm day^{-1} is reached, but predicts that 5 mm day^{-1}, 100 % will be mobilised. Concentrations of tyre wear within road runoff have been reported between 12 and 179 mg L^{-1} (Reddy and Quinn, 1997; Kuamta *et al*., 1997; Baunmann and Ismeier, 1998; Kumata *et al*., 2000; Kumata *et al*., 2002; Zeng *et al*., 2004; Wik and Dave, 2009). The length of the dry period prior to storm event is likely indicative of the particle load in the road off (POLMIT, 2002).

This runoff can flow into combined sewer systems, and subsequently be present wastewater plants. Concentrations of tyre wear within wastewater effluent discharge have been reported as 1 mg L^{-1} (Zeng *et al*., 2004). Runoff can also pass into storm drains, and discharge directly to surface waters. The sump at the bottom of storm drain is designed to capture some solids, in order to minimise blockages of pipework and also their entry to the environment. However, the retention of particles <50 µm is expected to be poor even when flow rate is slow (Vogeslang *et al*., 2018).

Unice *et al.* (2017) predicted tyre wear to be the largest source of microplastic export to European rivers. Little information however is available regarding concentrations and sources, sinks, and fluxes of tyre wear within this environmental matrix (Hurley *et al*., 2018; Wagner *et al*., 2018). Concentrations of tyre particles within surface waters have been reported 0.0037 – 3.6 mg L^{-1} (Kumata *et al*., 2000; Zeng *et al*., 2004; Ni *et al*., 2008., Unice *et al*., 2019a). Whilst providing a potential pathway to the sea, rivers and estuaries may also act as a sink via sedimentation of tyre wear. Previous reports suggest tyre concentrations to be higher in river sediments than in surface waters (Wagner *et al*., 2018), concentrations ranging between 0.4 and 155 g kg^{-1} d.w. (Spies *et al*., 1987; Reddy and Quinn, 1997; Kumata *et al*., 2002; Wik *et al*., 2008). Kumata *et al.* (2002) concluded concentrations of tyre wear are greater in river sediments in proximity to heavily trafficked areas, in rivers receiving storm water run-off.

Notably, there are few conclusive reports of the accumulation of tyre wear particles in the marine environment. Munari *et al.* (2017) investigated plastic pollution in Antarctic sediments. While fibres were found to be the most numerically abundant type of microplastics, synthetic rubber (SBS, polystyrene-butadiene-styrene) was the most abundant material by weight, with greatest concentrations in close proximity to the scientific base. Song *et al.* (2015) sampled the surface microlayer of coastal waters in South Korea, reporting synthetic rubber particles to contribute 8.3 % to the total microplastics recorded, but did not make estimations as to the origin of these particles.

Only one study that does attribute particles found at sea to be from tyre wear. Norén and Naustvoll (2010) undertook transect pelagic surveys from two coastal cities either side of the Skagerrak Sea, collecting particles between 10 - 500 µm, at depths of 0.1 to 1.5 m. Black particles were recovered between 8 L^{-1} and 779 L^{-1}, with the greatest concentrations collected near to the coast. They concluded some of these particles may be tyre tread in origin (analysed visually and by SEM-EDX).

In order to help illustrate the transport potential for tyre particles, we assessed rates of settlement in the laboratory.

3.5.1 Methods

Material containing tyre wear collected from the road surface and atmospheric deposition (representing particles transported to the environment by wastewater effluent and storm water runoff and atmospheric deposition) was introduced into a 10 cm beaker of deionised water, inverted three times, and left to settle for either 1 minute, 1 hour, or 1 week with three replicates at each time period. A composite blend of polyester (1.39 g cm^{-3}) and acrylic (1.18 g cm^{-3}) fibres were subject to settling tests in the same manner.

After these time periods, surface water and bottom water were separated from the water in suspension (the 'middle layer'), vacuum filtered onto Whatman glass microfiber 1.2 µm filter papers, dried (30 – 40 °C), and stored. Particles were photographed on a Leica M205C and counted in the same manner as explained in Section 2.2.4. This experiment was undertaken in a system with no energy; whereas in the natural environment turbulence is likely to have a considerable influence on sedimentation rate. Turbulence could have a range of effects including: increased surface mixing of articles that might otherwise be held in the meniscus, facilitating coagulation with other particulates potentially increasing settlement and may also lead to resuspension of particles that have settled on the seabed.

The approximate settling velocity of tyre wear particles was also calculated according to Stokes Law *i*) based upon the assumptions of uniform spherical particles, fresh water density, and a water body with a Reynolds number ≤ 1. This was calculated for the entire size distribution, 4 to 350 μm (according to Kreider *et al.*, 2010).

$$i) \qquad \omega = \frac{1}{18}\,\frac{(\rho\square - \rho)g\,D^2}{\mu}$$

3.5.2 Results

There was little difference in the settling behaviour of particles collected from the road surfaces and atmospheric deposition. Around one third of tyre wear material remained at the surface after a period of one minute. After 1 week, 10 - 20 % remained at the surface, and the remaining 80 - 90 % settled, see Figure 16. No material appeared to remain in suspension, all material was either at the surface or had settled to the bottom.

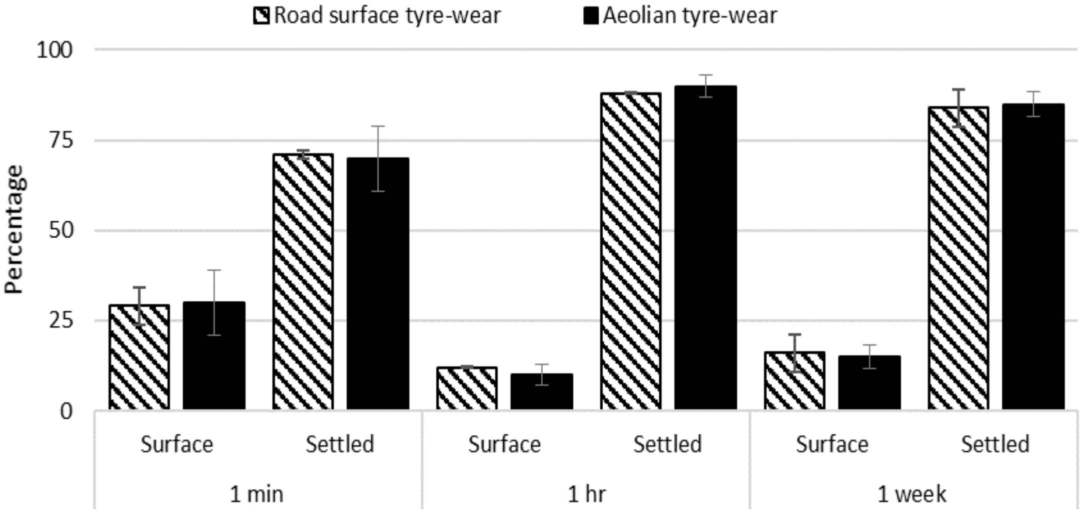

Fig. 16 Percentage of tyre wear particles, harnessed from atmospheric fallout and the road surface, at the surface vs tyre wear particles settled, after various time periods.

After one minute, the majority of synthetic fibres (80 %) remained at the surface. After one hour 30 % of acrylic, and 50 % of polyester fibres still at the surface, but after 1 week, roughly half of both polymers had settled (Figure 17).

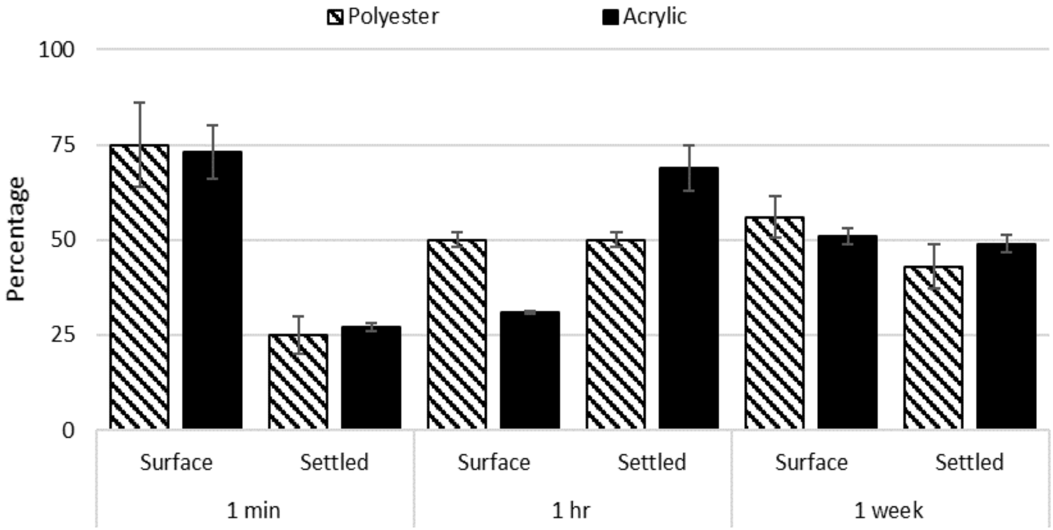

Fig. 17 Percentage of synthetic fibres particles, (composite blend of polyester and acrylic fibres), at the surface vs tyre wear particles settled, after various time periods.

The estimated settling velocity of tyre wear particles are displayed in Figure 18 (based upon the range of tyre wear particle size according to Kreider *et al*. (2010), 4 – 350 µm). The grey shaded area indicates the range in predicted densities of environmental tyre wear (1.2 to 2.5 g cm^{-3}). The black line represents a central estimate of 1.8 g cm^{-3} (Unice *et al.,* 2019a). Little difference was observed when the same parameters were plotted for saline water. Particle size appears to be the greatest influence on particle settling rates.

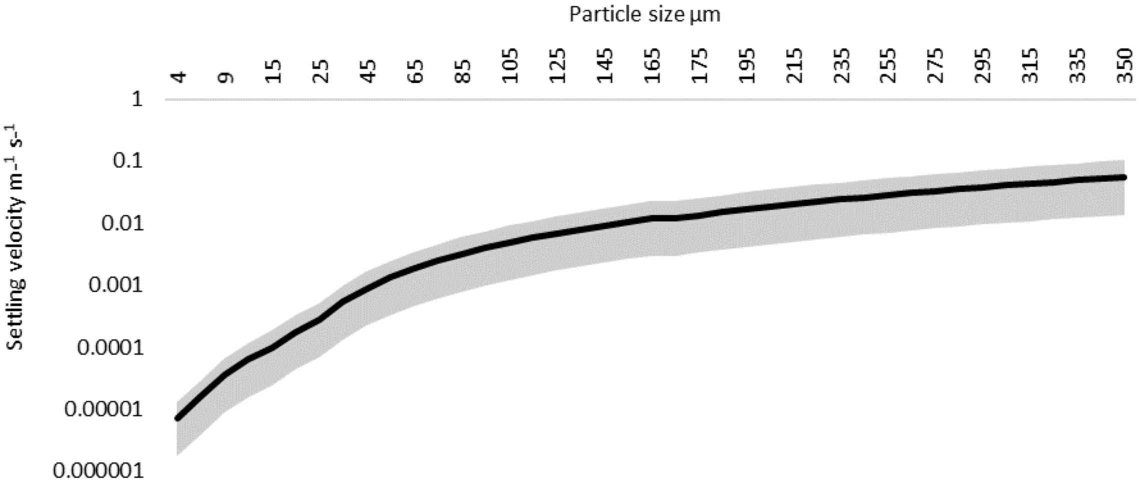

Fig. 18 Estimated settling velocities of tyre wear particles in fresh water (between 4 and 350 µm Kreider *et al*., 2010, and between 1.2 and 2.5 g cm^{-3} see 'environmental tyre wear', Fig3) calculated by Stoke's Law.

3.5.3 Discussion

In order to make estimations as to the transport potential of these particles within the environment studied based on the current state of knowledge, a number of assumptions are required. One, an average water flow rate (assumed uniform) calculated from tidal diamonds within 0.5 km of the coastline in Plymouth, averaged over spring and neap tides at high water flow. Two, an average depth (based upon an estuarine environment in Plymouth). Three, a size distribution provided by Kreider *et al.* (2010), see Figure 8 (% particles). And four, using Stoke's law to predict settling velocity with its associated assumptions of particle density and shape. These parameters suggest that in this environment tyre wear particles greater than 50 µm would settle close to their point of entry, travelling no more than a kilometre or so before reaching the seabed. Of the remaining particles (15 – 50 µm) could potentially travel much greater distances (1 – 15 km's), while the smallest particles (4 – 15 µm) could be transported considerably further from their point of entry, as was also evident by the laboratory settling experiments where around 15 % of particles remained at the water's surface after a 1 week settling period. These estimations were calculated at high water flow. Whilst the net movement of water in an estuary is export to the open ocean, the ebb and flow of the tide is likely to slow particle transport to the open ocean. Further empirical data would be required to confirm this. This is broadly in line with predictions by Unice *et al*. 2019b, who estimate considerable retention of particles within freshwater systems but also acknowledge that plausibly that export could range between 0.97 and 13 % (central estimate 2.2 %).

No analogous material exists for tyre wear particles. Clay presents some similarities (despite its higher density, 2.355 g cm^{-3}), therefore it seems reasonable to assume tyre particles could be deposited in environments where fine silt and clay accumulate, rather than in coarse or sandy deposits.

Particle size appears to be the greatest influence on settling velocity. Kooi *et al.* (2017) reviewed models which use other materials as proxies for microplastics, which also reported particle size to be the greatest influence on the removal of particles from the water column, with larger particles settling preferentially due to Stoke's Law. 75 - 90 % retention rate of tyre wear mass has been predicted within estuaries (Besseling *et al*., 2017; Siegfried *et al*., 2017; Unice *et al*., 2019b), due to sedimentation (Unice *et al*., 2019b). Factors including fresh water flow and tidal intrusions will further influence subsequent re-suspension (Vermeiren *et al*., 2016).

The most common fibres in this study (acrylic and polyester) have been reported within deep sea sediments (Woodall *et al*., 2014; Courtene-Jones *et al*., 2017), estuarine sediments (Peng *et al*., 2017), marine organisms including commercial fish species (Lusher *et al*., 2013; Neves *et al*., 2015), and remote environments such as the Arctic (Obbard *et al*., 2014). Given that fibres are widely documented in the marine environment, and that a good proportion of the tyre particles examined have similar transport potential, a lack of previous reporting of tyre wear particles in environmental samples is more likely a consequence in a lack of appropriate methods of detection, rather than a low environmental presence.

3.6 Objective 7) Potential contribution of microplastics from ropes used in maritime activities (supplementary to objective)

Microplastics can be released directly to the marine environment from lost or abraded rope and netting used in a number of maritime activities (Buchanan, 1971); including merchant and naval fleets, and recreational and commercial fishing activities. As such, rope and netting have been reported as the third most prevalent type of litter in the marine environment (Nelms *et al*., 2017). A considerable portion of this is likely to originate from fishing activities. In terms of fishing equipment, 88 % of fish landed by UK vessels in 2017 were captured using mobile gear, such as beam trawls, demersal trawls, nets, and dredges (Marine Management Organisation, 2017). Passive gear such as pots and traps were used to catch 43 % of the shellfish landed by the UK fleet (Marine Management Organisation, 2017).

Rope as a material is an assemblage of fibres, filaments, or wires which are compacted by being twisted or braided (plaiting) into a long, flexible line. By varying the number and thickness of the fibres, and how strands are laid, ropes of various dimensions, types and qualities can be produced.

Synthetic fibre ropes are preferential to their natural fibre counterparts because they have higher tensile strength, are more resistant to rotting, and can float on water (Coles, 2009). Rope fibres can be joined in many different ways. Because of the speed of their manufacturing, twisted ropes tend to be inexpensive to produce. Square-braided rope is made of eight strands that accompany each other in pairs. Monofilament is the name used for single filaments that are strong enough to be used alone. They can be used as fishing lines, but they are also spun in the manufacture of other forms of nets and ropes.

Most industrial fishing vessels are equipped with hydraulic net haulers or net drums; the hauling of ropes my cause considerable wear and abrasion. Exertion (weakening of the polymer structure), ageing, or direct physical damage of these ropes may cause them to fragment (Reddy *et al*., 2006; Andrady, 2011), see Figure 19 A & B.

Fig. 19 (A) 10-year-old Synthetic rope (polypropylene) previously used on a recreational yacht and stored outside, and (B) 2 year-old synthetic rope (polypropylene) that has previously been used to deploy nets on a fishing vessel.

Items that comprise abandoned, lost or otherwise discarded fishing gear (ALDFG) are extremely heterogeneous in terms of polymer type, size, shape and colour. For instance, some discarded or abandoned nets can be 100s of meters in length (UNEP, 2016), while offcuts are typically <1 m. The structure of synthetic rope is highly durable, but its plastic material is susceptible to embrittlement, cracking, and reduction in mechanical properties (Massey, 2006). This can lead to fragmentation and the formation of secondary microplastics (Arthur *et al*., 2009). Therefore the fragmentation could also result in the release of large quantities of microplastic particles into the marine environment (Welden and Cowie, 2017). Currently, there is little information on the importance of maritime activities in the generation of microplastics. Therefore, microplastic emissions from fishing gear was assessed by considering the following objectives:

a) Estimate the generation of microplastics from rope

b) Quantify fibres from rope and netting from environmental samples

3.6.1 Estimate the generation of microplastics from rope

The generation of microplastics from the abrasion of rope was compared between new and used rope. Four different rope types were examined; two of these were purchased new, and the other two had been used previously and were deemed to be at the end of their life service by their previous owners. The new ropes included a 12 mm and 16 mm diameter PolySteel rope. PolySteel rope is a mixture of polyethylene and polypropylene, a common choice for commercial fishing (personal communication with fishermen and retailers). The previously used ropes included: 1) 12 mm, polypropylene rope that had been stored outside on a boat for over 10 years; and 2) 16 mm, polypropylene rope that had been used regularly in fishing for two years.

Rope material was confirmed in the same manner as described in Section 2.2.2. Rope fragmentation was tested by the ropes being pulled by a hauler on a rig setup on a research vessel (Figure 20A) and in a laboratory (Figure 20B). The University of Plymouth's research vessel 'Falcon Spirit' was used to test microplastic generation from each rope type while at sea. Mechanical hauling was undertaken in water depths of 10 m where 15 m of each rope type (10-year old 12 mm diameter polypropylene rope; 2-year old 16 mm diameter polypropylene rope, new 12 mm diameter polysteel rope, new 16mm diameter polysteel rope) hauled up a 15 kg weight (replicates; n = 3). As the rope being hauled was wet, wide funnels were placed at 2 different friction points (Figure 20A). Microplastic pieces, released from the different rope types were collected together with water via funnels into a metal bucket and then transferred into glass vials.

To obtain the microplastic particles from this water, each sample was vacuum filtered through Whatman glass-filter paper (1.6 µm), then dried at 30 °C until at a constant weight. Once dry, particles were then visualised by scanning electron microscopy (JEOL, 7001F) imaging, to describe both whole particles and their topography.

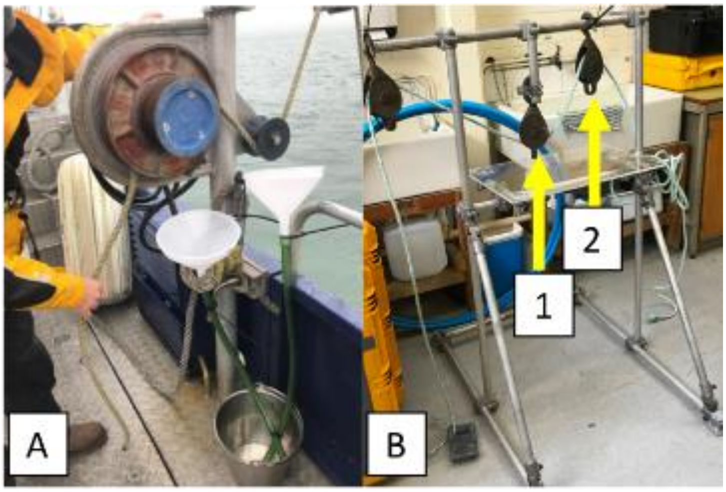

Fig. 20 (A) Experimental set up to collect microplastic released after mechanical hauling of rope. (B) Dry laboratory set-up replicated to the research vessel mechanical hauling; 1 & 2 are the friction points where released microplastic was collected onto a Pyrex sheet below.

A dry laboratory set-up was designed to replicate the experiment conducted on the research vessel (Figure 20B). This was necessary as the wet rope from the boat experiment could also bring up other foreign objects (e.g. sand), which affected abundance estimates.

Each replicate equated to 50, 1 m hauls of a 2.5 kg weight by hand on an untested section of rope. Microplastics that had fragmented from the main structure of the rope were collected onto a Pyrex sheet underneath the rig system; collection points were underneath pulleys 1 and 2 (Figure 20B). These were then brushed into a glass vial, using a goat hairbrush and a glass funnel. Since the used rope had been used for maritime activities in the past, any sand or non-plastic materials were extracted and separated from collected microplastics using Endecotts woven wire sieves of varying mesh size. The mass of the collected microplastic from rope was weighed by Precisa 2200C weighing scales. The null hypothesis was that the rope types differing in age and diameter would not significantly differ in the amount of microplastic fragments they produce when tested by the rig system. A Shapiro-Wilk normality test showed that the data did not fit normal distribution. Therefore, a Kruskal–Wallis test was performed ($p < 0.05$). This was followed by a post-hoc Nemenyi-Test (with tukey distance) to find which rope types significantly differed ($p < 0.05$).

A Malvern Mastersizer 2000 laser particle sizer (MM2) was used to measure the size-frequency distributions (SFDs) of the collected microplastics extracted using the dry rig setup. The resultant particle size distributions were expressed as a volume weighted mean from an average of twenty-five measurements per rope type (n = 5; 5 measurements for each replicate). The instrument assumes that the particles are spherical in shape. However, as the microplastics produced were typically cuboid shaped (see Figure 22), three prominent peaks were observed which corresponded to the length, height and width of the microplastic particle.

The number of fragments in each product, *N*, was estimated, assuming the fragments were of cuboid (Figure 21), using the following equations:

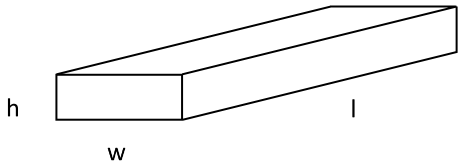

Fig. 21 a cuboid.

$$ii)\ V = l\ h\ w \qquad iii)\ Vt = \frac{Mt}{D} \qquad iv)\ N = \frac{Vt}{V}$$

where *Vt* is the total volume of plastic extracted, *Mt* is the total mass of plastic extracted, *D* is the density, *V(avg. fragment)* is the mean volume of one microplastic particle, *N* is number of microplastics, and length, height and width are l, h and w, respectively. For each rope type: equation *ii*) allowed calculation of the average volume of a microplastic particle from each rope type; equation *iii*) allowed calculation of the total volume of microplastics extracted; equation *iv*) allowed calculation of the approximate number of microplastics extracted during testing.

The shape and surface topography of the extracted microplastic particles from the rope hauling exercise (new 12mm diameter PolySteel rope) was visualised by scanning electron microscopy. The extracted microplastics were irregular shapes rather than fibres (Figure 22A & B). None of the fragments had a uniform shape and were of various sizes. On closer inspection, it appeared any fragments were themselves breaking down further (Figure 22C).

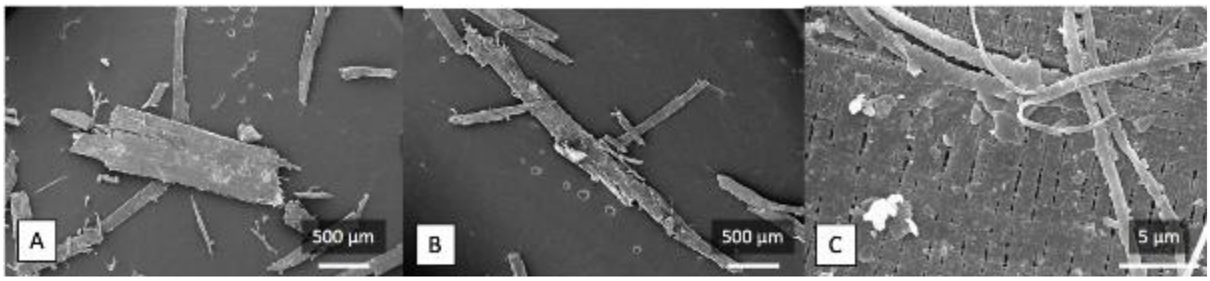

Fig. 22 -Scanning electron microscopy (SEM) images of a typical fragment from new fishing rope (new 12mm diameter PolySteel rope; 30X magnification). B- SEM of typical fragment from used fishing rope (new 12mm diameter PolySteel rope; 30X magnification). C- SEM of the cracks that appear in the fragment's topography (5000X magnification).

Microplastic generation from rope hauling was examined. The weight of microplastic extracted varied significantly between ropes (Kruskal-Wallis test, $p < 0.01$, Figure 23). The ropes which generated significantly more microplastic fragments were: 10 year old polysteel rope (12 mm diameter) compared to polysteel rope (12 mm diameter) (p <0.05); 2 year old polypropylene rope (16 mm diameter) compared to polysteel rope (16 mm diameter) (p <0.05); and ten-year old polypropylene rope (12 mm diameter) compared to new polyester rope (16 mm diameter) (p <0.01) (post hoc Nemenyi-Test).

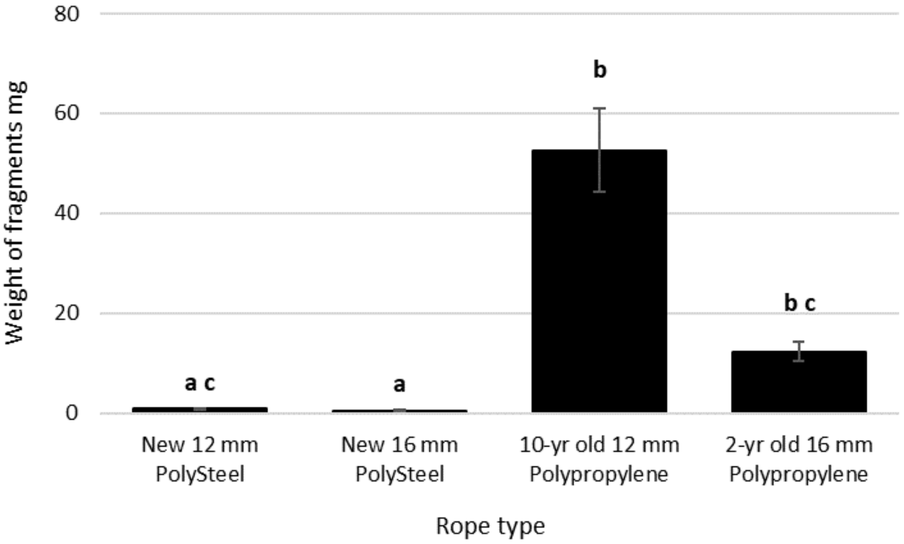

Fig. 23 Total mass of plastic fragments extracted from 4 rope types (10-year old 12mm diameter polypropylene rope, 2-year-old 16mm diameter polypropylene rope, new polysteel 12mm diameter rope, new polysteel 16mm diameter rope) for every 50 hauls with a 2.5 kg weight (n=5). The 10- (12 mm) and 2-year-old (16 mm) polypropylene ropes were found to generate more microplastic fragments than the new PolySteel counterparts. Letters a, b and c denote categories that are statistically different.

Size frequency distribution data presented three distinct peaks for each rope type, which were used to determine the microplastics length, width and height. Microplastic size, rather than the weight of microplastics generated, was found to have more influence in determining abundance estimates. After 50 hauls of 1 m with a 2.5 kg weight, the 10-year old 12 mm polypropylene diameter rope fragmented the most (52.59 mg). This was followed by the 2-year old 16mm diameter polypropylene (12.33 mg), the new 12 mm diameter polysteel (0.83 mg), and then the new 16 mm diameter polysteel (0.51 mg).

However, due to the average dimensions of the fragmented pieces released per haul, the 16 mm ropes were found to have the most microplastics per mg. The new 16 mm diameter rope was estimated to produce 3327 microplastics per mg, followed by the 2-year old 16 mm diameter rope with 2919 per mg. The new 12 mm diameter rope was estimated to produce a similar amount with 2788 per mg, see Table 1.

Table 1. The dimensions of an average microplastic fragment from four different rope types. The dimensions then allowed for an estimation of the number of microplastics released from a rope per mg. This included: two new rope types (12 mm and 16 mm); and two used ropes (12 mm:10 years old and 16 mm:2 years old).

Rope type	Length µm	Width µm	Height µm	Microplastics/mg
10-year old, 12 mm diameter polypropylene	545	115	24	730
2-year old, 16 mm diameter polypropylene	545	162	4	2919
New 12 mm diameter polysteel	1091	115	3	2788
New 16 mm diameter polysteel	917	115	3	3327

Focusing on hauling, this data indicates that new rope could release between 34 – 46 microplastic fragments per meter hauled. For older rope, this was substantially higher; it was estimated to release between 720 – 767 release per meter hauled. The quantity of plastic fragments was calculated by estimating fragment dimensions measured by laser particle size analyser, which assumes all particles are spherical in shape. Additionally, these estimates were calculated using data collected using a 2.5 kg weight. Most maritime activities could be hauling up much heavier loads, creating more friction and potentially more fragments.

3.6.2 Quantify fibres from rope and netting from environmental samples

To analyse the amount of abandoned, lost or otherwise discarded fishing gear within the marine environment, citizen science beach clean data was obtained from the Marine Conservation Society (MCS). Only beach surveys of 100 m in length and with complete data sets were included; this resulted in data from 1356 beach cleans. Data was collected by volunteers who walked along a linear transect (100 m along the beaches strand-line). Volunteers recorded litter in 101 item categories. These classifications were pre-determined by MCS. Both litter identification guides and face-to-face training was provided by beach survey organisers. The specific categories obtained from the data set were those relating to fishing activities, such as rope or line:

1) Plastic / Polystyrene: Fishing line
2) Plastic / Polystyrene: Fishing net and net pieces: 0-50 cm (small)
3) Plastic / Polystyrene: Fishing net and net pieces: 50 cm+ (large)
4) Plastic / Polystyrene: String/cord/rope: thickness 0-1cm
5) Plastic / Polystyrene: String/cord/rope: thickness 1 cm+

Independently of MSC surveys, additional beach cleans were undertaken at 3 beaches in South Devon, and 3 in North Devon. Beaches were chosen to provide a range of sandy and rocky substrate, high and low energy, and micro and macrotidal ranges. These beach cleans were conducted by our team who supervised 3 to 5 volunteers using the MCS parameters. These categories were split into more specific classifications and compared proportionally to the MCS data. The main categories included twisted rope, braided rope, rope from knotted net or single filaments (Table 2; description of rope categories described in the results).

Table 2. The categories of rope from beaches in the South West UK.

Categories of Rope			
Braided Rope	**Twisted Rope**	**Filaments**	**Knotted**
Square-braided rope	1-stranded rope	Single filament	Rope from knotted net
	2-stranded rope	Tangled ball of filament	
	3-stranded rope		
	4-stranded rope		
	<4-stranded rope		
	Cable rope		

To quantify the number of microplastic pieces that each category of rope could potentially produce, a sample size of up to 5 random pieces in each category and from each location was used to indicate the mean number of filaments and their length. The number of visible filaments which formed part of the main rope structure was counted from the end of the rope piece (Fig. 24A). Considering that microplastics are defined as pieces <5 mm in size, for every 5 mm of rope the mean number of filaments represented the maximum number of microplastics that could theoretically be generated (Fig. 24B). Clearly this is a simplification as each of the fibres generated could subsequently fragment in to more pieces. Hence our assessment is intend to give a first approximation of the initial potential for microplastic generation as the rope disintegrates.

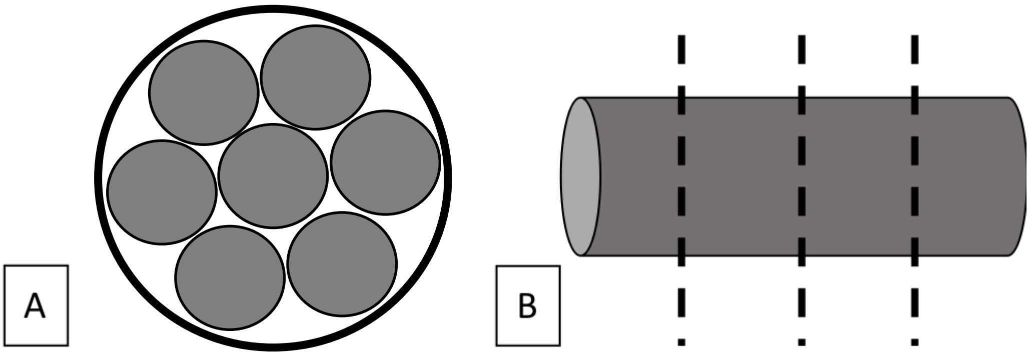

Fig. 24 A- Illustration showing the hypothetical composition of a rope from filaments; each smaller circle represents one filament. B- For every 5 mm of rope, the number of filaments represents the maximum number of microplastics that could be generated (based on the premise that micropalstics are < 5mm).

Results.

Results from MCS beach clean data (2011 - 2018), found the category of litter which had increased the most since 2011 was 'string/cord/rope: thickness 0-1cm' with a 71 % increase. 'Fishing line' was second highest (increasing by 46 %), and then 'string/cord/rope: thickness 1 cm+' (increasing by 32 %). By contrast, 'Fishing net and net pieces: 50 cm+ (large)' and '0-50 cm (small)' had a decreased in abundance with a reduction of – 55 % and – 32 %, respectively. Cumulatively however, the amount of fishing related debris found on beaches has remained relatively constant (Table 3).

Table 3. The average quantity of fishing related debris (e.g. rope) collected from 100 m of 1356 beaches between 2011 – 2018. Data was analysed from reports using MCS beach clean data.

Year	Number of beaches	No. of pieces recovered				
		Fishing line	Fishing net and net pieces: 0-50 cm (small)	Fishing net and net pieces: 50 cm+ (large)	String/cord/rope: thickness 0-1 cm	String/cord/rope: thickness 1 cm+
2011	95	18 ± 2.21	41 ± 3.66	13 ± 3.46	31 ± 1.68	15 ± 1.39
2012	150	31 ± 1.43	36 ± 1.59	12 ± 1.59	46 ± 1.07	23 ± 1.00
2013	113	28 ± 1.50	33 ± 2.78	10 ± 2.91	52 ± 1.52	23 ± 1.19
2014	157	35 ± 1.59	35 ± 1.34	7 ± 1.24	43 ± 0.96	33 ± 1.92
2015	167	27 ± 1.53	35 ± 1.60	8 ± 1.15	50 ± 0.92	30 ± 1.26
2016	209	22 ± 1.50	23 ± 1.97	5 ± 1.68	60 ± 0.61	20 ± 1.57
2017	207	32 ± 0.97	28 ± 0.94	8 ± 0.43	72 ± 0.84	25 ± 0.59
2018	258	26 ± 0.77	28 ± 0.96	6 ± 1.1	52 ± 0.67	20 ± 0.62

From the six additional beach cleans, included as part of this project, 1027 rope related litter items were obtained. These were separated into 10 categories (Table 4). These categories were chosen as they were the most prominent from the samples collected. The abundance of items varied significantly between the different categories (Kruskal-Wallis test; df = 9, $p < 0.01$). However, the only categories which were significantly different from each other were single filaments, which were more abundant than 4-stranded twisted rope ($p < 0.05$) and cable rope ($p < 0.05$) (post hoc Nemenyi-Test).

On average, single filaments were the most abundant type of rope found in the beach litter (61 items, Table 4). Square-braided rope was the second most abundant (46 items) and then tangled balls of filaments (23 items), see Table 3. The least abundant item was cable rope (1 item). However, cable rope was found to have the highest number of filaments which formed the main rope structure. Therefore, cable rope could potentially disintegrate into the highest numerical amount of microplastics (411 for every 5 mm of rope), whereas 1-stranded rope was estimated to produce the lowest numerical quantity of microplastics (10 for every 5 mm of rope) as it had the least filaments.

Table 4. Average (mean) quantity of different rope types found on beaches together with the mean number of filaments per rope piece.

Rope Structure	Average quantity per Beach	Number of Filaments
Square-braided rope	46	31
1-stranded rope	14	10
2-stranded rope	3	101
3-stranded rope	6	26
4-stranded rope	2	19
>4-stranded rope	3	53
Cable rope	1	411
Single filament	61	1
Tangled ball of filament	23	1
Rope from knotted net	9	35

It is important to recognize that some degree of fishing gear loss is inevitable and unavoidable as a consequence of fishing effort, gear conflicts, extreme weather, and operator error (FAO, 2016). However, abandoned or otherwise discarded fishing gear is essentially intentional and therefore avoidable. For all rope types collected from our beach cleans, large variability was recorded for rope length, but there was little variety in the width. Some of this rope may have been cut and discarded at sea. Therefore, behaviour and policy change focussing on rope offcuts may be effective for mitigating entry of marine related rope debris into the environment.

Pieces of rope, cord, and fishing line are frequently reported within the most abundant litter items in by beach cleaners (Smith *et al*., 2014). It is estimated that 640,000 t of fishing gear is lost to the marine environment every year (Macfadyen *et al*., 2009). Rope debris from maritime activities is mostly polyethylene and polypropylene fragments, whose densities (0.92 – 0.96 g cm^{-3}) are less than that of seawater (1.02–1.03 g cm^{-3}) (if devoid of significant fouling). Hence, this material can be readily washed up on beaches (Turner, 2017). Our results found single filaments were the most abundant fishing related debris on beaches. These are likely to have detached off from a larger segments of rope of which it was woven into or be the protective threads of dolly rope from trawling.

"Dolly rope" (also referred to as "chafe" or "chafer" in the UK), consists of bundles of orange or blue threads made of polyethylene (e.g., UHMWPE), polypropylene, or nylon that are attached to the lower side of a fishing net. It is used to buffer and protect the net from wear and tear and is designed to fray and lose strands as the net is dragged along the seabed (FAO, 2002). Dolly rope frays easily, and 10 – 25 % of the dolly rope tears off and accumulates in the marine environment (DollyRopeFree, 2019; Murray and Cowie, 2011). A large proportion of the single filaments found in this study were nylon and orange in colour, and therefore could be Dollyrope. Further assumptions about the origins of plastic beach litter may be made based upon the polymer type and the dominant maritime activity in the area.

In terms of microplastic emissions from mechanical hauling, we estimate that new ropes could release roughly 40 microplastic fragments per meter hauled and older ropes around 750. To put this into perspective, depending the length of vessel and the depth of at which fishing takes place, rope length could be up to between 120 fathoms (220 metres). Assuming 200 metres of rope is used and hauled back on-board, we estimate new rope to potentially release up to 8000 microplastics and older rope up to 150,000 per 200 m of haul. Here we also how that microplastics generated from rope wear were irregular fragments, rather than fibres (Figure 22A, B & C). More work would be needed to establish how the dimensions of these fragments might vary with rope type.

Rope age is an important factor when considering replacement. This varies according to a rope type and usage. For example, some fishing practices state that they run new lines and ropes every six months, whereas others decide to replace rope after inspection, or after 18 months. Presently, there are no standards or regulations when ropes and lines should be replaced. However, recommendations include that ropes should be stored away from heat and sunlight, if possible, in a separate compartment which is dry and well ventilated, away from containers of chemicals, detergents, rust removers, paint strippers and other substances capable of damaging them. Rope should be inspected internally and externally before use for signs of deterioration, undue wear or damage (MCA, 2010). The greatest mass shed from ropes subject to mechanical hauling was the oldest rope, that had also be exposed to long term UV (Figure 23), suggesting that UV increases deterioration of ropes.

When considering the potential consequences of the release of microplastics from commercial fishing into the environment, if any, it is important to consider both the mass of plastic, and the number and size of the particles. The latter will have direct influence on the probability of encounters with wildlife.

4.0 Synthetises of findings and comparison with previous modelling studies

The pattern of relative emissions between urban, rural, and motorway settings, was relatively consistent for both tyre particles and synthetic fibres with variation occurring mostly being between sampling dates. However, there was no clear pattern evident from weather data collected in the study e.g. no apparent changes in the presence of tyre particles or fibres with respect to ambient air temperatures, wind direction, and speed. Further work would be needed specifically addressing these parameters.

The abundance of synthetic fibres recorded in this study were similar to previous reports from atmospheric fallout and wastewater effluent. Tyre particle concentrations within storm water run-off and wastewater effluent were in similar orders of magnitude to, but toward the lower end of previous estimates.

With regards to the relative importance of tyre particles versus synthetic fibres, the units used to quantify tyre wear particles (mass) and synthetic fibres (abundance) do not allow direct quantitative comparisons. However, *results qualitatively indicate that, the presence of tyre particles measured at the points of entry to the marine environment examined in this study (WWT effluent, storm water runoff and aeolian deposition) is far greater than that of synthetic fibres*. To draw quantitative conclusions would require much more comprehensive, and detailed volumetric (shape and size) characterisation of both tyre particles and synthetic fibres. Notably, this finding does not suggest that previous estimates of fibres in the environment are incorrect, but that previous reports have underestimated, or overlooked tyre wear. Comprehensive empirical data regarding the abundance of tyre particles and synthetic fibres away from their points of the entry to the environment is now needed in combination with a better understanding of their transport potential once in the marine environment. Given the extent a which tyre wear is generated, coupled with the apparent overwhelming presence at entry points to marine environments, and that a small portion of tyre particles appear to have the potential for long range transport (Figure 16), there is currently no reason to doubt that tyre particles, like synthetic fibres, have the ability to become as widely dispersed in the ocean, reaching remote environments such as the poles or the deep sea.

Fallout from the atmosphere was a substantial pathway for both tyre particles and synthetic fibres. Our data indicated tyre particles and fibres were deposited at least 50 m from roadways. More work would be needed to establish exactly how far these particles can travel in the air. Based on the assumption that these particles could travel at least 50 m from a roadside we calculated that in Plymouth, that a surface area of approximately 125,000 m^2 of river, and 175,000 m^2 of estuarine or coastal waters was available for settlement of particles. For the whole of the UK, this equates to roughly 100,000,000 m^2 of river and 58,000,000 m^2 of estuarine or coastal waters.

The frequency of storm water drains far outnumbered wastewater treatment plants. Storm water drains were found to occur every few hundred meters along the river, estuary, or coastline from the regions sampled in Plymouth and Bristol and wastewater treatment plants surveyed could serve areas of up to 20 km^2. That said, wastewater plants release effluent continually, while storm water drains only release effluent during periods of intense rainfall. The frequency of storm water events likely to result in the release of tyre wear to surface waters was calculated based upon the occurrence, duration, and intensity of rainfall events, as well as immediately preceding weather conditions. Data for Plymouth and Bristol were obtained from the Met Office, and synthetized to give empirical values (see Appendix 2 for detailed calculations). This indicated that these events occurred on average 44 times a year, typically lasting around 90 minutes. It is not known how long it takes for tyres or fibres to be flushed out, or if their emission are continual for the duration of the rain event. Hence, it would seem likely that storm water runoff presents the most important pathway for tyre particles to reach aquatic environments.

How do the findings of this report compare to existing modelling predictions? It is important to look at the results of this study in context with research that has already been undertaken to quantify the release of microplastics into the environment. A study by Eunomia for the European Commission (hereafter referred to as the EU study) was used as a key part of the EU plastics strategy and in Defra's initial research into the issue. As an influential report in terms of policy making on the subject it is therefore helpful to ascertain whether the results of the present study would change the conclusions of the EU study and whether this has any wider policy implications.

The key difference between the EU study and the present study is that the EU study used a 'top-down' approach using emissions and activity data to develop a model for the occurrence of microplastics in the aquatic environment. The present study directly identifies, measures and quantifies the macroplastics as found in the open environment. It is almost impossible to make these two approaches marry up to the point where a full mass balance can be developed. This is because we simply do not know how and where all the particles end up and the myriad factors which can affect this. Nevertheless, the relative abundance in the environment should, at least, agree to some degree with what is expected to be emitted at source.

The following observations have been made in relation to how the results from the present study would in influence the findings of the EU study and the implications of this:

- The EU study estimates emissions of tyre wear emitted from wastewater treatment to be in the same order of magnitude as the emission of fibres, yet the present study estimates the presence of tyre wear to be orders of magnitude greater than fibres. The present study suggests this is because tyre particles are more prevalent than previously reported, rather than there are fewer fibres than previously reported. The reasons for the vast difference in their prevalence are unclear at this stage.

- The main pathway for tyre particles to the marine environment appears to be storm water runoff, which both studies agree on. There are also likely to be far more storm water outlets than wastewater effluent outlets (albeit not always releasing) which further emphasises this pathway as the most important for tyre particles.

- The pathway of atmospheric fallout was not considered for either fibres of tyre wear in the EU Study (or any other similar studies at the time). This is because of the lack of data concerning these pathways. Particularly for fibres, the main pathway to the marine environment was always considered to be through the washing of clothing. The present study indicates that the magnitude of the atmospheric deposition of fibres—presumably as a result of everyday wear and tear—could be emitting fibres in similar orders of magnitude to emissions reaching the sewer system from laundering. Similarly, for the EU study the atmospheric deposition of tyre particles was known to occur (and contribute to overall air pollution), but the magnitude was unknown. As a result of the present study, there are early indications that this pathway could result in a significant increase in the suspected emissions of tyre wear particles into waterways—this may be especially true for rural areas where the road system has direct water run-off into sewer systems. Further work would need to be undertaken to verify this.

- The sampling of fibres in storm water run-off is also a pathway not considered by the EU study. It was assumed that all garments laundered would release fibres into the sewer system which was separate from storm water. Finding fibres in this effluent suggests that another pathway exists. We can hypothesise that these fibres come from atmospheric deposition before being washed away from roads and streets. Again, this is a further pathway not considered in the EU study due to lack of evidence, but could even be much more substantial; whilst the mass of fibres per litres of storm water is half that of waste water effluent, as previously mentioned, there are far more storm water outlets. It would be a worthwhile exercise to develop a scalable model for wastewater effluent and storm water release quantity and frequency (i.e. for every litre of effluent, how many litres of storm water enter a catchment per year). Applying this to the microplastic emission rates in the present study could determine whether the focus should shift towards storm water management for the mitigation of fibres as well as tyre particles.

- The EU Study suggested there was some evidence that acrylic released more fibres during washing than other materials, but at the time this was not substantial enough to incorporate into the model or lead to any specific conclusions. Interestingly, almost half of the fibres identified in the present study were acrylic and only around one third were polyester. The market share of polyester is around double that of acrylic, therefore there may be some credence in the assertion that acrylic garments shed relatively larger amounts of fibres. This also suggests that there is merit in identifying the fibre types that shed the most and therefore adds weight to the recommendations from the EU study that a measurement method should be developed that allows comparison between different fibre types, construction methods and garments. This recognises that it should be a priority to reduce fibre release from the garment rather than mitigate or capture these once they are in the environment. While it has been recognised for some time that rope was a likely source of fibres the present study provides the first quantitative data and indicates this may be a substantial additional source of microplastic directly to the environment.

5.0 Future research

Data presented here gives a consistent comparison of the relative proportions of tyre particles to synthetic fibres within each pathway. Further work should focus on scaling up current understanding of these pathways to give a clearer picture of the relative importance. There were some clearly significant patterns in the data, however, some apparent trends fell short of significance and so greater levels of replication could help future work. More fieldwork also needs to be undertaken to further our understanding on the distribution of tyres and fibres in the marine environment, as estimation of the transport potential of these particles in this study were based upon laboratory experiments.

Future research should take a mass balance approach assessing concentrations of tyre wear and synthetic fibres along the entire transport pathway, and should also include sampling under high and low rainfall conditions of both storm runoff and wastewater discharge. Seasonal effects should also be quantified in order to help confirm annual inputs to the environment. Sampling in the present study was focused on roadways and consequently tyre wear emissions, more work is needed to sample areas with high footfall, but fewer roads, which may have some bearing on the relative importance of each contaminant type. It is also important to establish the transport potential via air at much greater distances from potential sources. Our study sampled at 50 m from roadways but recent work has shown the potential for fibres to travel up to 95 km. Sampling both tyre particles and fibres at greater distances is advised to improve our understanding of their transport potential.

While it has been recognised for some time that rope used in maritime activities was a likely source of fibres, the present study provides the first quantitative data and indicates this may be a substantial additional source of microplastic directly to the environment. More work is needed to establish that factors in the design, use and storage of ropes that might influence fibre shedding.

6.0 Further research and possible mitigation actions

Our data indicate the potential for substantial emissions of synthetic fibres to the marine environment from atmospheric deposition in addition to those from wastewater. Once a fibre is in the atmosphere it is difficult to establish its source (clothing, upholstery, carpets etc.). The importance of this pathway suggests that fitting filters to washing machines or wastewater treatment plants in order to collect fibres may be less beneficial than directly modifying any textile properties that influence fibre shedding. There is already a good indication that differences in textile design can have a significant effect on emissions (Napper and Thompson, 2016), with some garments releasing considerably more fibres than others. More research is needed to assess the potential for features in textile design to be used to reduce fibre emissions during use and during laundering. It would also be worth assessing whether features of rope design can be utilised to reduce shedding during maritime activities.

Discharge from storm water will drain directly into surface waters and presents a major pathway for particle contamination to aquatic environments. In addition, our findings indicate that overflow events during high rainfall also cause substantial quantities of particles to escape from wastewater treatment. Further research to examine the efficacy of various storm drain sumps could therefore be useful to establish the potential to increase particle retention at the roadside. In addition, it would be useful to establish the potential to increase particle retention at the roadside, and to establish the extent to which the amount of material in the sump of these drains influences their ability to retain particulates. It is clear that once the sump is at capacity it will no longer effectively trap particles. However, due to the relatively low density of tyre and fibre particles the efficiency of the sump in interception of particles may be limited even if the sump is empty; more work would be needed to examine this.

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Appendix

Appendix 1. Detection of tyre particles by Raman spectroscopy and FTIR

Methods

Raman spectroscopy. Five individual reference particles, artificially generated from tyre tread (high performance summer tyre for passenger car manufactured by Prestivo) were transferred with steel forceps to a steel substrate. Raman spectroscopy was performed using an inVia™ Raman microscope (Renishaw Plc, Wotton-under-Edge, UK) equipped with a 785 nm diode laser and 600 lines/mm diffraction grating. The system was calibrated using an internal silicon sample with a characteristic band at 520 cm^{-1} before use. Reference spectra were acquired in the extended (over the full range of Raman shifts for a user-defined point in a sample) mode through a 20x/0.40 air objective with 10 s integration time (a 30 s integration time did not improve spectral quality). Given the high fluorescence of tyre wear particles, laser powers ranging from 0.05 – 5% (19 mW = 10%) were used to avoid saturation of the CCD. Three acquisitions were collected at 2 sites of the same particle and averaged, for five particles. Black carbon, an ingredient in synthetic vehicle tyres, is hypothesized to be a large contributor to the fluorescence observed in tyre particulates' Raman fingerprint. To evaluate whether it's possible to discriminate between tyre and black carbon, 1000 narrow spectra (912 – 1668.1 cm^{-1}) of black carbon and tyre reference material were obtained with 2 s integration times.

Spectra of environmental tyre particles from an urban atmospheric deposition sample (Plymouth) were acquired in the extended (over the full range of Raman shifts for a user-defined point in a sample) mode through a 50x/0.75 air objective with integration times ranging from 10 to 30 s to improve spectral quality. Environmental particles elicited higher fluorescence and hence laser power ranged from 0.0001 to 0.05% to avoid saturation of the CCD.

All spectra were processed and plotted using hyperSpec in RStudio (Beleited and Sergo: 'hyperSpec: a package to handle hyperspectral data sets in R', R package version 0.99-20180627). A polynomial baseline was fit of an order of 3 – 5, using the 'baseline' package (Liland and Mevik: 'baseline', R package version 1.2-1). Reference and sample spectra were matched to a spectral library (BioRad KnowItAll® Informatics System - Raman ID Expert software) and composition was estimated based on a combination of Hit Quality Index (HQI), matching peak wavenumber positions and relevance in the context of the reference particles, sample type and morphology.

The 1000 spectra obtained for black carbon and tyre were standard normal variate and normalised to ensure spectral alignment. The dataset was then mean centred and analysed using a Principal Component Analysis (PCA) in Python.

Results

Raman spectroscopy. High fluorescence led to poor quality spectra for tyre reference particles, with no accurate matches in the spectral library (hit indices generally below 70). Some generated band (D-band and G-band ~1350 and ~1580 cm^{-1}, respectively), characteristic of blank carbon materials, but it was not consistent among all reference particles, which was not improved by base-line correction (Figure 29) It also suggests the carbon black additive in the tyre particle overrides any signal from the synthetic rubber. Using a higher NA lens, high confocality set-up and use of a spot laser (Renishaw, personal communication). The most frequent matches of tyre reference materials were calcium hypochlorite and 3,3’ diaminobenzidine. Further processing using the software may improve this. Moreover, there is a potential that longer wavelength lasers may acquire Raman spectra with lower fluorescence.

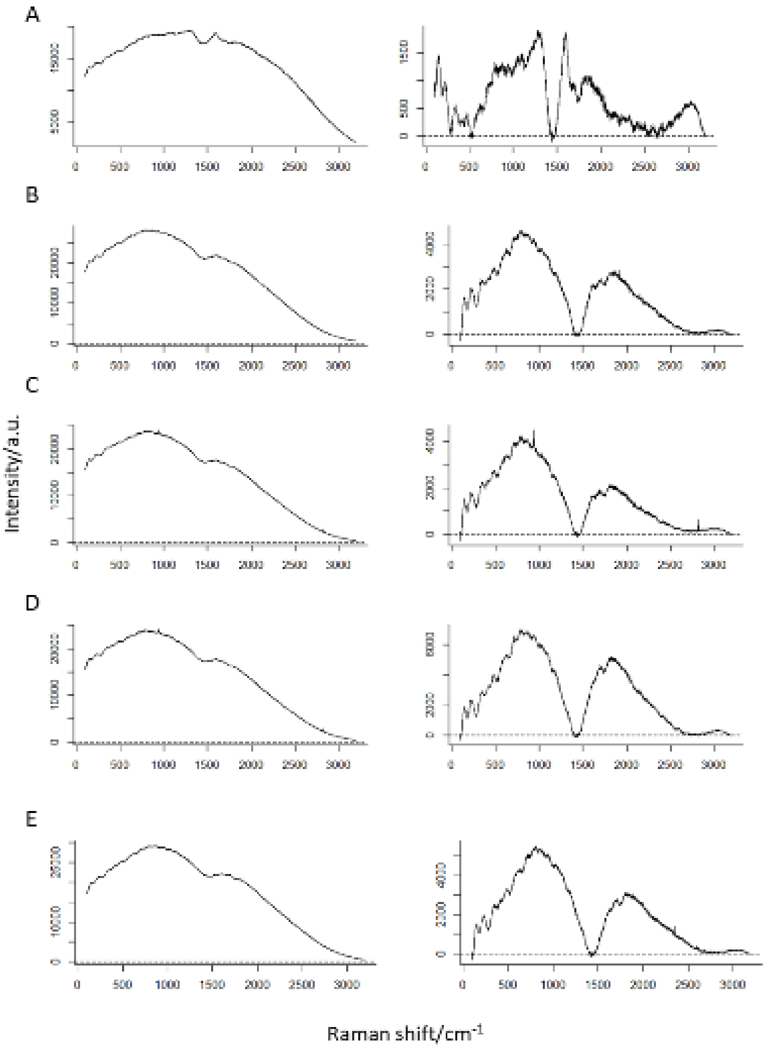

Fig 29. Unprocessed (left) and polynomial baseline-corrected (right) spectra of reference tyre particles (A-E).

Environmental tyre particles (collected from atmospheric deposition from an urban environment) exhibited higher fluorescence than the reference material. Whilst their spectra (Figure 30) were similar to reference particles, KnowItAll software was unable to match them to a reference spectrum in the library.

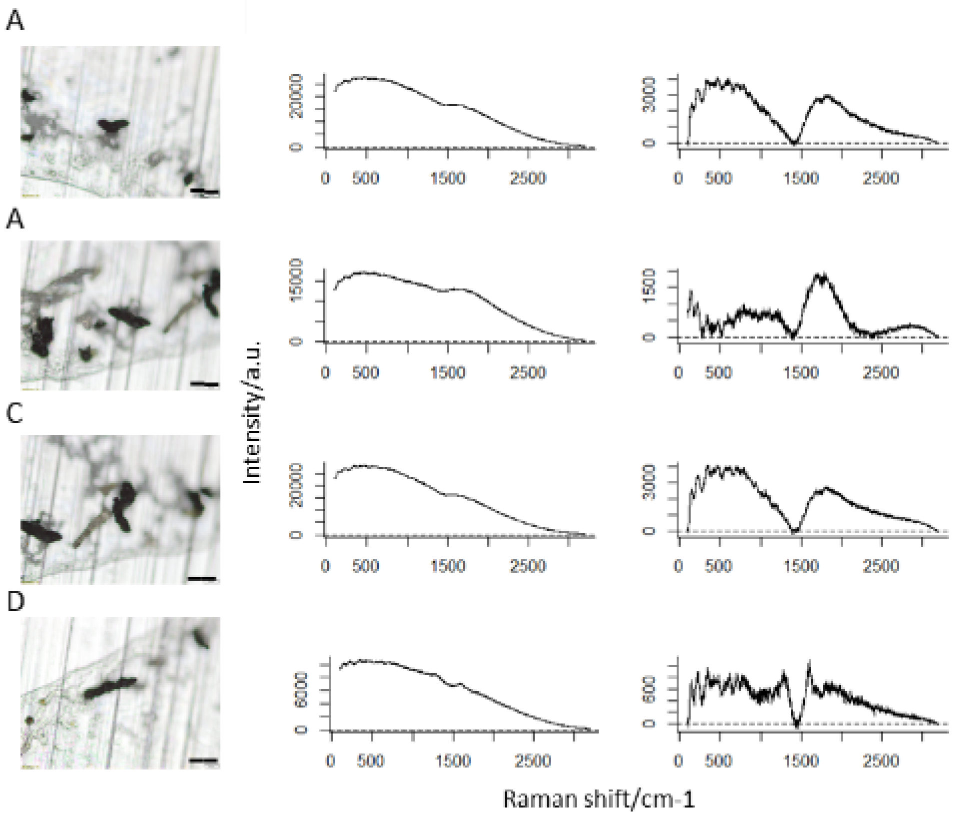

Fig 30. Example spectra for potential tyre particles collected from urban atmospheric deposition, with corresponding unprocessed and baseline-corrected spectra. Scale bar = 40µm

Identification of individual tyre particles was unsuccessful due to high fluorescence. A more in-depth Raman analysis of environmental particulate matter is needed to improve classification of tyre particles versus other common black particles such as soot and asphalt. This may improved by adopting a longer wavelength laser and spectral processing. Micro-FTIR has potential, following the same sample preparation as outlined for Raman. Environmental tyre particles have been successfully matched to polymerised petroleum resin using BioRad's KnowItAll software, which has applications in rubber, amongst other materials. Potentially, a combination of rubber/tyre-associated additives identified using spectroscopy, combined with morphological criteria, will infer whether particles are tyre.

Appendix 2. Frequency of storm event storm event calculation

The average number of rainfall events that exceeded the predicted flush out threshold annually were counted (removing events that occurred on consecutive days due to likelihood of a total flush out of tyre and fibres from the road surface), in location one and two, averaging 44 times a year

(2017), typically lasting 1.6 hours, equating to figure in L^{-1} yr^{-1}. This works on the assumption that tyre wear is released for the duration of the rainfall event, where in reality it is not known how long it takes for a flush out. The frequency of storm water discharge points were counted along the sampled river/estuary in location 1 and 2, occurring approximately every 350 m. This frequency was agreeable in both locations, however there was large variability, and is not necessarily transferable or applicable to any estuary or full river catchment, therefore the relative proportions should be met with caution. The frequency of storm water drains were counted alongside sampled river catchments in location 1 and 2, typically occurring every 350 m.