

**Microplastics and Contaminants of Concern in the
Strategic Road Network**

**Appendix A: Quantifying tyre wear particles and
other microplastics from the Strategic Road
Network**

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Appendix A. Microplastics and Tyre Particles

A.1. Abstract

Road drainage has been identified as a major pathway for microplastics (MPs) to enter aquatic environments, and particles generated from the abrasion of vehicle tyre tread against road surfaces are thought to represent the dominant share. This project aimed to quantify: 1) the contribution of tyre wear particles (TWPs) and other types of microplastics from the National Highways Strategic Road Network (SRN) to aquatic environments; 2) whether TWPs and other microplastics varied in magnitude between straight and curved sections of the network and 3) the effectiveness of existing management approaches to retain TWPs and other microplastics pollutants in surface water runoff, such as retention ponds and wetlands, to capture TWPs and other microplastics. Findings from this project also aim to inform approaches to minimise microplastics release from the SRN to natural aquatic environments.

In order to examine whether characteristics of the SRN might influence the generation of microplastics, TWPs and other microplastics were quantified within direct runoff draining from both curved and straight sections of the SRN over multiple rainfall events. To examine the efficacy of highway drainage systems in retaining microplastics, water samples were collected from the influent and effluent of three wetlands and three retention ponds over three rainfall events. Sites were located in the South-West and in the Midlands of the UK. Tyre wear was quantified using pyrolysis gas chromatography–mass spectrometry (Py-GC-MS). Other forms of microplastics such as fibres and fragments were identified using Fourier-transform infrared spectroscopy (FTIR).

Retention ponds and wetlands captured both TWPs and other microplastics particles. Typically resulting in a substantial reduction in concentration between influent and effluent. However, there was considerable variability among sites and sampling occasions and the effect was only statistically significant for reductions in tyre wear particles by retention ponds.

The concentration of TWPs in pond sediment was several orders of magnitude greater than in water samples, indicating particles were accumulating. There was a positive correlation between the concentration of TWPs in direct runoff and the content of total suspended solids (TSS), indicating TSS could perhaps serve as a proxy for TWPs in future studies, though further targeted investigation is recommended. The removal of other microplastics, such as fibres and fragments, by retention ponds and wetlands was inferior and less consistent ($39.6\% \pm 31.6$), possibly attributable to the lower densities of some of the polymers identified ($0.9 - 1.43 \text{ g cm}^3$). Although TWPs can have densities as low as 1.2 g cm^3 they can also reach up to 2.5 g cm^3 . The mass of TWPs within pond sediment and direct runoff (pond influent and drainage from curves and straights) was considerably greater than the estimated mass of other forms of microplastics, however the mass of TWPs and other microplastics was similar exiting the ponds within effluent.

Future research should consider the extent to which increasing the frequency of removal of sediments from highway drainage systems such as retention ponds or roadside sumps and installing ponds with long flow paths might further increase capture efficiency of TWPs. Further work should also examine the efficiency of TWP and microplastic retention in other highway drainage systems, as well as establishing the relative importance of tyre design and composition, vehicle maintenance and driver behaviour.

A.2. Introduction

Microplastics (MPs) are described as small pieces of plastic debris (<5 mm) that are insoluble in water, solid in state, persistent in the environment, and synthetic in composition (Verschoor, 2015). They can enter the environment directly as micro sized particles (primary microplastics e.g. microbeads from cosmetics), originate from the wear and tear of items during use (e.g. textiles fibres or tyre wear particles (TWPs)), or be generated as a consequence of the fragmentation of plastic in the environment (secondary microplastics).

Road drainage has been identified as a major pathway for microplastic pollution (Jarlskog *et al.*, 2020; Moruzzi *et al.*, 2020; Wang *et al.*, 2020; Xu *et al.*, 2020; Parker-Jurd *et al.*, 2021).

Concentrations of anthropogenic particles in surface stormwater drainage tend to be higher than other pathways, such as treated wastewater effluent which undergoes substantial treatment prior to its discharge to aquatic waters (Werbowski *et al.*, 2021). Particles generated from the wear of vehicle tyre tread are thought to represent the dominant share of the pollution load in stormwater drainage (Overdahl *et al.*, 2021), however, stormwater from road networks can also carry other microplastics, such as fragments generated from the breakdown of larger items from intentional and unintentional littering, or microplastics such as fibres generated from the wear of textiles that have been transported via the atmosphere and deposited on road surfaces. By necessity TWPs and other microplastics are quantified by different methods and have different units (mass and abundance respectively). Consequently, they are presented separately in this report and hereafter are referred to as 'tyre wear particles (TWPs)' and as 'other microplastics'.

A typical passenger tyre weighs around 11.8 kg and will last approximately 40,000 km over which it can wear approximately 3.5 kg of its mass before reaching its safety limit. Passenger tyre treads are primarily comprised of a mix of synthetic and natural rubbers (Kole *et al.*, 2017), while HGVs typically have a greater proportion of natural to synthetic rubbers. In addition to rubbers, tyre treads also contain a complex blend of chemical compounds including potentially hazardous chemicals that can leach into aquatic waters with potential toxic effects (Peter *et al.*, 2018). The wear of tyre tread occurs due to friction at the tyre-road interface, incorporating varying amounts of amounts of mineral encrustation from the road surface (Dall'Osto *et al.*, 2014). Consequently, their density is highly variable (~1.2 - 2.5 g cm³) (Verschoor *et al.*, 2016; Sommer *et al.*, 2018; Vogeslang *et al.*, 2018; *et al.*; Kovochich *et al.*, 2021).

Concentrations of TWPs are correlated with traffic volume, population density and urbanisation (Bondelind *et al.*, 2020; Su *et al.*, 2020; Goßmann *et al.*, 2021; Jarlskog *et al.*, 2021; Mengistu *et al.*, 2021). Braking, accelerating and cornering are also among the most frequently reported factors influencing TWP generation (Dannis, 1974; Councell *et al.*, 2004; Knight *et al.*, 2020; Mengistu *et al.*, 2021). Seasonal effects have also been reported with greater wear during the summer (Jarlskog *et al.*, 2020; Jarlskog *et al.*, 2021), accumulation during periods of dry weather and transportation during storm events (Su *et al.*, 2020). However, road wetness, temperature, and seasonal effects have been suggested as less influential than factors such as vehicle, tyre, and road types, road curvature and driving style (European TRWP Platform, 2019; Liu *et al.*, 2021).

Few studies exist quantifying other forms of microplastic within stormwater in drainage management assets such as retention ponds, bioretention cells, or rain gardens (e.g. Reddy and Quinn, 1997; Klöckner *et al.*, 2020; Werbowski *et al.*, 2021). However, stormwater ponds have been suggested as a potential preliminary barrier to reduce the release of microplastics into the wider environment (Grbic *et al.*, 2020; Moruzzi *et al.*, 2020; Smyth *et al.*, 2021; Mengistu *et al.*, 2021).

A.3. Aims and objectives

This project aimed to quantify the contribution of tyre wear particles and other types of microplastics from the SRN to aquatic environments. More specifically, it examined the influence of road characteristics on their generation, and the efficacy of some existing highway drainage systems such as ponds for the retention of TWPs and other microplastics. Both topics are currently lacking primary data (Shruti *et al.*, 2021). It is anticipated this report will guide approaches to minimise the release of TWPs and other microplastics from the SRN to the natural environment.

A.4. Methods

A.4.1. Experimental design

Two factors were considered, the influence of road curvature which had two levels curved and straight, and in a separate experimental design the effect of highways drainage systems for

stormwater management, comparing retention ponds and wetlands. Where possible sites were selected to cover a range of traffic volumes and some geographic spread in order to integrate across variations in climate and traffic density.

Sampling followed the experimental design detailed in Figure A.1.

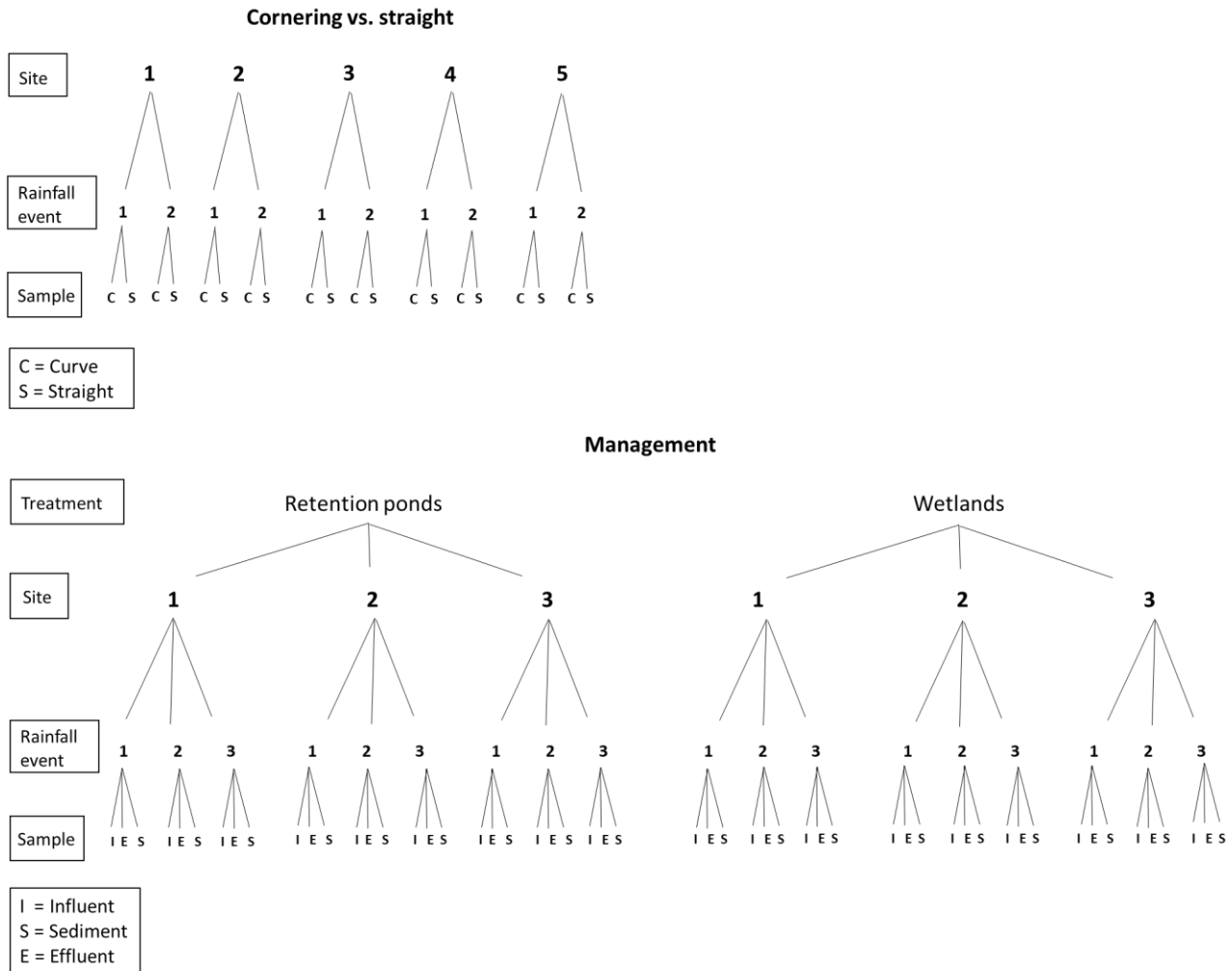


Figure A.1: Detailed breakdown of the experimental design for sampling direct drainage from curved and straight sections of the SRN and the influent, effluent and sediments of highways drainage systems (retention ponds and wetlands).

A.4.2. Site selection

A ‘curve’ on the road network was determined according to the Design Manual for Roads and Bridges (volume 6, section 1 CD109) parameters (Highways England, 2020). For example, a road with a 70 mph speed limit should be designed with a minimum radius of 1020 m and minimum superelevation of 5 %. An excerpt of the DMRB (National Highways, 2022) is provided in Supporting Information (Section A10.1). Superelevation is defined as the transverse slope between each side of the road designed to counteract the effects of centrifugal force and reduce the tendency of vehicles to overturn and skid laterally when navigating into and through a bend. Bends in the road network were identified where the radius or superelevation fell short of the minimum requirements for the speed limit. Superelevation and radius were estimated on Google Earth Pro. Samples were collected from outfalls that drained from curved and straight sections of the road network. In each instance these paired sites were located in as close proximity to one another as possible to ensure key site characteristics such as rainfall duration and intensity and traffic loads were comparable. In each instance other characteristics such as slope angle, road width, vehicle speed, or congestion may differ.

According to the National Highways standards for the Design of Highways Drainage Systems, a retention pond is defined as ‘a pond that generally retains some water at all times. Can have permeable base or banks. Primarily designed to attenuate flows by accepting large inflows, but discharging slowly. Can also treat water by allowing suspended solids to settle out.’ A wetland is described as ‘a pond with a high proportion of shallow zones that promote the growth of bottom-rooted plants, and which can be used for the treatment of pollution.’ (National Highways, 2022). Retention ponds and wetlands were selected based upon their designation on the internal Highways Agency Drainage Data Management System (HADDMS). Site selection was further determined by the following prerequisites, including: permission to access and sample from the regional National Highways drainage team, and safe, or off network access to sample as opposed to access from the live carriageway. Example retention pond and wetlands are shown in Figure A.2.

Key site characteristics are detailed in Table A.1. Across the selected sites, annual average daily traffic (AADT) volumes ranged between ~17,500 - >100,000, approximate impermeable catchment areas ranged between 0.0012 km² and 0.095 km² and were located mostly in the South West with three sites located in the Midlands. Runoff sampled drained from both A-roads and motorways. Approximate impermeable catchment area was determined on HADDMS using assets details and a digital terrain model contour layer (1 m). Calculation of estimated catchment areas was verified with the local regional National Highways drainage engineer. Further site details are provided in the supporting information A10.4.

Table A.1: Details of key site characteristics. Further site details (including site names) are provided in the supporting information (supporting information A10.4). AADT at curve vs. straight 4 includes drainage from a section of road where the AADT is variable.

Site name	Road	Region	~AADT	~Impermeable catchment area [km ²]	~Pond surface area [m ²]	Shortest flow path [m]	
Retention pond							
1	CS	A30	SW	36,000	0.022	1710	36
2	P12	A30	SW	35,000	0.0065	960	41
3	PBN	A43	Midlands	35,000	0.0410	2227	75
Wetland							
1	BP	A38	SW	17,500	0.0137	640	70
2	KEG	A50	Midlands	>100,000	0.0189	1567	100
3	DON	A453	Midlands	30,000	0.0952	517	16
Curve vs. straight							
1	OKE	A30	SW	28,000	0.039		
2	ASH	A38	SW	40,000	0.0064		
3	NEW	A30	SW	32,500	0.027		
4	CH	A38	SW	41,000 (80,000)	0.012		
5	HH	A38	SW	40,000	0.0012		



Figure A.2: Example of a wetland (left, wetland 1) and a retention pond (right, retention pond 1).
Source: Florence Parker-Jurd University of Plymouth, 2022.

A.4.3. Field sampling

Sampling was conducted between 28th October 2021 and 30th September 2022. Water samples were collected during the onset or initial period of a rainfall event after runoff was generated. Samples were collected from direct drainage points (e.g. Figure A.3 right). The paired sites were located in close proximity (1.2 – 9.5 km apart) in order to ensure site characteristics were as comparable as possible. Each site was sampled on two occasions, with the site within the pair that was sampled first alternated between sampling occasions.

For wetlands and retention ponds water samples were collected over a period of ~20 minutes from the inlet to the pond (see example in Figure A.3 left) during the onset of the precipitation event with the goal of capturing the first flush. A change in colour and/or flow of the influent was typically noted as the point at which to start sampling. Samples were collected from the outlet of the pond after a period of at least 20 minutes or until the effluent was starting to flow, or in some cases after the 'normal' baseflow increased. A minimum of 6 litres of influent and 6 litres of effluent was collected at each site into glass bottles. All samples were transported to the laboratory for processing and analysis. Each pond was sampled during three separate precipitation events.

On three occasions autosamplers (ISCO 6712) were used in an attempt to aid sampling at retention ponds and wetlands. Autosamplers were programmed to trigger sampling in excess of 2 mm hr⁻¹ of rain, collecting 250 ml every minute, mimicking manual sampling. See table in Section A10.3 for use of autosamplers.

For other microplastics three procedural blanks were collected to replicate manual sampling, and three to replicate autosamplers. These were used to quantify any contamination originating from the sampling apparatus or procedure rather than from the sample itself.



Figure A.3: Example of drainage points at which water samples were collected from a retention pond inlet (left) and a direct drainage outfall (right). Source: Florence Parker-Jurd University of Plymouth, 2022.

Sediments were collected at each retention pond and each wetland on three occasions. Samples were collected using a prewashed container strapped to an extendable pole. Where possible, samples were collected from three different locations across the pond. Sediments were collected either prior to rainfall events or during periods of dry weather when the water levels of the ponds were low enough to enable collection as close to the centre of ponds as possible, where most sediments accumulated.

A.4.4. Laboratory protocol

Samples were processed in a purpose-built clean two-tier laboratory (ISO clean room class 7 and 8) at the University of Plymouth with positive pressure and controlled airways (filtered to 0.5 μm). The room is restricted in its access where laboratory shoes and cotton laboratory coats are worn at all times to minimise microplastic contamination. Due to their colour and carbon black content, tyre wear particles cannot be reliably identified using the approach typically used for other form of microplastics, where particles are individually identified using spectroscopy. Tyre particles were instead, by necessity, quantified by mass using a bulk chemical analysis. Consequently, each sample was homogenized and separated in two to allow for both analyses (see below).

A.4.4.1. Tyre wear particle analysis

Water samples were homogenised and inverted five times after which 20 % of the total volume was transferred into a clean beaker. The remaining 80 % was first passed through 30 μm and 15 μm sieves and backwashed with deionised water into a clean beaker before being vacuum filtered over a 1.6 μm Whatman glass microfibre filter paper.

Sediment samples were placed in a low temperature drying oven until at a thick consistency and mixed thoroughly until homogenous. A subsample (~1.5 g) was resuspended in deionised water and filtered over a 1.6 μm Whatman glass microfibre filter paper and placed in a drying oven at a low heat until the mass as a dry weight (d.w.) could be recorded.

Benzothiazole was used as a chemical marker for the presence of tyre wear within environmental samples, quantified using Py-GC-MS (method adapted from Parker-Jurd *et al.* (2021)). Our approach targeted molecules that are bound into a polymer which is cross-linked with sulphur into the elastomeric materials based on isoprene, butadiene and styrene-butadiene, rather than compounds present in the free solvent-extractable fraction. Hence our approach maximised the detection of solid tyre wear particles as opposed to tyre wear leachates. Full details of the analytical method are given in the supporting information (A10.2).

In order to relate the spectral response to an estimated mass of TWPs present in the samples, benzothiazole was quantified from the pyrolysis products of fragments from seven common passenger tread tyre treads (Bridgestone, Continental, Goodyear, Michelin, Nokian, Pirelli and Vredestein). These were analysed in the same manner as the water and sediment samples (SI A10.2). The response of the instrument was measured using a calibration curve of peak intensity versus the weight of an authentic standard of benzothiazole averaged over three pyrolysis runs ($R^2 > 0.99$). Data were then converted to give a mass of TWPs per sample and normalized by the volume or mass of sample collected. The limit of detection was ~ 1 ng per mg of sample.

A.4.4.2. Analysis of other microplastics

The remaining 20 % of the total volume of the water sample was filtered over multiple 1.6 μm Whatman glass microfibre filter papers, the volume on each filter paper determined by the colour i.e. the material sparse enough so that any potential microplastics were visible under a dissection microscope (LEICA S9E).

A subsample of the sediment (~ 1.5 g) was also dried until at a thick consistency and mixed thoroughly until homogenised. The subsample was transferred into a pre-washed beaker and placed in a drying oven on a low heat ($\sim 35^\circ\text{C}$) until a dry weight could be taken. The dried sediment was then resuspended in deionised water. As for the water samples, the sample was filtered over multiple 1.6 μm Whatman glass microfibre filter papers, sparsely enough to identify any potential microplastics under a dissection microscope.

Each potential microplastic was measured at its longest length, the colour and form (e.g. sphere, fragment, fibre, or film) of the particle was also recorded and then subject to FTIR. Particle identification using FTIR was performed in transmission mode in the range $400\text{-}6000\text{ cm}^{-1}$ (and a background scan performed between each particle) with a Hyperion 1000 microscope coupled to a Vertex 70 spectrometer by Bruker. For each particle spectra were recorded with 32 scans and identified against a spectral database (BPAD polymer and synthetic fibres ATR).

A.4.5. Data Analysis

The statistics package Minitab (V18) was used to perform all the data analysis. Analysis of variance (ANOVA) was used to compare concentrations of TWPs in drainage between; curved and straight sections of the SRN, influent and effluent of highway drainage systems, and different drainage asset types (wetlands vs. retention ponds). Homogeneity of variance was assessed prior to ANOVA (Anderson-darling) and transformations applied if appropriate (log transformation). In each instance treatment (influent or effluent), asset type (wetland or retention pond) and road type (curve or straight) were fixed and site was random. Treatment, asset type and road type were nested within site. The interaction of TWPs and microplastic concentrations (dependent variable) and weather and site characteristics (e.g. AADT, flow path, antecedent conditions, independent variable) in direct runoff (curve vs straight or pond influent) were also analysed in Minitab (V18) and examined using a linear regression. The same approach was taken for microplastics. Standard error was used to show deviation of the mean across sampling events. All results are presented as the mean plus-minus the standard error ($\bar{x} \pm \sigma_M$) throughout.

A.5. Results

In total TWPs and other microplastics were quantified across a total of 70 samples (52 water samples and 18 sediments samples) across 14 sites. On only one occasion were concentrations

below the limit of detection where no microplastics were detected in the sediment of a wetland. Raw data are provided in the supporting information (A10.6).

Autosamplers were found to be of minimal use due to failures in the unit being triggered or difficulties in locating discrete placement at sampling sites. On two occasions at retention pond 3, effluent water samples were collected as pooled water next to the outlet due to there being insufficient rainfall to fill the pond and generate effluent. This approach was considered a fair approximation as the pooled water would be the first to become displaced if sufficient rainfall had occurred.

The rainfall events sampled varied between 1 mm and 34.6 mm ($12.87 \text{ mm} \pm 1.5$), which on average was after $5.14 \text{ mm} \pm 0.6$ of rain, see supporting information A.10.3 for more details. Manual procedural blanks found 0.67 MP/sample and autosamplers 1.3 MP/sample.

Runoff that was collected directly from roads (curve and straight drainage points) and samples that were collected as pond influent are referred to as 'direct runoff' or 'direct drainage' as they have not undergone any form of treatment. Runoff that passed through wetlands and retention ponds and collected at the outlet of the ponds are referred to throughout as effluent.

The following section will present the results from the water samples, focusing initially on TWPs and other microplastics in drainage from curved and straight sections of the SRN and then, assessing the removal efficiency of retention ponds and wetlands. Results from the sediment sampling collected in the wetlands and ponds are also presented. Finally, the characteristics of the other microplastics as well as the potential influence of site and weather characteristics across all sites are considered.

A.5.1. Tyre wear particles and other microplastics in drainage from curved and straight sections of the SRN

A pair of curved and straight outlets was not sampled successfully as per the experimental design (Figure A.1) due to a misconnection or out of date drainage map not permitting the collection of a water sample at location (Supporting Information A10.4, see curve vs. straight site 5).

Direct drainage from curved and straight sections of the road network contained between 0.01 and 3.21 mg/L of TWPs ($0.62 \text{ mg/L} \pm 0.23$). Runoff from curved sections of the road network contained $0.77 \text{ mg/L} \pm 0.38$ of TWPs, overall this was ~40 % higher than found in runoff from straight sections of road at $0.47 \text{ mg/L} \pm 0.37$, but this pattern was not consistent between sites (see Figure A.4), and was not significant overall (ANOVA, $df=1$, $p>0.05$). On average 3.1 other microplastics ± 0.7 ($0.67 - 8.52 \text{ MP/L}$) were released to receiving waters per litre of direct drainage from curved and straight sections of the SRN (Figure A.5). There were no significant differences in emissions between curved and straight road types (ANOVA, $df=1$, $p=>0.05$).

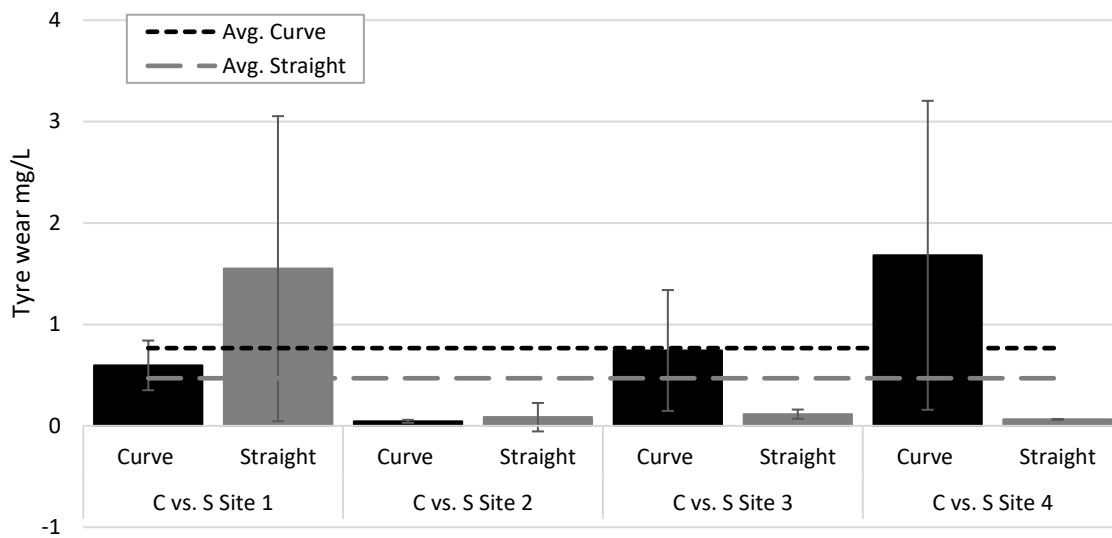


Figure A.4: Concentrations of TWPs mg/L in direct runoff drainage from pairs of curved and straight sections of the SRN over two separate rainfall events. Error bars represent standard error of the sampling events. Dashed lines represent the average concentration across all sites and rainfall events.

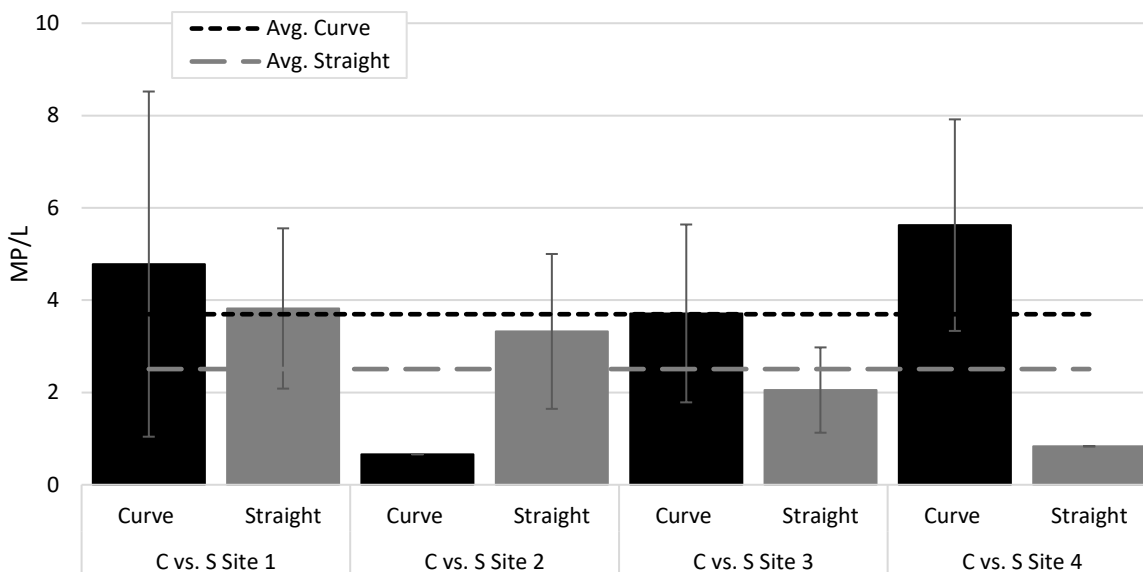


Figure A.5: Concentrations of other microplastics (MP/L) in direct runoff drainage from pairs of curved and straight sections of the SRN over two separate rainfall events. Error bars represent the standard error of the sampling events. Dashed lines represent the average concentration across all sites and rainfall events.

A.5.2. Tyre wear particles and other microplastics in the influent and effluent of retention ponds and wetlands and their removal efficiency

Our sampling compared the concentration of TWPs and other microplastics between the influent and effluent of both wetlands and retention ponds. This resulted in 12 comparisons with three replicate sampling occasions within each. For 10 of these 12 comparisons the highway drainage system assessed led to a reduction in the concentration of TWPs and other microplastics released to waterbodies when compared to the influent. While at wetland 3, the average concentrations of TWPs and other microplastics within the influent was similar to that of the effluent. This was the only site that did not on average lead to a reduction in TWPs and other microplastics (Figure A.6).

On average wetlands removed $72.6 \% \pm 14.5$ of tyre wear (13.6 – 99.7 %). Wetland influent contained on average $5.6 \text{ mg/L} \pm 1.92$ of TWPs and effluent $0.71 \text{ mg/L} \pm 0.38$ (Figure A.6). However, this trend in the concentrations of TWPs was not statistically significant (ANOVA, $df=1$, $p \geq 0.05$).

Retention pond influent contained between 0.17 and 29.8 mg of TWPs per litre (average 4.1 ± 3.22), and effluent contained $0.22 \text{ mg/L} \pm 0.13$ (Figure A.6), removing on average $77.2 \% \pm 7.4$ (38.4 – 99.9 %). This effect was found to be significant (ANOVA, $df=1$, $p < 0.05$).

Removal of other microplastics by both wetlands and retention ponds was highly variable ranging between 0 % and 98.1 % in efficiency. On three occasions, concentrations of microplastics were greater in the effluent leaving the pond than in the influent.

Wetland influent contained between 2.1 and 10.8 other microplastics per litre (5.6 ± 0.9), while each litre of effluent contained between 0.42 and 7.8 microplastics (3 ± 0.8). This effect was not significant ANOVA, $df=1$, $p \geq 0.05$, (Figure A.6). For retention ponds, on average, 6.4 ± 2.3 other microplastics were recorded per litre within influent (between 0.87 – 22.5 MP/L), and 1.6 ± 0.3 recorded per litre within effluent (0.45 – 2.85), Figure A.6. This effect was not significant (ANOVA, $df=1$, $p \geq 0.05$).

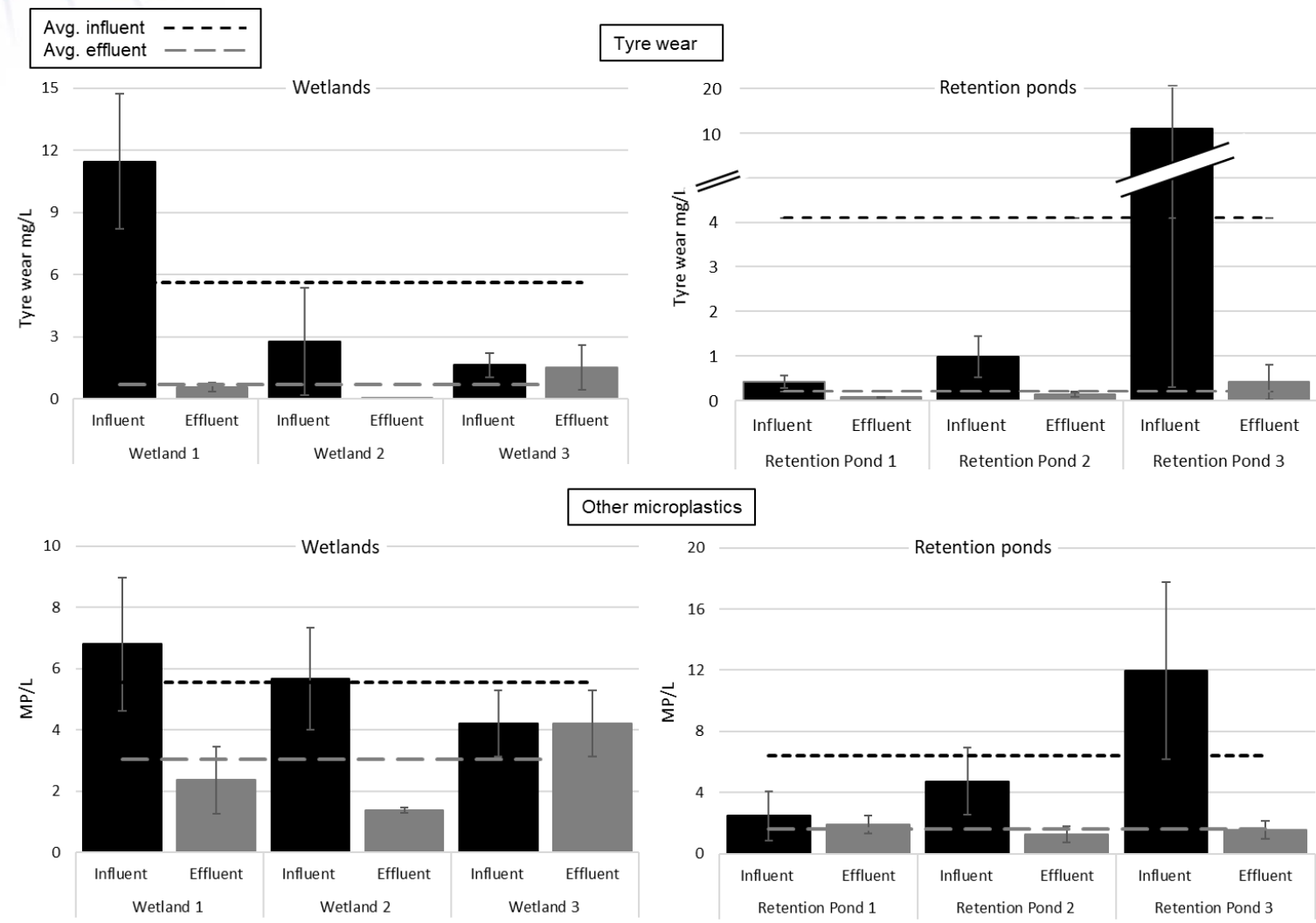


Figure A.6 Concentrations of TWPs (mg/L) and other microplastics (MP/L) in the influent and effluent of three wetlands (left) and three retention ponds (right), averaged over three separate rainfall events. Error bars represent standard error over the three sampling occasions. Dashed lines represent the average concentration across all sites and rainfall events.

A.5.3. Tyre wear particles and other microplastics in wetland and retention pond sediments

Sediments retained by wetlands and retention ponds contained between 0.21 and 11.32 mg of TWPs per gram (d.w.) (Figure A.7). The average concentration was 3.83 mg/g \pm 3.78, far exceeding concentrations recorded in the water samples.

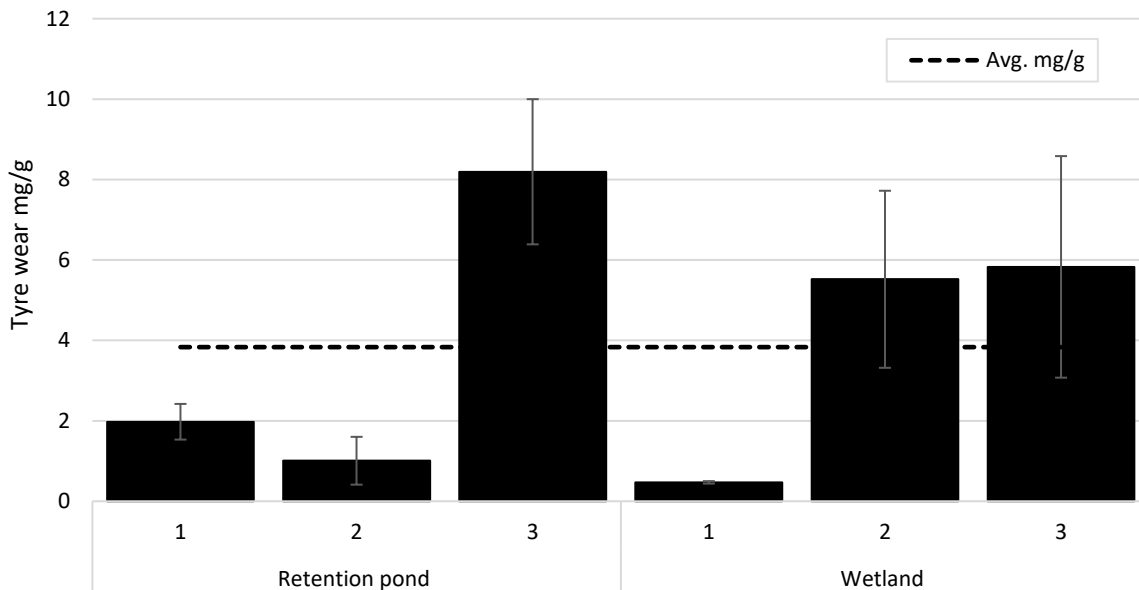


Figure A.7: Concentrations of TWPs mg/g in the sediment from three wetlands and retention ponds, averaged over three separate occasions. Error bars represent standard error of the three sampling events. Dashed lines represent the average concentration across all sites and sampling events.

On average 4.22 \pm 3.84 other microplastics were recovered per gram of dry pond sediment (n=18), Figure A.8. The highest recorded concentration was 14.29 microplastics per gram. On one occasion, no other microplastics were identified.

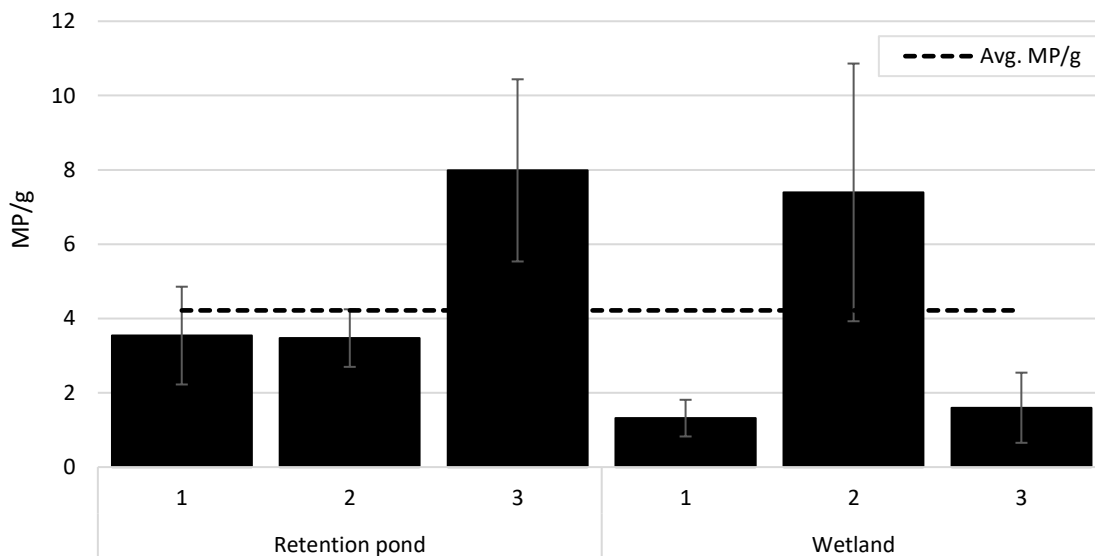


Figure A.8: Concentrations of microplastics MP/g within the sediments of three wetlands and three retention ponds collected over three separate occasions. Error bars represent standard error of the three sampling events. The dashed line represents the average concentration across all sites and sampling events.

The TSS by dry mass in pond influent ranged between 0.02 and 1.82 g/L, on average 0.23 g/L \pm 0.1 and in effluent between 0.012 and 0.231 g/L, average 0.052 g/L \pm 0.016. Retention ponds and wetlands typically removed 56 % \pm 42.5 of TSS prior to discharge to waterways. On one occasion the TSS content increased. The removal rate of TSS at each site largely reflected the removal rate of TWPs. TWPs contributed between 0.081 and 6.14 % of the total solid mass within each sample (average 1.4 % \pm 0.21). The relationship between TWPs and TSS content were significantly correlated ($p=0.000$, F-value 98.75, $df=1$, $R^2 = 86$). Concentrations of other microplastics in direct runoff was also positively correlated with TSS content ($p=0.000$, F-value 28.07, $df=1$, $R^2 = 63.7$).

A.5.4. Characteristics of other microplastics in direct drainage from the SRN

Of the 313 microplastics identified within direct drainage (wetland and retention pond influent and drainage from curved and straight sections of the SRN), the majority of microplastics were fibres and fragments (Figure A.9). The most commonly identified polymers are shown in Figure A.9, all other polymers; acrylic, co-polymers, polyethylene terephthalate (PET), polyvinyl alcohol (PVA), polybutylene terephthalate (PBT), polyethylene (PE), polycarbonate (PC), polystyrene (PS), acrylonitrile butadiene styrene (ABS), styrene-acrylonitrile resin (SAN), and polyphenyl ether represented less than 5 % of the total particles (Figure A.10). The most common colour was blue, followed by black, and red. All other colours accounted for less than 10 % each. At their longest length, particles measured on average 1311 $\mu\text{m} \pm 1847$ ($\bar{x} \pm \sigma_M$), the largest particle was 14000 μm and the smallest 50 μm (Figure A.11).

Of the 93 synthetic particles within effluent from wetland and retention ponds, fibres accounted for the majority, followed by fragments and spheres (Figure A.11). The most common polymers within effluent are shown in Figure A10. PBT, co-polymers, low-density polyethylene (LD PE), and PC all contributed less than 5 % of the total. Blue and black were the most common colours (>70 %), on average particles measured 1788 $\mu\text{m} \pm 2127$, the largest 12500 μm .

Microplastics within pond sediments ($n=103$) measured on average 1475 $\mu\text{m} \pm 2132$. Fibrous particles accounted for 53.7 % of the total, fragments 41.7 % and films 4.6 %. The most common polymers were polyvinyl chloride (PVC), polyester (PES), and polyamide (PA). Blue was the most dominant colour followed by black and red.

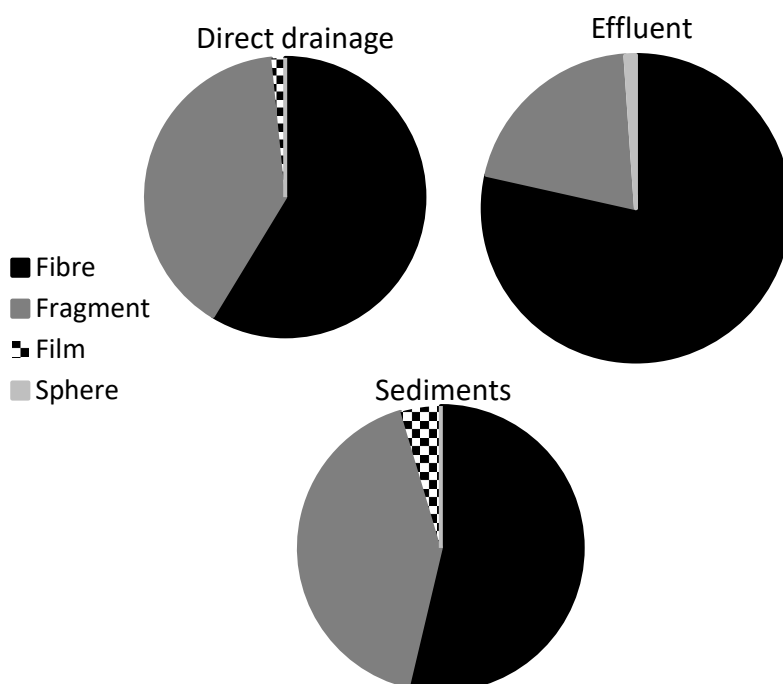


Figure A.9: The percentage of microplastics classified as fibres, fragments, films or spheres within direct runoff, effluent and pond sediments.

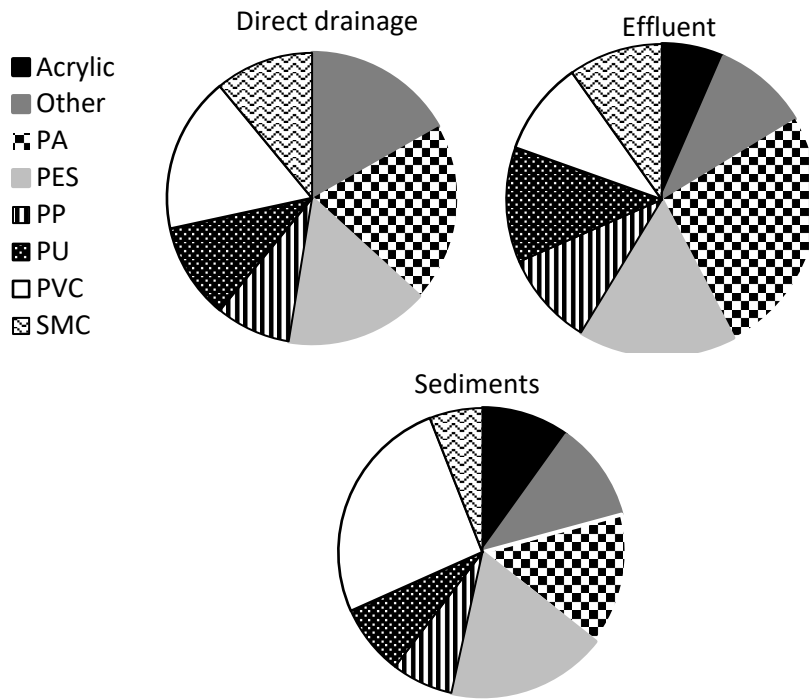


Figure A.10: The percentage of microplastics identified as various polymers within direct runoff, effluent and pond sediments.

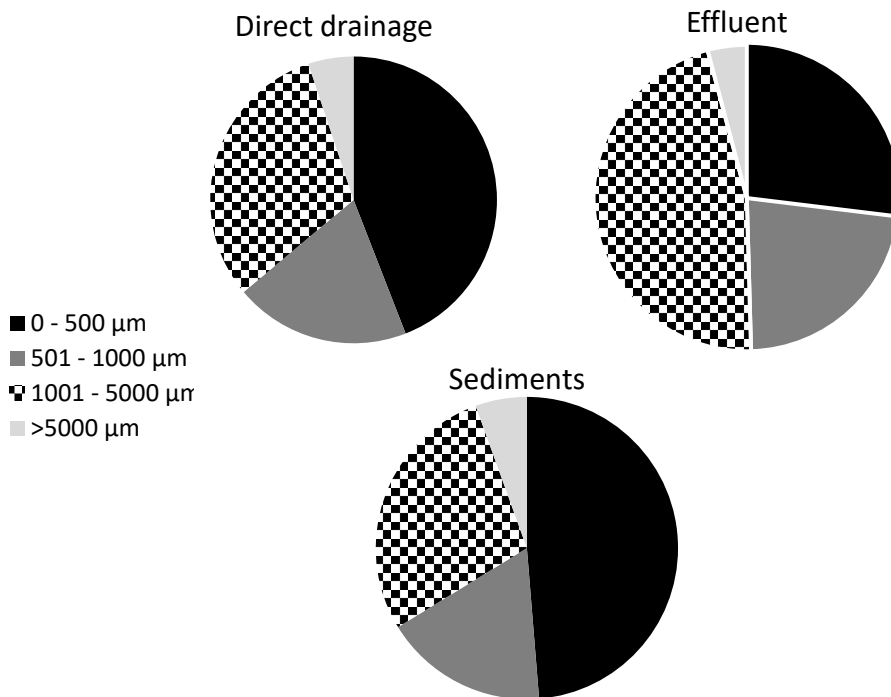


Figure A.11: The percentage of microplastics across various size fractions (measured at their longest length) within direct runoff, effluent and pond sediments.

Of the 1381 particles subject to FTIR analysis 63 % were identified as cellulose, rayon, or viscose which are generated from naturally occurring materials such as wood pulp. However, due to the large number of process and chemicals used in the production of these fibres they are widely considered to be 'semi-synthetic'. It is not readily possible to distinguish natural cellulose from reconstituted cellulose which is considered semi-synthetic. Therefore, these particles were not included in the main body of results or analysis. Of the 872 cellulosic particles, nearly half (47.7 %) were blue, 38.2 % were black and 5.8 % red, while the other colours made up less than 2 % each. Coloured fibres are unlikely to occur in nature and it seems likely that the majority of these cellulosic fibres were semi synthetic in origin.

A.5.5. The influence of site and weather characteristics on tyre wear and other microplastic concentrations in drainage from the SRN

Previous work has suggested a link between antecedent conditions and concentrations of tyre wear particles in drainage from the SRN. Concentrations of TWPs and other microplastics found in this study were positively correlated with the duration of dry antecedent conditions. Dry conditions were considered as days where rainfall did not exceed 2.5 mm/d, the estimated mobilization threshold of TWPs (Brodie, 2007). However, when an outlier (46 days with no rain >2.5 mm/d) was removed this relationship was not significant ($p \geq 0.05$, F-value 0.07, $df=1$, $R^2=0.46$). The same was true for other microplastics ($p \geq 0.05$, F-value 1.79, $df=1$, $R^2=0.04$).

The relationship between tyre wear concentrations in direct road drainage and AADT and catchment area, and tyre wear removal and flow path length and pond surface area were explored, but no significant relationships were found. The same approach was applied to other microplastics, where one significant correlation was observed; microplastic removal increasing with flow path length ($p=0.004$, F-value 11.08, $df=1$, $R^2=40.92$).

A.6. Discussion

TWPs were found to be present in all environmental samples (70/70). Microplastics were present in all but one sample, within sediment from a wetland (69/70). This section will first discuss the results of the water sampling; from direct drainage from curved and straight portions of the SRN, followed by, the efficacy of wetlands and retention ponds for the removal of TWPs and other microplastics.

A.6.1. Tyre wear particles

Concentrations of TWPs reported in this study sat at the lower end of the ranges previously reported in the academic literature. Table A.2, largely adapted from Wik and Dave (2009), compares the range in measured and estimated concentrations of TWPs reported in surface water runoff, motorway pond sediments, motorway pond water and also in freshwater and freshwater sediments across the present and previous studies. Where the study quantified the concentration of a tyre wear marker but did not convert into an estimated mass of TWPs, Wik and Dave (2009) converted using reported concentrations of markers within tyre tread. Studies from Wik and Dave (2009) are marked with an asterisk (*). Direct comparisons between the studies in Table A.2 should be made with caution due to a lack of standardized approaches, the variety of markers employed and potential sources of chemical markers to the environment other than tyre tread.

Table A.2: Comparisons of concentrations of tyre wear in the present study compared with that reported in previous studies. Data presented as averages; ranges are given in brackets where available. Data largely adapted from Wik and Dave (2009) showing measured and estimated concentrations of TWPs in surface water runoff, motorway pond and sediment basin sediments, settling pond water, river water and sediments, using a variety of chemical markers. BT = benzothiazole, 24MoBT = 2-(4-morpholinyl)benzothiazole, NCBA = N-cyclohexyl-2-benzothiazolamine, Zn = zinc, HOBT = 2-hydroxybenzothiazole.

Environmental matrix	Concentration	Marker	Region	Study	
Water	Surface water runoff [mg/L]	2.5	BT	UK	Parker-Jurd <i>et al.</i> (2021)
		2.8 (0.01 - 28.9)	BT	UK	This study
		12	24MoBT	Japan	*Kumata <i>et al.</i> (2002)
		87	HOBT	USA	*Reddy and Quinn (1997)
		92	24MoBT	USA	*Zeng <i>et al.</i> (2004)
		93	24MoBT	Japan	*Kumata <i>et al.</i> (1997)
		97	BT	Germany	*Baumann and Ismeier (1998)
		179	24MoBT	Japan	*Kumata <i>et al.</i> (2002)
	Motorway drainage pond water [mg/L]	2.3	24MoBT	USA	*Reddy and Quinn (1997)
		0.46 (0.01 - 3.6)	BT	UK	This study
River water [mg/L]	0.5	24MoBT	China	*Ni <i>et al.</i> (2008)	
	1.6	24MoBT	USA	*Reddy and Quinn (1997)	
	3.6	NCBA	Japan	*Kumata <i>et al.</i> (2000)	
Sediment	Motorway drainage pond sediments [mg/g]	0.35	24MoBT	USA	*Reddy and Quinn (1997)
		3.7 - 20 mg/g	Zn	Germany	Klößner <i>et al.</i> (2020)
		3.8 (0.2 - 12.5)	BT	UK	This study
	(motorway sediment basin)	360 - 480 mg/g	Zn	Germany	Klößner <i>et al.</i> (2020)
	Sediments (river, lake estuary) [mg/g]	0.4	HOBT	USA	*Reddy and Quinn (1997)
		3.9	24MoBT	Japan	*Kumata <i>et al.</i> (2002)
		11	Extr. Org. Zn	Sweden	*Wik <i>et al.</i> (2008)
		155	24MoBT	USA	*Spies <i>et al.</i> (1987)
		40	Zn	Germany	Klößner <i>et al.</i> (2020)

A.6.2. Do concentrations of tyre wear particles differ in direct drainage from curved and straight sections of the SRN?

Driving behaviour (braking, accelerating and cornering) have all been reported as being factors influencing the generation of tyre wear particles (Dannis, 1974; Council *et al.*, 2004; Knight *et al.*, 2020; Mengistu *et al.*, 2021 *et al.*). Dannis (1974) reported an average tread wear rate of 0.09 g/km, ranging from 0.024 g/km when cruising at 75 mph, but this could reach as high as 0.49 g/km when cornering at 30 mph at a 2-degree slip angle. This was also evidenced by Knight *et al.* (2020) who reported larger size, and a greater abundance of TWPs in roadside drain sumps located on roads subject to frequent braking and accelerating compared with straight roads even when carrying high traffic loads. In the present study the mass of TWPs was on average 40 % greater in drainage from curved sections of the SRN compared with straight sections, but this pattern was not statistically significant. Notably in only one of the four paired drainage sites, the tyre wear concentration was consistently higher at one site than the other.

In road runoff, TWPs have previously been quantified in the range of 2.5 – 179 mg L⁻¹ (Kumata *et al.*, 1997; Reddy and Quinn, 1997; Baumann and Ismeier, 1998; Kumata *et al.*, 2000; Kumata *et al.*, 2002; Zeng *et al.*, 2004; Wik and Dave, 2009; Parker-Jurd *et al.*, 2021). This study reports concentrations in direct runoff, from influent of ponds and curved and straights sections of the road

network to be generally lower (0.01 – 28.9 mg/L) but in the same orders of magnitude as the previous studies (Table A.2). Lower concentrations may be attributable to differences in analytical approach, climatic conditions, and notably in traffic volumes and density or urban environments in places such as the USA and Japan being higher than the sites sampled here.

Concentrations of tyre wear previously reported in rivers are not directly comparable with samples collected here as road drainage will be substantially diluted as it mixes with river water. However previous reports of tyre wear in river water range between 0.5 and 3.6 mg/L (Reddy and Quinn, 1997; Kumata *et al.*, 2000; Ni *et al.*, 2008; Wik and Dave, 2009), some of which exceed concentrations reported in pond effluent and direct drainage from curved and straight sections of road in the present study (Table A.2). The three previous studies in question collected water samples from underneath a major trunk road (in the Pawtuxet River, Rhode Island), from central Tokyo in a metropolitan region described as one of the most urbanised areas in the world (Kumata *et al.*, 2000), and from the Pearl River Delta, one of the most populated and developed areas in China (Ni *et al.*, 2008). The location of these sampling campaigns may explain the higher concentrations than reported in the present study.

A.6.3. The effectiveness of retention ponds and wetlands at removing tyre wear particles

Comparing the concentrations of TWPs in the influent and effluent of both retention ponds and wetlands led on most occasions to a reduction in TWP loading (Figure A.7). However, some sites (notably wetland 3 and retention pond 3) deviated from the average considerably. Retention pond 3 had a far higher TWP loading within pond influent, and no effect in concentrations of TWPs was observed between the influent and effluent. While both retention ponds and wetlands appear to offer considerable potential to trap both TWPs and other microplastics the results obtained here indicate considerable between-site variability. Hence further sampling would be advisable to better understand the main factors causing this variability in order to guide the placement and design of wetlands and, to a lesser extent, retention ponds.

Wetland 3 had the lowest and most inconsistent retention efficiency at $26 \% \pm 32$. It had the smallest surface area and the shortest flow path of the six ponds examined (Section A.10.4), resulting in a very short residence time which perhaps did not allow for effective removal of TWPs from suspension. On one occasion, the mass of TWPs was higher in the effluent than the influent at this site. This may be further attributable to the resuspension of previously settled TWPs during intense rainfall events, which in a dry pond (Wetland 3, does not typically hold water) will occur more readily. Due to space and infrastructure constraints, the inlet and outlets of ponds may not be located at the maximum distance apart. Of the six ponds sampled, flow paths ranged between ~15 and 220 m and only one had an outlet at the furthest possible distance from the inlet, (see Section A.10.4). Wetland 2 had on average the highest retention rate of tyre wear ($98.5 \% \pm 0.9$) and performed the most consistently. Wetland 2 had the longest flow path and the second largest surface area (after retention pond 3). However, no correlation was observed between TWP removal between pond surface area or flow path.

The National Highways Design Manual for Roads and Bridges dictates that assets such as retention ponds and wetlands are maintained on 5 or 10-year cycles where they will be de-silted, though partial de-silting may occur at a greater frequency in some cases. In the past removed material was de-watered and treated, but would now be disposed of as hazardous waste. The same principle applies for roadside gullies, but due to their smaller capacity these are maintained on a more regular basis (annually), or at a greater frequency if known to fill quickly. However, most regions have adjusted to maintain assets as and when required to be determined by inspection (reactive maintenance), which may result in drainage assets such as ponds going longer than the recommended period without maintenance.

More regular de-silting of gullies and ponds would potentially see an improvement in retention rates of TWPs, particularly in gullies which will fill quicker than ponds before reaching capacity.

According to the National Highways 'Design of highway drainage systems' (National Highways, 2022) retention ponds and wetlands are estimated to remove 60 % of TSS. This was accurately

reflected in the present study where the 6 ponds examined removed on average 56 % of TSS, not dissimilar from the rate of TWPs removal efficiency (~75 %). On one occasion the TSS content was greater in the effluent than influent (retention pond 3 on 13/02/2022). On this date organic matter such as reeds and algae was observed to be blocking the outlet and these items were likely dislodged and released into the effluent when pond levels rose following heavy rainfall. The transport processes affecting microplastics have previously been thought to be similar to those of TSS. Therefore, it has been proposed TSS modelling can be used to predict microplastic transport in systems such as attenuation ponds (Smyth *et al.*, 2021). This study provides evidence that this may be possible for TWPs but is less accurate for other forms of microplastics such as fibres and fragments which were less effectively removed.

Density is an important factor in determining the fate and transport of particles in aquatic environments. The density of TWPs is variable (~1.2 - 2.5 g cm³) partly due to their complex and numerous chemical formulations, but largely attributable to the variable mineral incrustation of road wear and other materials (Verschoor *et al.*, 2016; Sommer *et al.*, 2018; Vogeslang *et al.*, 2018; Unice *et al.*, 2019). A study by Parker-Jurd *et al.* (2021) conducted laboratory based settling experiments and estimated TWPs ranging in size between 4 and 350 µm to have a settling velocity somewhere between 0.00001 and 0.1 m/s. It also observed around 15 % of TWPs to remain in suspension in fresh water (with no turbulence) after a period of one week. With an average retention of ~75 % over the six ponds examined, this study was agreeable with previous findings. Particles that exited the settling ponds within effluent likely had insufficient time to settle, reached the ponds via atmospheric deposition, or were resuspended due to mixing of waters and disturbance of sediments during rainfall. The density of polymers of other microplastics observed in this study ranged between 0.90 and 1.43 g cm³, typically lower than TWPs. Previous studies have estimated the settling velocities of other microplastics to be at the slower end of the estimated settling rate of TWPs. Elagami *et al.* (2022) examined the settling velocities of PS, PA and PVC as fragments to range between about 0.0003 and 0.05 m/s, with settling rate slowing with particle diameter. While Nguyen *et al.* (2022) examined the settling velocity of polyester fibres to range between 0.0001 and 0.00055 m/s.

Reddy and Quinn (1997) reported TWPs in water collected in a motorway settling pond at a concentration of 2.3 mg/L. In the absence of previous estimates of TWPs exiting roadside drainage ponds this is most comparable to effluent pond samples collected during this study as this water is the first to become displaced as effluent during the onset of a rainfall event and falls well within the ranges reported here 0.01 – 3.6 mg/L (Table A.2).

Pond sediments contained on average 3,833 mg/kg of TWPs, equivalent to 3,833 mg/L, several orders of magnitude greater than found in the influent. This provides further evidence that highway drainage ponds are effective at capturing tyre wear. Concentrations found in pond sediments were agreeable with previous studies, aside from Klöckner *et al.* (2020) who reported concentrations far higher within a motorway sediment basin. The motorway sediment pond sampled was positioned ahead of a wetland and therefore may intercept much of the pollutant load before the runoff is discharged to the wetland. Of the six ponds studied, four had either oil separators or pollution control tanks (Section A10.4), large under and over ground tanks designed to intercept oils and sediments prior to the water being discharged to the ponds, ahead of the pond inlets while wetlands 2 and 3 had catchpits. Catchpits are small underground drain gullies with sumps designed to intercept silt and solids to prevent pipe blockage but are much smaller in capacity and consequently have a shorter retention period, therefore the likelihood of sediment being intercepted particularly at high flow speeds is lower. Likewise, if either pollution control tanks or oil separators are not maintained on a regular basis, they may be rendered ineffective when they reach capacity.

Reports of TWPs in fresh and estuarine sediments by Spies *et al.* (1987), Reddy and Quinn (1997), Kumata *et al.* (2002) and Klöckner *et al.* (2020) (Table A.2) are not directly comparable to those collected here but serve an interesting comparison as they were reported in similar orders of magnitude and in some cases exceed those reported here. These studies however collected samples from areas that are far more heavily populated and urbanised than those sampled here

e.g. San Francisco bay, Nogawa river in central Tokyo (Kumata *et al.*, 2002), and from Lake Tegel in Berlin.

TWPs are reported to measure as little as 0.01 µm, and up to ~ 350 µm (Cadle and Williams, 1978; Dahl *et al.*, 2006; Kreider *et al.*, 2010). Coarser TWPs are thought to be more effectively retained in gully pots and channels compared with the finer fraction (Baensch-Baltruschat *et al.*, 2020) which have also been observed to be greater in abundance and are suspected to be more harmful (Wik and Dave, 2009). During sampling (and site visits by National Highways employees), observations were made that organisms including ducks, deer, frogs, invertebrates and other insects, and even protected species such as great crested newts (*Triturus cristatus*) were living or utilising retention ponds and wetlands. While these ponds may not reflect environmental concentrations across common habitats, their use by an array of organisms suggests they may provide isolated opportunities for high levels of exposure. As is their primary role, they do provide protection to habitats downstream.

A.6.4. The influence of weather and site characteristics on concentrations of tyre wear in drainage from the SRN

Although short of significance, a positive correlation was observed between TWP emissions and antecedent weather conditions prior to sampling, agreeable with previous reports of TWPs accumulating during periods of dry weather and being transported at higher concentrations during storm events (Su *et al.*, 2020). Looking more broadly at the climate, the South West experiences warm and wet summers and mild and wet winters. Rainfall events are common due to varying altitudes, but primarily due to its strong maritime influence (Met Office, 2016a) which also helps regulate the temperature compared with more sheltered regions like the Midlands, where the temperature fluctuates more readily and to greater extremes (Met Office, 2016b). The more frequent wet weather events in the Southwest may produce a more chronic pattern of TWP release compared to the Midlands where the discharges may be less frequent but more intense due to longer periods of accumulation. This was observed at retention pond 3 where the highest recorded concentration across the entire study (28.9 mg/L) followed a period of 15 days with no rain and 46 days with no rainfall events >2.5 mm/d (Section A10.3). Wetter road conditions in the South West may also mitigate tyre wear as friction at the tyre-road interface will be lessened during wet conditions. The effects of antecedent conditions may have been better observed with a greater number of samples, or sampling following a greater variety of antecedent conditions.

While some factors such as the impermeable catchment area, flow path and pond surface area will stay consistent between sampling events, other factors such as how full the ponds were prior to the sampled rainfall event, the intensity and duration of rainfall, the traffic volume, the season, and antecedent conditions were variable. Concentrations of TWPs draining from pairs of curved and straight portions of the SRN was not consistently higher at one site across the two rainfall events sampled. This indicates that factors other than those that remain consistent were responsible for the more polluted site varying between sampling occasions, these could include possible congestion occurring at one pair but not the other, very localised variations in rainfall intensity, or in the time taken moving between the paired sites (~15 minutes) not allowing capture of the same point in the pollution load of the rainfall event.

While previously reports have suggested a link between traffic density and tyre wear, no correlation was observed here. Some sites took drainage from portions of adjacent roads and from slip roads where AADT is not reported, for example retention pond 1 and 3 and wetland 2 and 3 (see site cards in supporting information B10.4). In the case of wetland 2 the AADT for that stretch of the M1 is approximately 100,000 vehicles a day, however the AADT for the slip road, which makes up a large portion of the estimated drainage catchment area at that site, is likely to be much lower. In addition, the AADT was reported as an average for the year where seasonal variations in traffic densities likely occur. Instances such as these as may mask the influence of AADT on tyre wear in drainage from the SRN.

A.6.5. Other microplastics

Concentrations of other microplastics in this study within stormwater direct from roads, as wetland and retention pond influent, drainage pond effluent and within drainage pond sediments are largely comparable with existing data, see Table A.3. It is worth noting that these studies will vary in their sample collection, their means of isolating and analysing particles and in their detection limits, therefore it is not appropriate to directly compare reported concentrations. Variations in the abundance of microplastics across all these studies will also vary with population and other characteristics of the drainage area and river catchments.

Table A.3 Comparisons of concentrations of other microplastics found within present study with existing literature.

Environmental matrix	Concentration	Region	Study
Drainage pond influent [MP/L]			
(Bioretention basin)	0.8	USA	Boni <i>et al.</i> (2022)
(Wetland)	0.9	Australia	Ziajahromi <i>et al.</i> (2020)
(Rain garden)	1.6	USA	Gilbreath <i>et al.</i> (2019)
	1.9	USA	Werbowski <i>et al.</i> (2021)
	5.98 (0.87 - 22.5)	UK	This study
Motorway pond effluent [MP/L]			
(rain garden)	0.16	USA	Gilbreath <i>et al.</i> (2019)
(Rain garden)	0.7	USA	Werbowski <i>et al.</i> (2021)
	2.32 (0.42 - 7.83)	UK	This study
(Wetland)	4	Australia	Ziajahromi <i>et al.</i> (2020)
(Retention pond, collected during dry weather)	270	Denmark	Olesen <i>et al.</i> (2019)
Stormwater runoff [MP/L]			
	0.3 - 0.37	USA	Boni <i>et al.</i> (2022)
	3.1 (0.66 - 8.52)	UK	This study
	12 to 2054	Mexico	Piñon-Colin <i>et al.</i> 2020
Stormwater sampled after mixing with receiving waters [MP/L]			
	1.1 - 24.6	USA	Werbowski <i>et al.</i> (2021)
	2.3 - 29.4	Canada	Grbić <i>et al.</i> (2020)
Pond sediments [MP/kg]			
	320 - 595	Australia	Ziajahromi <i>et al.</i> (2020)
	4220 (0 - 14290)	UK	This study
	17490 (1511 - 127,986)	Denmark	Liu <i>et al.</i> (2019)

A.6.6. Do concentrations of other microplastics differ in drainage from curved and straight sections of the SRN

We had no hypothesis relating to concentrations of microplastics in drainage between curved vs. straight portions of the SRN, and no patterns were observed. Concentrations of microplastics found within direct drainage from curved and straight portions of the SRN sat directly between previous reports by Boni *et al.* (2022) in the USA and Piñon-Colin *et al.* (2020) in Mexico (Table A.3) who sampled drainage directly from stormwater outfalls. Concentrations found by Piñon-Colin *et al.* (2020) at the highest end of the spectrum were attributed to grey or industrial water being connected to highway drainage systems. It is rare, but possible in the UK that drainage assets can take grey water, but this was not thought to occur at any of the sites sampled here. A handful of other studies have reported concentrations of microplastics in rivers that are fed by stormwater. In Toronto, Canada, concentrations were reported between 2.3–29.4 particles L⁻¹ in stormwater runoff collected from urban rivers (average 15.4 microparticles/L ± 7.9) (Grbić *et al.*, 2020). Werbowski *et al.* (2021) quantified anthropogenic particles in tributaries around San Francisco Bay that were fed by stormwater drainage outlets. While concentrations are similar to those reported here, it included particles described as ‘rubbery fragments’, likely originating from tyre wear which

were largely identified by visual means in addition to other microplastics. However, it also only quantified particles larger than 106 µm, and employed a density separation step where some materials may be lost. The stormwater was also diluted due to the mixing with tributary water which may compensate for the inclusion of suspect TWPs.

A.6.7. The effectiveness of retention ponds and wetlands at removing other microplastics

A handful of studies (Gilbreath *et al.*, 2019; Ziajahromi *et al.*, 2020; Werbowski *et al.* 2021) have previously quantified microplastics in roadside ponds, in both the influent and effluent of wetlands and rain gardens. In a rain garden Gilbreath *et al.* (2019) reported a microplastic retention of 96 % and Werbowski *et al.* (2021) around 60 %. However, Ziajahromi *et al.* (2020) reported the opposite, an increase of around 80 % between the inlet and outlet of a wetland (Table A.3). This variability reflects findings from this study with inconsistent removal of microplastics from highway drainage ponds. This is likely due to input sources other than runoff. With large exposed surface areas, these ponds will accumulate particles by atmospheric deposition which has been evidenced to pollute even remote environments with low footfalls (e.g. Allen *et al.*, 2019; Stanton *et al.*, 2019; Napper *et al.*, 2020; Napper and Parker-Jurd *et al.*, 2022). Boni *et al.* (2022) also quantified microplastics at the inlet of a roadside drainage pond (a bioretention basin), at concentrations around 0.8 MP/L but did not report microplastics in the effluent to allow calculation of removal efficiency. Olesen *et al.* (2019) sampled water from a motorway pond in Denmark during dry weather conditions and reported concentrations far higher than reported here or in previous studies at 270 MP/L (Table A.3). This type of drainage most closely resembles the effluent samples collected in this study as it has been subject to a settling period and will become discharged as effluent once a rainfall event occurs. The retention pond sampled by Olesen *et al.* (2019) is described as taking drainage from areas including retail and car parks, which likely correlate to increased footfall. Therefore, the samples may be subject to higher levels of contamination from atmospheric pollution compared this study where the drainage points were located in remote and sparsely populated locations.

One or two studies have previously quantified microplastic concentrations in motorway pond sediments (Table A.3). Ziajahromi *et al.* (2020) collected sediment near the inlet and outlet of constructed floating wetlands in Australia reporting concentrations to range between 320 and 595 particles/kg respectively, lower than reported here. While Liu *et al.* (2019) quantified microplastics in a motorway retention pond in Denmark far higher than this study at 17,490 items/kg. Interestingly, sediment concentrations found in this study are similar to previous reports in freshwater sediments e.g. from lakes in the UK (539 particles/kg, Tuner *et al.*, 2019) and in China at 388 – 502 particles kg (Jiang *et al.*, 2018). While more diluted, freshwater lakes may be sensitive to a greater variety of diffuse and point input sources and act as an accumulation zone.

A.6.8. The influence of weather and site characteristics on concentrations of microplastics in drainage from the SRN

Antecedent conditions were observed to correlate with concentrations of microplastics in direct drainage from the SRN. This suggests that like TWPs and other particles present on the road surface, other forms of microplastics also accumulate during periods of dry weather and are mobilised and transported during rainfall events where they are discharged into highway drainage treatment systems and into waterways.

Although microplastics concentrations in drainage from the SRN may relate to varying traffic loads where microplastics can originate from fragmentation of intentional or unintentional littering of road users or escape of fibres from passengers in vehicles from car windows, no correlation was observed between AADT and microplastic concentrations in direct drainage.

A.6.9. Characteristics of other microplastics within drainage from the SRN

The polymers most commonly identified were similar across direct drainage, in pond effluent and pond sediments samples (Figure A.10). However, the diversity of polymers in the pond effluent and sediments was lower than reported in the direct runoff.

Previous studies have also reported a variety of polymers within in fresh waters fed directly by stormwater outfalls. Aside from sheet moulding compound (SMC) the most commonly identified polymers in direct drainage were polypropylene (PP), PET, PA, acrylic, co-polymers, PES, PU, agreeable with previous findings (Grbić *et al.*, 2020; Werbroski *et al.*, 2021; Boni *et al.*, 2022). While some studies choose to combine polyester and polyester PET, this study chose to separate the two given that polyester fibres likely originate from a different source (i.e. textiles) than polyester PET fragments (i.e. food and drink packaging).

Likewise, the common polymers found within effluent (Figure A.10) were largely agreeable with those found in previous studies by Olesen *et al.* (2019) in pond effluent (PP) and Werbowski *et al.* (2021) in rain garden effluent (PES/PET followed by PE, acrylic and polyacrylamide).

In drainage pond sediments, Liu *et al.* (2019) reported the most abundant polymers to be PP followed by PA -> PES-> PE-> PS-> polyurethane (PU) -> acrylic -> and PVC, very similar to the common polymers reported here (Figure A.10). Liu *et al.* (2019) concluded that the presence of low-density polymers in sediments indicated that density was not the only factor in determining microplastic sedimentation. It is also possible that some of the microplastics recovered from the sediment did not fall out of suspension but became 'beached' when water levels dropped.

While fibres were the dominant form of other microplastics, fragments represented around 40 % of the particles within direct runoff from the SRN (Figure A.9). A study conducted in the same region as the majority of sites in the present study, non-tidal freshwaters in Devon and Cornwall, found fragments contribute on average only half as much to the total (20%, collected between 2020 – 2022 (personal communication)), further indicating that the breakdown of intentional or unintentional litter on highways contributes to microplastic loads from the SRN.

The polymers identified across this study have a wide range of applications, some of which are unlikely to reach the SRN or highway drainage systems. Sources that do have the potential to reach these locations may come from atmospheric pollution (i.e. fibres most commonly from textiles), or the breakdown of macro waste (by passing vehicles) by the side and central reservations of roads which are challenging, expensive, and potentially dangerous to clear. This can come from both intentional littering and unintentional littering such as broken car parts or mismanaged waste. Waste could potentially also originate from neighbouring land (e.g. agricultural waste).

Of the non-fibrous particles most were identified as PVC followed by PP, PU, and PA. While PA is used primarily for textiles it is also used in food and beverage packing, and in the automotive industry for engine covers, handles, wheel covers, fuel caps and lids (AEROUSA, 2022). Likewise, polyester PET is used most commonly in food and drink packaging but is also used for moulded car parts and for linings and seat covers (SpecialChem, 2022b). PU is utilised in a variety of applications including textiles, building and construction, electronics, medical, packaging but also in automotive applications for bumpers, car body parts, doors and windows, and for interior uses including foam PU for car seats. Similarly, PP is used in flexible and rigid packaging, but also for vehicle bumpers, door trims and interior trim (SpecialChem, 2022c). Unplasticised PVC or PVC-U, is used in construction as well as drainage systems and interior and exterior automotive parts (Turner and Filella, 2021).

Some polymers that are not commonly reported in environmental samples but were found in the present study to have applications in the automotive and packaging industries, see Table A.4. These polymers are less commonly reported in environmental samples, possibly attributable to materials such as SMC, which is a reinforced polyester, being counted as 'polyester', or these materials not being present in the spectral libraries used. Given their application in the automotive or packaging industries it's also likely their presence is attributable to collecting samples close to the source, compared to river or sea samples which have a much higher diversity of inputs. For

example, Liu *et al.* (2019) quantified microplastics in roadside drainage pond sediments in Denmark and also reported particles as Acrylonitrile Butadiene Styrene (ABS) and Styrene Acrylonitrile copolymer (SAN).

Table A.4 Uses of polymers less commonly reported in environmental samples within the automotive industry.

Polymer	Abbreviation	Uses relating to automotive industry	Reference
Polyurethane RIM	PU RIM	Manufacture of vehicle bumpers.	Rapitypes (2022)
Sheet moulding compound	SMC	Composite material widely used in automotive industry including body panels.	Brooks (2000)
Acrylonitrile Butadiene Styrene	ABS	Automotive body parts, wheel covers, door handles, door trim (exterior), navigation system housing (interior).	McKeen (2010)
Styrene Acrylonitrile copolymer	SAN	Ridged, heat resistant, thermal stable & and chemically resistant material used for used in automotive applications, consumer goods and packaging.	S&P Global (2022)
Polybutylene terephthalate	PBT	Windshield wiper covers, mirror housing (exterior), fuse boxes, ignition system components (interior).	SpecialChem (2022a)

It could be hypothesised that many of the 872 particles identified by FTIR analysis such as rayon, viscose, or cellulose, particularly when they are not naturally occurring colours, are anthropogenically altered and should be considered semi synthetic. Furthermore, blue was by far the dominant colour of cellulosic fibres which is the UK's most popular garment colour (Jordan, 2015).

Microplastics in pond effluent measured on average slightly larger and contained a slightly greater proportion of larger particles (1001 – 5000 μm) to smaller particles (0 – 500 μm) than the influent and sediments, as shown in Figure A.11. However, with such large variability in particle size it is difficult to draw conclusions in terms of which size of particles were more effectively removed from suspension. Furthermore, particles found in the sediment may represent particles that have become 'beached' when water levels dropped, or were deposited from the atmosphere, rather than solely ones which have become sedimented. Grbić *et al.* (2020) found particles recovered from rivers fed by stormwater to be smaller than in the present study at 900 $\mu\text{m} \pm 900 \mu\text{m}$ but these were also highly variable. In drainage pond sediment Liu *et al.* (2019) reported the majority of particles to measure between 10 – 50 μm . In the current study no particle recovered from pond sediments measured less than 100 μm at their longest length.

The ratio of fibres to fragments in direct drainage and pond sediments was higher than in effluent suggesting fragments are more readily removed from suspension compared to fibres (Figure A.9). In the influent of a rain garden Werbowski *et al.* (2021) reported similar ratios of particle morphologies at; 53 % fibres, 19 % firm fragments, 5 % rubbery fragments, or suspect TWPs, with a much higher proportion of fibres in the effluent (86 % fibres, and 14 % fragments). The higher proportion of fibres within roadside drainage pond effluent is likely attributable to the surface area to volume ratio of fibres which typically results in a slow settling velocity. Furthermore, fibres are a common form of microplastic contamination in atmospheric deposition (Stanton *et al.*, 2019; Napper and Parker-Jurd *et al.*, 2022) which may contribute to the increased ratio of fibres to other forms of plastic in the pond effluent.

A study by Parker-Jurd *et al.* (2020) quantified atmospheric fallout of synthetic fibres in four locations in the UK adjacent to the SRN (up to 50 m from the roadside) and reported an atmospheric deposition rate between 0 – 56.5 fibres m² d⁻¹ (\bar{x} = 24 m² d⁻¹). The approximate surface of the six ponds surveyed here ranged between 517 and 2,227 m² (1270 ± 672 m², \bar{x} ± σ). This could equate to somewhere in the range of 15,000 - 50,000 synthetic fibres being deposited on the surface of each pond daily. These fibres may have been transported from more densely populated areas, originate from local sources such as the occasional walker or farmers, or out of car windows. Even particles that may have settled on the roadside could be mobilised and reach the ponds surfaces in windy conditions. Inputs of TWPs from atmospheric deposition will also be occurring, previously shown in the range of 3.92 – 97.04 mg m² d⁻¹ in areas beside arterial roads (Parker-Jurd *et al.*, 2021), potentially equating to 2,500 to 215,000 mg of TWPs a day reaching each pond surface daily.

A.6.10. The relative importance of tyre wear vs. ‘other’ microplastics

Quantifying TWPs by mass and other forms of microplastics by abundance makes direct comparisons about the relative importance of each challenging. In order to draw a conclusion about whether TWPs or microplastics discharging from the SRN are more prevalent, microplastic concentrations were converted from abundance (MP/L) to an estimated mass (~mg/L), see Section A10.5 for full details. This calculation was based upon a number of assumptions; therefore any direct comparisons should be treated as an estimation.

On average the mass of tyre wear determined from Py-GC-MS analysis was considerably greater than the estimated mass of other microplastics in both direct runoff from the SRN and in motorway pond sediments. This agrees with desk-based estimates (Sundt *et al.*, 2014; Essel *et al.*, 2015; Lassen *et al.*, 2015; Magnusson *et al.*, 2016; Boucher and Friot, 2017; Eunomia, 2018) which suggest TWPs contribute a substantial portion of microplastic emissions to the natural environment. It is also in agreement with a previous field study by Parker-Jurd *et al.* (2020) who quantified tyre wear and synthetic fibres at principal pathways to the marine environment, wastewater treatment, surface water drainage, and atmospheric deposition and reported the presence of TWPs to be greater than that of synthetic fibres.

However, after passing via wetlands and retention ponds, the mass of both TWPs and other forms of microplastics being released to aquatic waters in pond effluent were similar, furthering evidencing TWPs were more readily removed than other forms of microplastics (see Figure A.12).

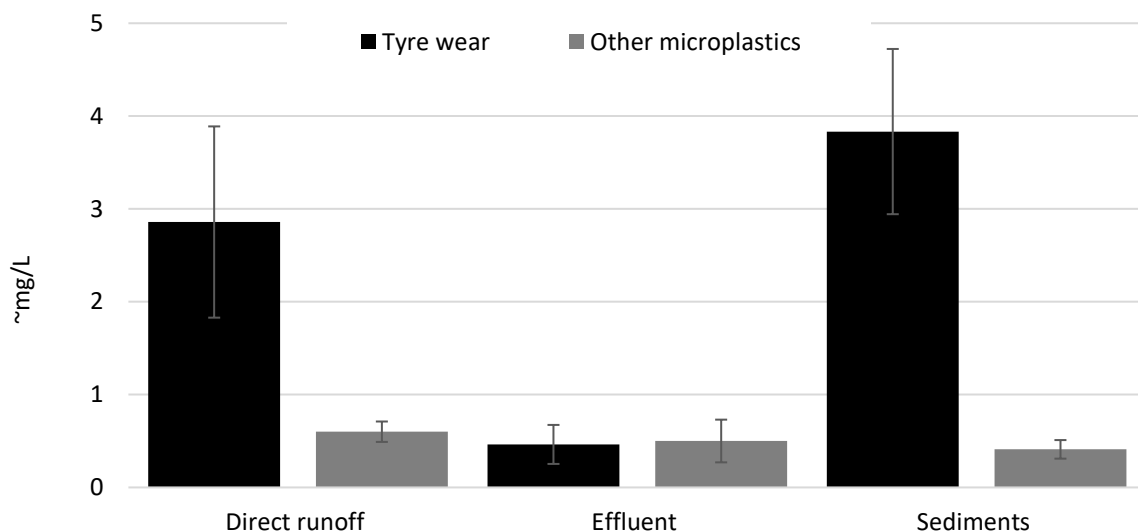


Figure A.12: The relative mass of tyre wear (mg/L or mg/g) vs. the estimated relative mass of other microplastics (mg/L or mg/g) within direct drainage, pond effluent and pond sediments.

A.7. Potential study limitations

In addition to water flow from the impermeable road surface, highway drains also receive water from the permeable or natural catchment such as agricultural land, roadside verges, or in some instances misconnected grey water. This dilution by natural flow could therefore introduce variability to the comparison in the emissions of TWPs per litre of effluent from curved and straight sections of the road network as well as the particle removal rate of highway drainage systems. A thorough examination of the contribution of natural flow, i.e. quantifying natural flow across a range of weather and antecedent conditions could help account for this dilution during further study.

While efforts were in place to minimise contamination, some may originate from the field and laboratory procedures. The total number of microplastics found in environmental samples was on average 7.2 ± 0.8 microplastics per sample, higher than found in the procedural blanks from manual sampling which on average contributed $0.33 \text{ MP/sample} \pm 0.33$ and from sampling with the aid of autosamplers ($1.3 \text{ MP/sample} \pm 0.33$).

Despite water samples for microplastic analysis being filtered down to $1.6 \mu\text{m}$, the limit of detection when using the FTIR is between $10 - 20 \mu\text{m}$, some microplastics therefore could be present within the sample without detection.

The study aimed to conduct all water sampling following antecedent dry periods of at least 24 to 48 hours but in some instances, largely attributable to unpredictable weather forecasting, some rainfall did occur within this time frame prior to sampling, see supporting information in A10.3.

Furthermore, weather data which were taken from Shoothill GaugeMap (<https://www.gaugemap.co.uk/>), may not fully represent local variations in rainfall due to the closest weather stations being located between 2.5 and 8.5 km away ($\bar{x} = 5.8 \text{ km}$) from each site.

As highlighted in section A.6.3. the presence of drainage systems such as pollution control tanks or oil separators ahead of retention ponds and wetlands may also influence particle removal by ponds. A targeted investigation into the capacity of these systems to treat the first flush prior to being discharged as influent compared with ponds which take runoff direct from the road may also prove informative into the installation of future ponds.

Lastly, due to safety constraints and the shelving of pond banks, it was not possible to sample sediments from the deepest central part of the ponds where the majority of particles will likely settle out of suspension. Consequently, despite sediment samples being collected during dry periods where pond levels were low, the sediment samples may not fully reflect the concentrations of TWPs or other microplastics intercepted by the attenuation ponds.

A.8. Conclusions and scope for further study

This study adds considerably to our understanding of the sources and extent of TWPs and other microplastics associated with the SRN, potentially aiding considerations in the design, location (placement of highway drainage systems) and maintenance management strategies. Findings from this study are agreeable with previous research which also concludes stormwater runoff to be a significant source of anthropogenic debris, including microplastics, to aquatic ecosystems, with TWPs contributing a greater mass than other forms of microplastics.

Key findings are summarised below:

- Tyre wear particles (TWPs) and other forms of microplastics (MPs) were quantified by Pyrolysis–gas chromatography–mass spectrometry (Py-GCMS) and Fourier-transform infrared spectroscopy (FTIR) respectively in drainage from curve and straight sections of the Strategic Road Network (SRN), and in the influent and effluent of two types of drainage management systems (wetlands and retention ponds). TWPs were present in every environmental sample examined (70/70). Other microplastics were present in all but one sample (69/70)
- Surface water drainage from curved and straight sections of the road network contained between 0.01 and 3.21 mg of TWPs per litre

- The mass of TWPs was on average 40 % greater in drainage from curved sections of the SRN ($0.77 \text{ mg/L} \pm 0.38$) compared with straight sections (0.47 ± 0.37) but this pattern was not statistically significant due to variation between sites
- Direct drainage from curved and straight sections of the road network contained other microplastics in concentrations of between 0.66 and 8.52 particles per litre. No significant difference was observed in concentrations of other microplastics between road type (curve or straight)
- Comparison of the concentration of TWPs and other microplastics between the influent and effluent of both wetlands and retention ponds found that for 10 of the 12 comparisons the highway drainage system assessed led to a reduction in the concentration of TWPs and other microplastics released to waterbodies when compared to the influent.
- Removal of other microplastics by both wetlands and retention ponds was highly variable ranging between 0% and 98.1% in efficiency.
- Wetland influent contained on average $5.6 \text{ mg/L} \pm 1.92$ of TWPs and effluent $0.71 \text{ mg/L} \pm 0.38$ of TWPs, yet this difference was not statistically significant. On average wetlands removed $72.6 \% \pm 14.5$ of tyre wear but their performance varied by site 13.6 – 99.7 %
- Retention pond influent contained on average $4.1 \text{ mg/L} \pm 3.22$ of TWPs and effluent contained significantly less at $0.22 \text{ mg/L} \pm 0.13$ of TWPs. Retention ponds removed on average $77.2 \% \pm 7.4$ of tyre wear particles (38.4 – 99.9%)
- Wetland and retention ponds sediment contained on average 3.83 mg/g or 3832.9 mg/kg of TWPs, several orders of magnitude greater than in pond water indicating TWPs are accumulating and therefore highway drainage ponds are effective at capturing TWPs.
- Retention ponds and wetlands typically removed $56 \% \pm 42.5$ of total suspended solids (TSS).
- TWPs contributed between 0.081 and 6.14 % of the total solid mass within each sample ($1.4 \% \pm 0.21$). TWPs and TSS content were significantly correlated but more study is recommended prior to TSS being adapted as a proxy for tyre wear
- Wetland influent contained on average 5.6 ± 0.9 other microplastics a litre, and effluent $3 \text{ MP/L} \pm 0.8$, this difference was not significant. On average wetlands removed $36.5 \% \pm 15.7$ of other microplastics, but on 3 occasions microplastic concentrations were greater in the pond effluent than the influent
- Retention pond influent contained on average $6.4 \text{ MP/L} \pm 2.3$ other microplastics, while effluent contained $1.6 \text{ MP/L} \pm 0.3$ but this was not significant. Retention ponds removed on average $42.7 \% \pm 16.4$ of other microplastics, but on one occasion microplastic concentrations were greater in the pond effluent than the influent
- Concentrations of TWPs reported in this study were at the lower end of the ranges previously reported in the literature. Concentrations of other microplastics typically sat within ranges previously reported in the literature
- The most commonly identified polymers among other microplastics in runoff from the SRN were polypropylene, polyethylene terephthalate, polyamide, acrylic, co-polymers, polyester, and polyurethane. The majority of microplastics identified within direct drainage were fibres and fragments. Of the 93 synthetic particles within effluent from wetland and retention ponds, fibres account for the majority, followed by fragments and spheres.
- The estimated mass of TWPs was considerably greater than that of other microplastics in both runoff from the SRN and in pond sediments; this was agreeable with desk-based estimates suggesting TWPs contribute a substantial portion of total microplastic emissions to the natural environment

- After passing via wetlands and retention ponds, the mass of both TWPs and other forms of microplastics being released to aquatic waters in pond effluent were similar, suggesting TWPs were more effectively retained by wetlands and retention ponds than other forms of microplastics

More regular cleaning and maintenance of roadside litter could potentially help reduce the rate at which microplastics are generated by fragmentation of larger waste by mechanical action of passing vehicles or by strimming or mowing of roadside banks. The removal of microplastics from the ponds examined in this study was inconsistent and inferior compared with TWP removal. This is not surprising given microplastics such as fibres will not be readily removed from suspension which is the principal factor in the ponds examined here that results in the accumulation of particulates. Other interventions such as oil separators may perform better at removing other microplastics as they are designed to remove both sedimented and floating waste. We recommend further research to examine the efficiency of highway drainage systems under a variety of rainfall events and antecedent conditions before and after maintenance in order to better understand the variability introduced by these factors.

While in the present study there was variability among sites and the performance of retention ponds was more consistent than that of wetlands it was apparent that having highways drainage systems in place to intercept other forms of pollution can also facilitate effective removal of microplastics. We recommend further work to examine the extent to which the following features might increase the efficacy of these assets in retaining microplastics a) cleaning or dredging assets periodically and more often to minimise resuspension of trapped particles; b) creating larger ponds with longer flow paths; and c) increasing the height of the pond effluent drain in order to increase residence time.

Any modifications to mitigate contamination from TWPs and other microplastics should be implemented with consideration of requirements for flood risk management. Tests conducted by Michelin in 2021 examined the loss in mass of tyre tread from a variety of passenger tyres driven under the same conditions for 20,000 km and found wear rate to vary considerably indicating intervention at the design stage of vehicle tyre tread could offer a key approach to help minimize particulate release (Michelin, 2021). Investigating what permutations of tyre tread design influence wear rates will be hugely valuable to mitigate emissions at the source, potentially presenting a more viable option than retrofitting drainage assets across the SRN and capturing particles once in the environment. Intervention at the design stage will also address emissions of TWPs to the atmosphere.

When comparing the concentrations of TWPs and other microplastics in the influent and effluent retention ponds and wetlands, led on most occasions, to a reduction in the concentration of TWPs and other microplastics. However, on some occasions there was no difference in concentrations possibly due to a limited flow path and small surface area of the pond. Investigating the influence of pond design features, potential drivers in the performance of the highway drainage systems, is recommended to better inform future placement and design of assets.

Given the apparent parallels in the behaviour of TSS and TWPs in highway drainage systems it is worth subsequent studies further examining the suitability of TSS to be used as a proxy for TWPs, TWPs being more costly and challenging to quantify, would also be beneficial for future monitoring purposes.

It is important to note the variability among sites examined here and we recommend further studies incorporate increased replication at a greater range of spatial and temporal scales in order to better inform actions to reduce and intercept TWPs and other microplastics from the SRN. A more detailed examination into relative importance of the effects of influencing of factors such as driving style and vehicle maintenance by choosing study sites that receive drainage from areas including features such as junctions, roundabouts, or a mix of landuses would also prove insightful.

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A.10. Supporting Information

A.10.1. Examples of Design speed related parameters sampled from Design Manual for Roads and Bridges, National Highways (volume 6, section 1 CD109)

Speed Kph/mph	120/75	100/62	85/53	70/44	60/37	50/31
Minimum radius with adverse camber and without transitions	2880	2040	1440	1020	720	520
Horizontal curve [m] minimum radius with super elevation of 2.5 %	2040	1440	1020	720	510	360
Horizontal curve [m] minimum R with super elevation of 3.5 %	1440	1020	720	510	360	255
Horizontal curve [m] minimum R with super elevation of 5 %	1020	720	510	360	225	180

A.10.2. Detailed Py-GC-MS method statement for tyre particle analysis

A.10.2.1. Pyrolysis-gas chromatography-mass spectrometry

The Py-GC-MS method is adapted from the one described in Parker-Jurd *et al.* (2021). Pyrolysis was carried out using a Frontier Labs single-shot pyrolyser 3030S (Frontier Laboratories Ltd., Koriyama 963-8862, Japan). Samples (typically ~ 20 mg) were added with internal standards (see below) to stainless steel cups and then loaded into the pyrolyser using an auto-shot sampler (Frontier Labs AS-1020E). The pyrolysis unit was interfaced to an Agilent 7890A/5975C GC-MS. The pyrolyser furnace temperature was held at 610 °C and the interface at 300 °C. Helium carrier gas was supplied to the gas chromatograph (GC) via the pyrolyser. The analysis was performed in constant pressure mode (107 kPa) and transferred onto the column in splitless mode (1 minute). The GC inlet temperature was held at 240 °C. The purge flow to split vent was 20 mL/min after 1 minute. The separation was performed using an HP-5ms capillary column (60 m x 0.25 mm i.d. (internal diameter)) coated with (5%-Phenyl)-methylpolysiloxane stationary phase (film thickness 0.25 µm). The GC oven was initially heated at 50 °C for 5 minutes, next it was heated at a rate of 5 °C/min to 320 °C and maintained at that temperature for 15 minutes. The transfer line temperature was 315 °C. The mass spectrometer (MS) ion source temperature was 230 °C and the MS electron ionisation energy 70 eV. The mass analyser was operated in scan mode with mass range m/z 50 – 550.

A.10.2.2. Sample preparation

The total weight of each sample was recorded prior to pyrolysis preparation. Pyrolysis cups (80 µL, 3.8 mm i.d., deactivated stainless steel; Frontier Labs PY1-EC80F) were weighed empty and then containing typically ~20 mg sample. The exact sample weights were recorded to 3 decimal places. Sample cups were spiked with 30 µL of benzothiazole-D4 (5 ng/mL in dichloromethane) internal standard and 30 µL of androstane (5 ng/mL in dichloromethane) recovery standard.

A.10.2.3. Calibration of benzothiazole against internal standards using pure authentic standards of benzothiazole, androstane and benzothiazole-D4.

Approximately 15 mg of a glass microfibre filter were placed in a pyrolysis pot and spiked with the following amounts of authentic standards. A = Benzothiazole 5 ng/mL in dichloromethane, B =

Benzothiazole 50 ng/mL in dichloromethane, C = Androstane 5 ng/mL in dichloromethane, D = Benzothiazole-D4 5 ng/mL in dichloromethane

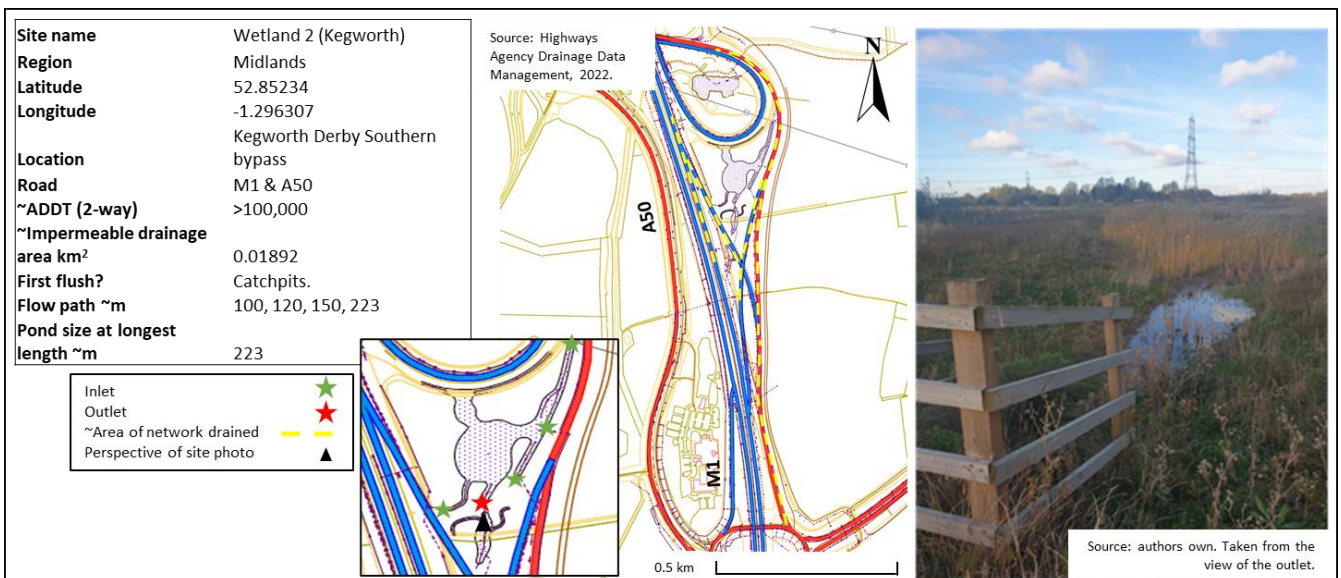
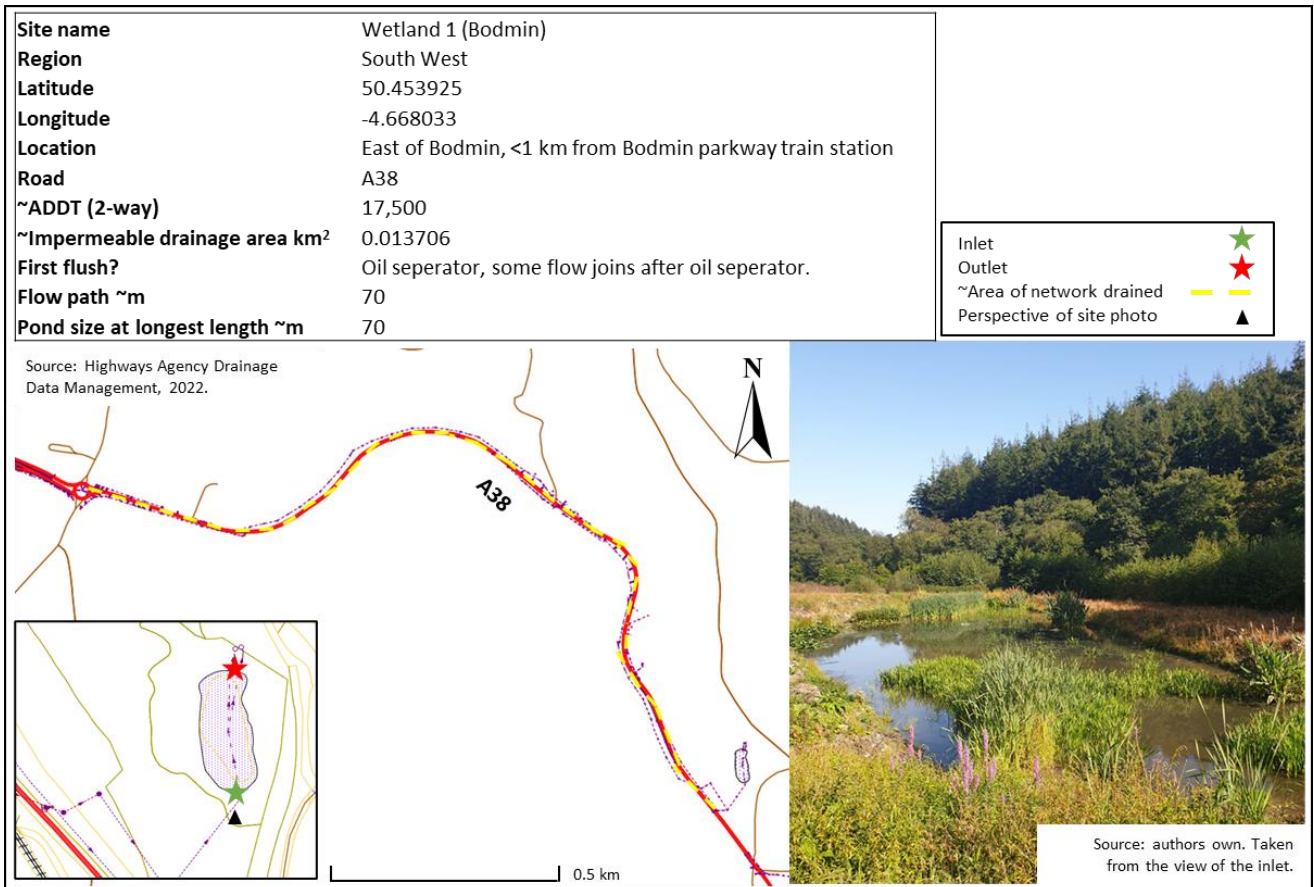
Cal. Std.	Vol. (mL) (A)	Vol. (mL) (B)	Vol. (mL) (C)	Vol. (ml) (D)	Benzothiazole (ng/cup)	Benzothiazole-D4 (ng/cup)	Androstane (ng/cup)
0	0	0	30	30	0	150	150
1	10	0	30	30	50	150	150
2	30	0	30	30	150	150	150
3	0	10	30	30	500	150	150
4	0	25	30	30	1250	150	150
5	0	50	30	30	2500	150	150
6	0	100	30	30	5000	150	150

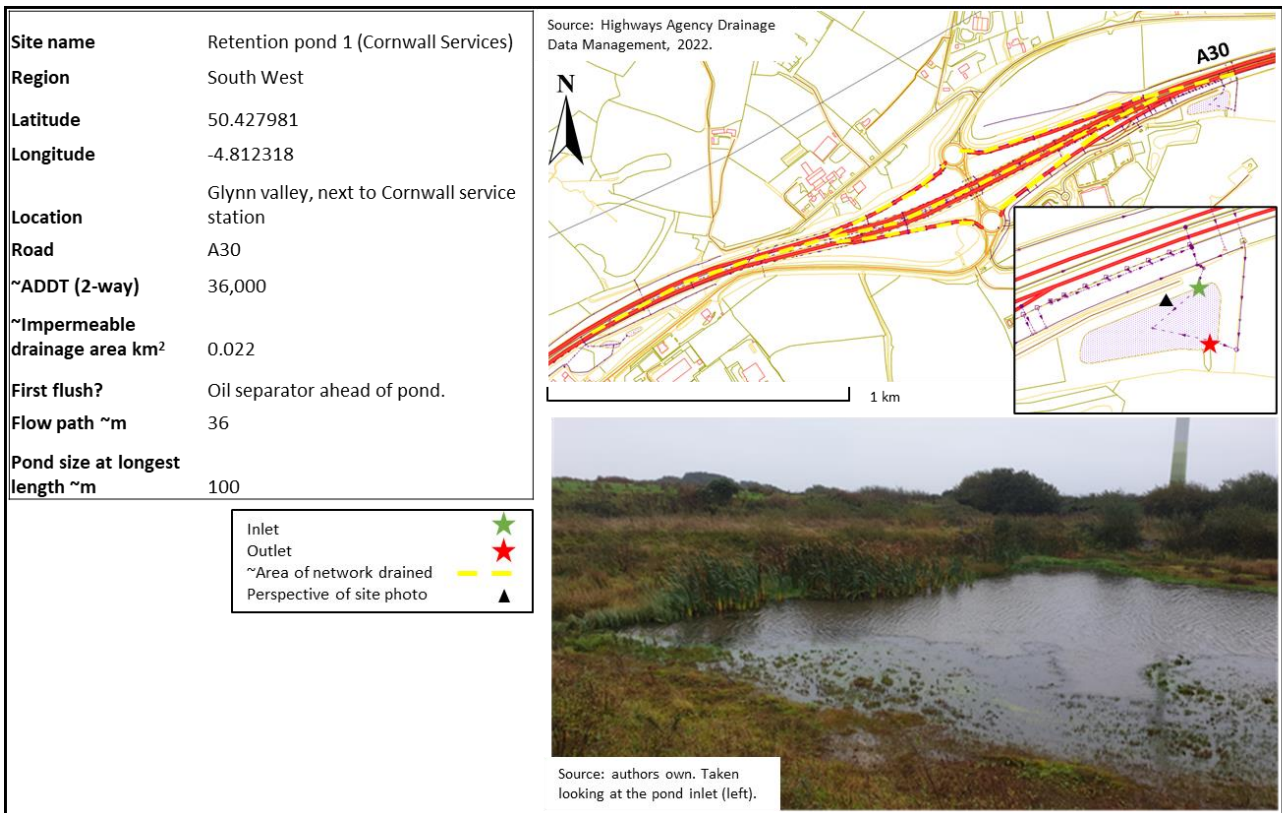
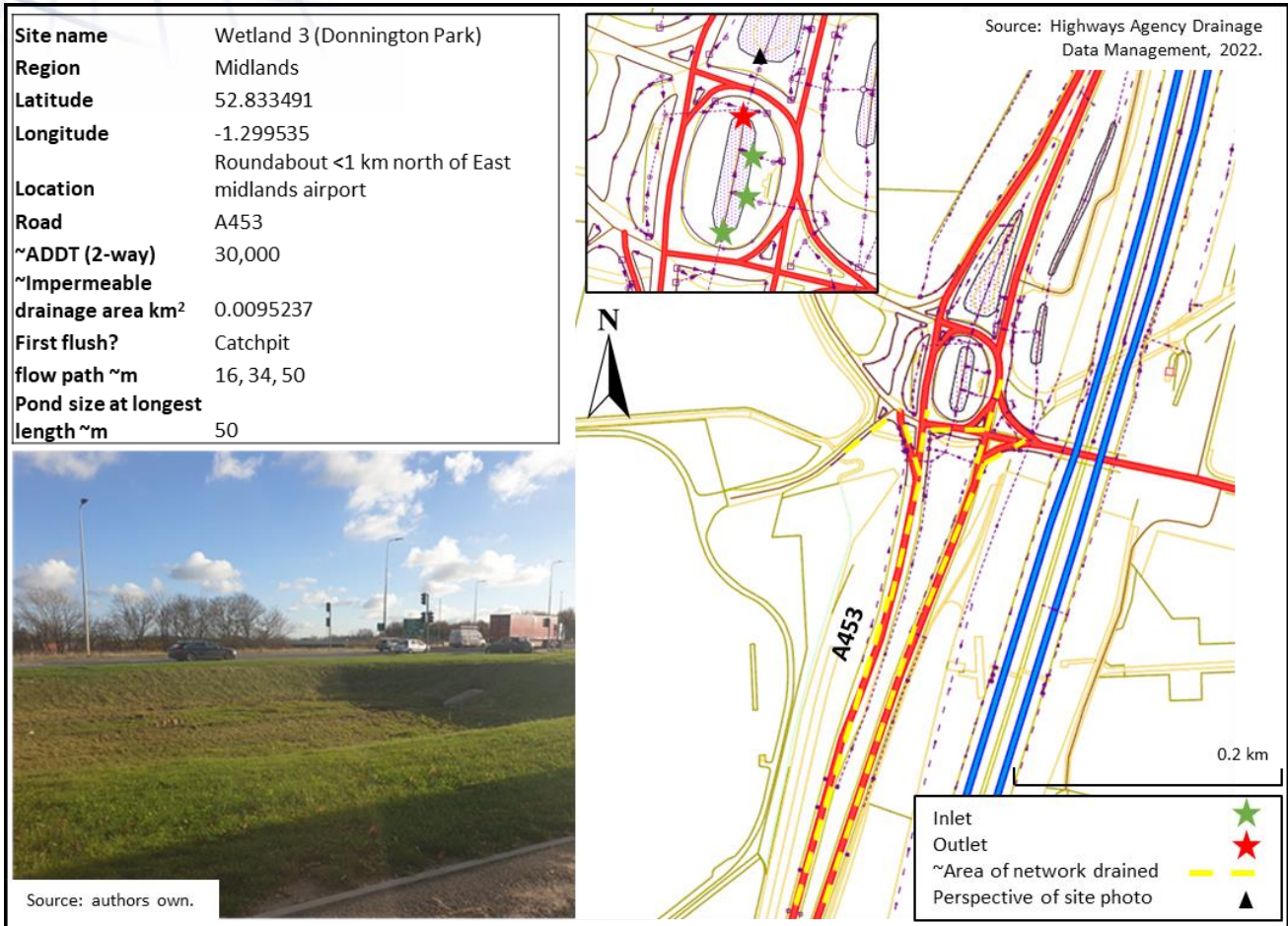
A.10.3. Summary table of sampling details. Antecedent conditions taken from the closest weather station from Shoot Hill GaugeMap

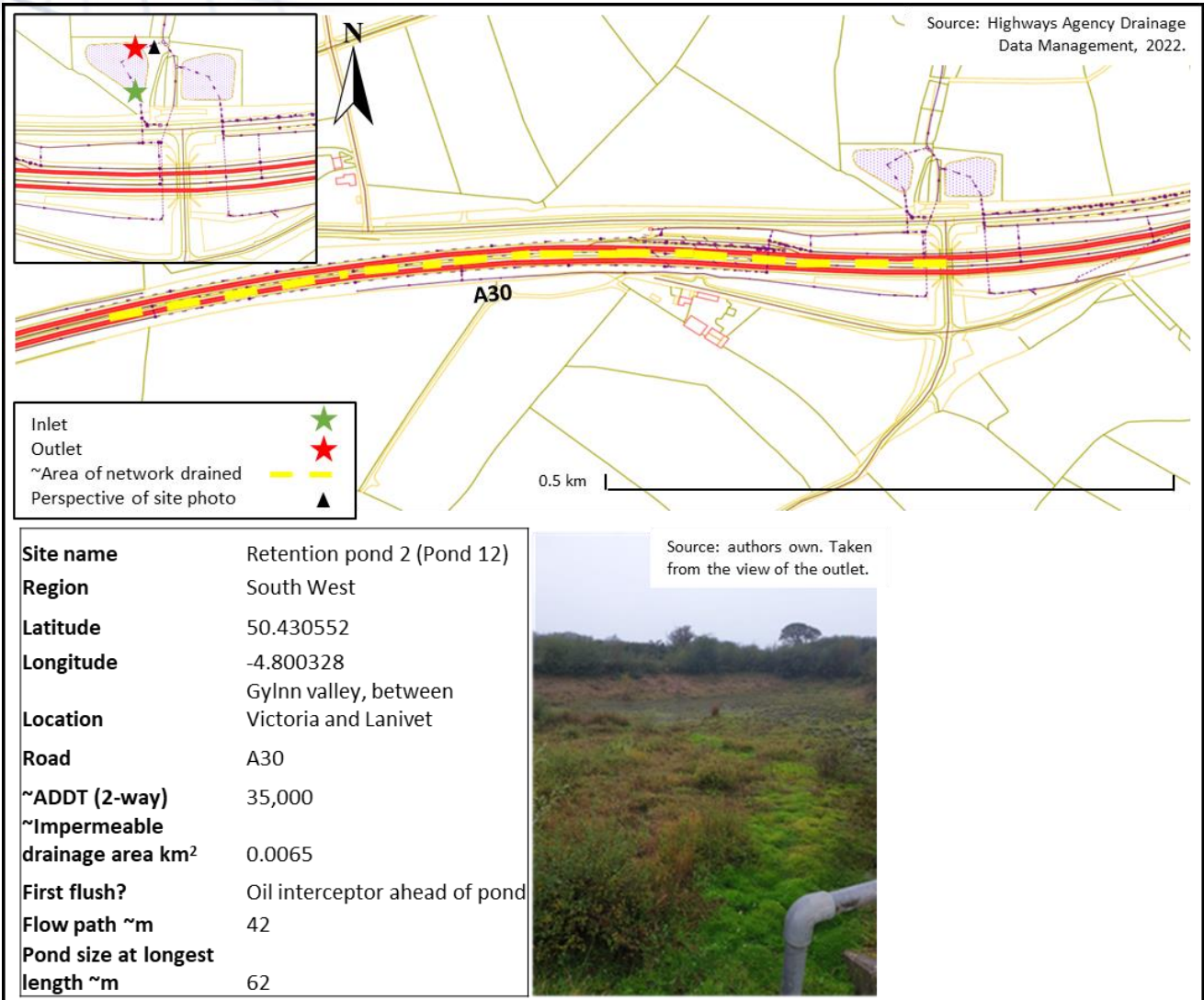
	Site	Date sampled	Distance between weather station & drainage point [km]	Antecedent period [days, 0 mm]	Antecedent period [days, < 2.5 mm]	Rainfall fallen prior to sampling [mm]	Rainfall event sampled [Total, mm]	Manual	A.sampler
Curve vs. straight	1	06/01/2022	Curve 6.72,	1	3	6	7.2		
		04/02/2022	Straight 2.5	0	4	6.6	7.6		
	2	07/12/2021	Curve 3.42,	0	0	12.2	17.5		
		08/03/2022	Straight 6.52	4	4	1	1		
	3	06/01/2022	Curve 6.96,	0	3	1.6	6.2		
		19/02/2022	Straight 8.28	1	2	1.6	1.2		
	4	23/05/2022	Curve 5.34,	2	2	7.4	8.5		
		28/06/2022	Straight 6.94	0	0	2.2	10.1		
Retention Ponds	1	28/10/2021		0	2	4.4	24.8		
		28/02/2022	7.69	0	3	6.4	14.6		
		09/03/2022		0	0	2.4	15		
	2	28/10/2021		0	2	8.3	24.8		
		08/01/2022	8.55	0	0	9.5	13.6		
		28/02/2022		0	3	4	14.6		
	3	13/02/2022		0	6	3.6	10.1		
		16/08/2022	7.96	15	46	0	17.6		
	30/09/2022		0	6	3.7	10.1			
Wetlands	1	03/12/2021	3.6	0	0	11.8	21.3		

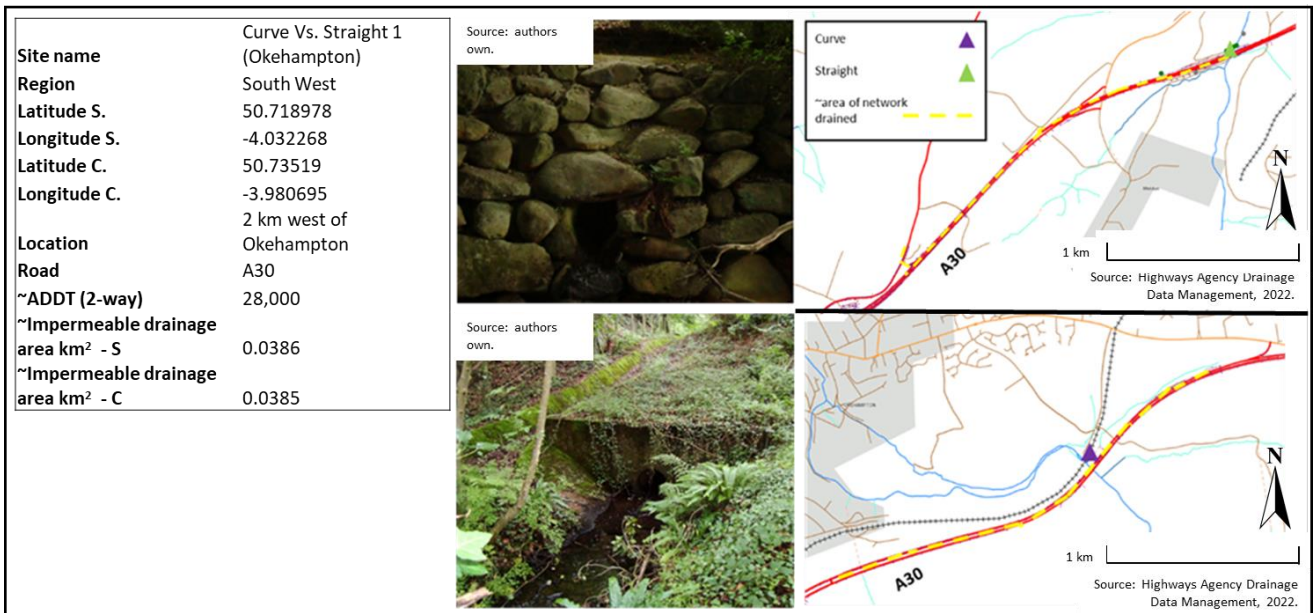
Site	Date sampled	Distance between weather station & drainage point [km]	Antecedent period [days, 0 mm]	Antecedent period [days, < 2.5 mm]	Rainfall fallen prior to sampling [mm]	Rainfall event sampled [Total, mm]	Manual	A.sampler
	28/10/2021		0	3	8.3	34.6		
	28/02/2022		0	3	8	12.3		
	16/03/2022		2	4	6.6	16.6		
2	11/05/2022	3.68	0	4	3.2	8.4		
	18/06/2022		8	11	2.6	6		
	16/03/2022		2	4	6.6	16.6		
3	11/05/2022	3.15	0	4	3.2	8.4		
	18/06/2022		8	11	2.6	6		

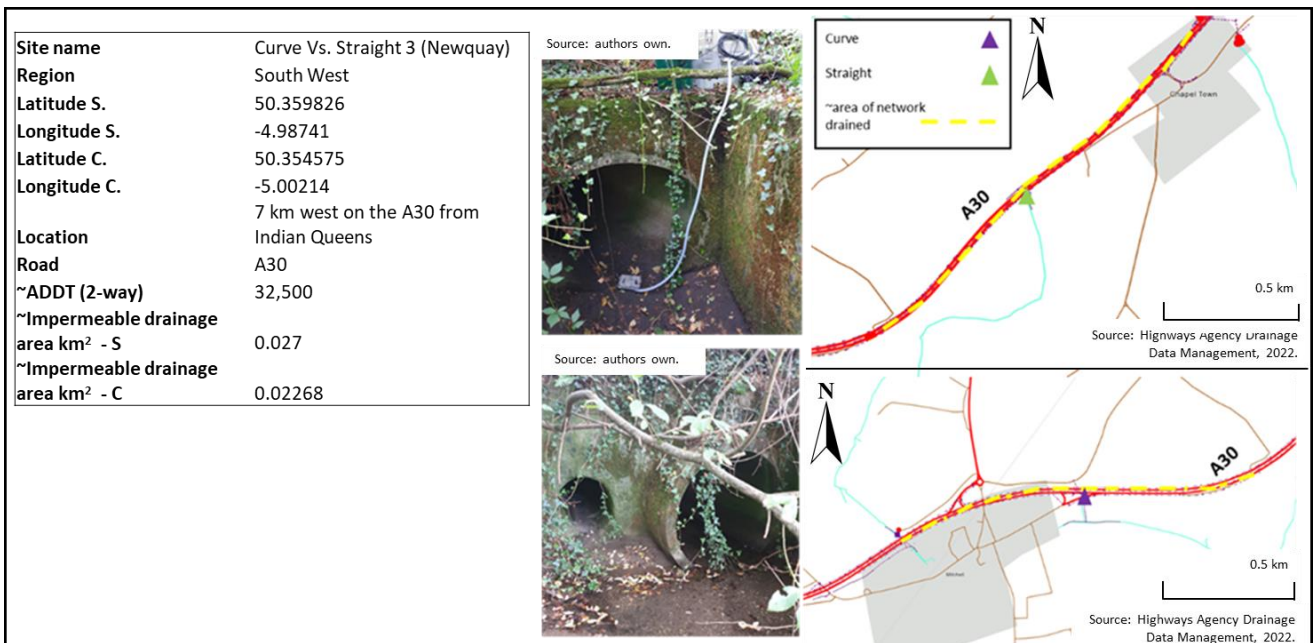
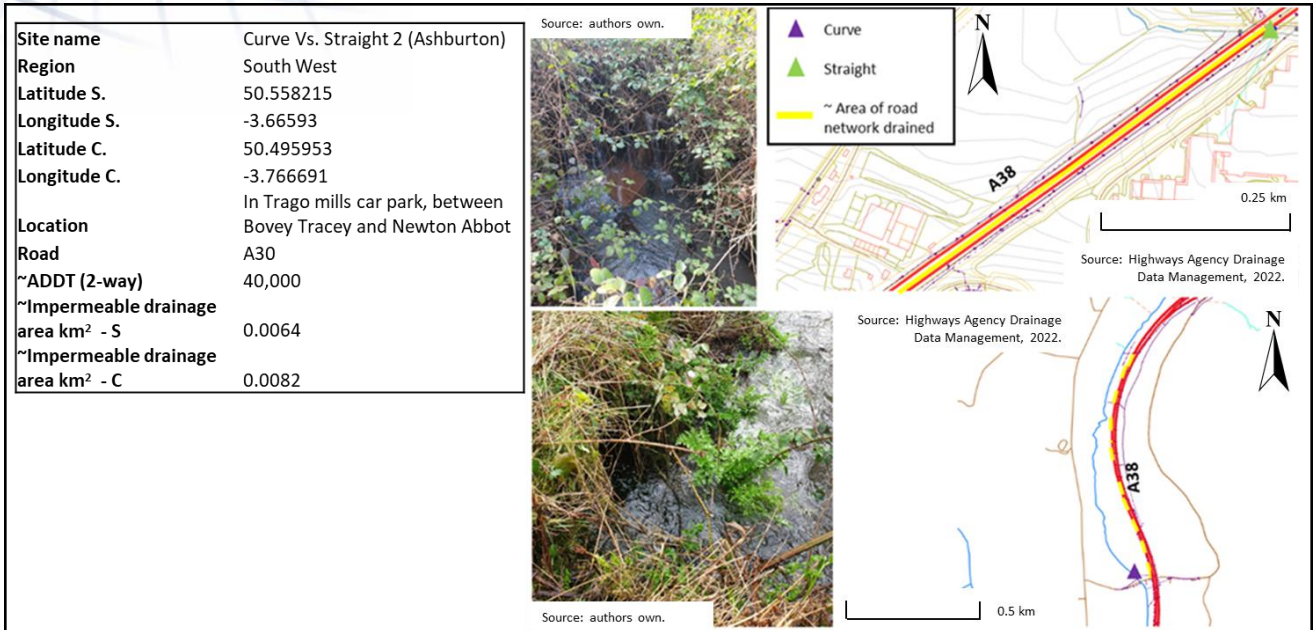
A.10.4. Site cards showing detailed site characteristics.

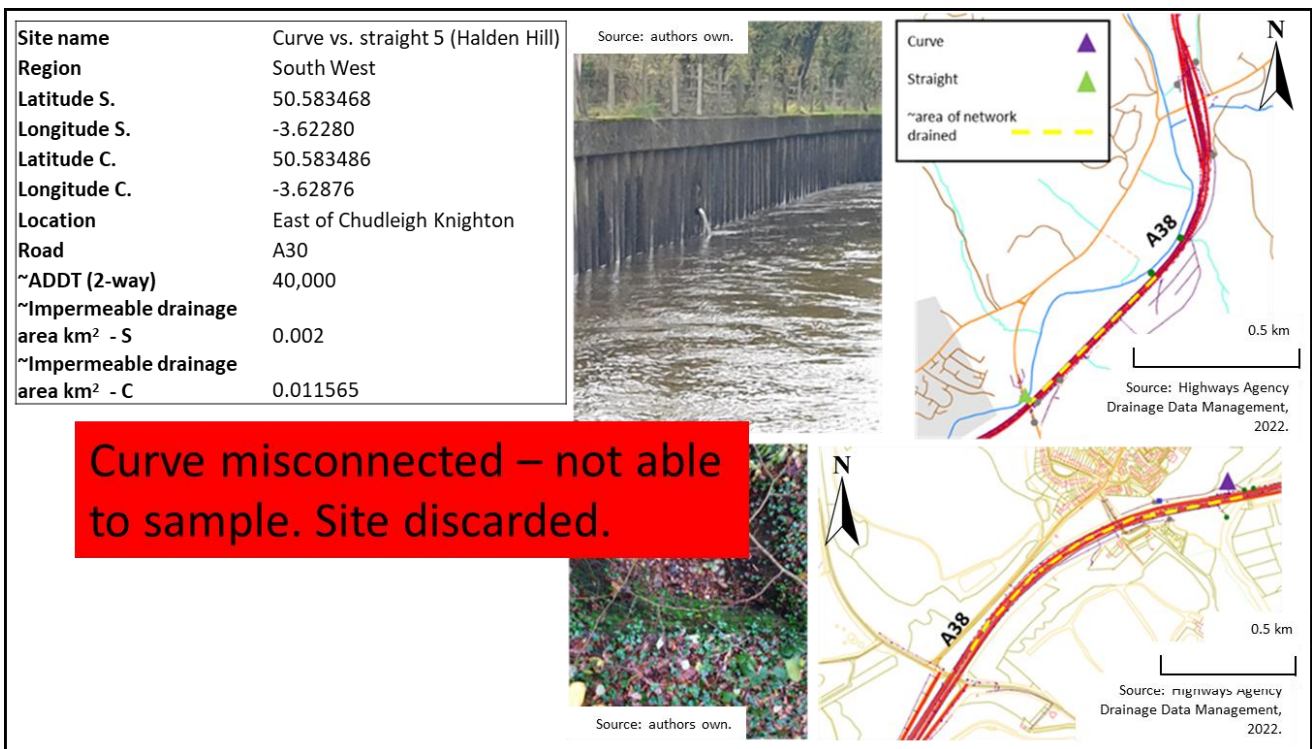
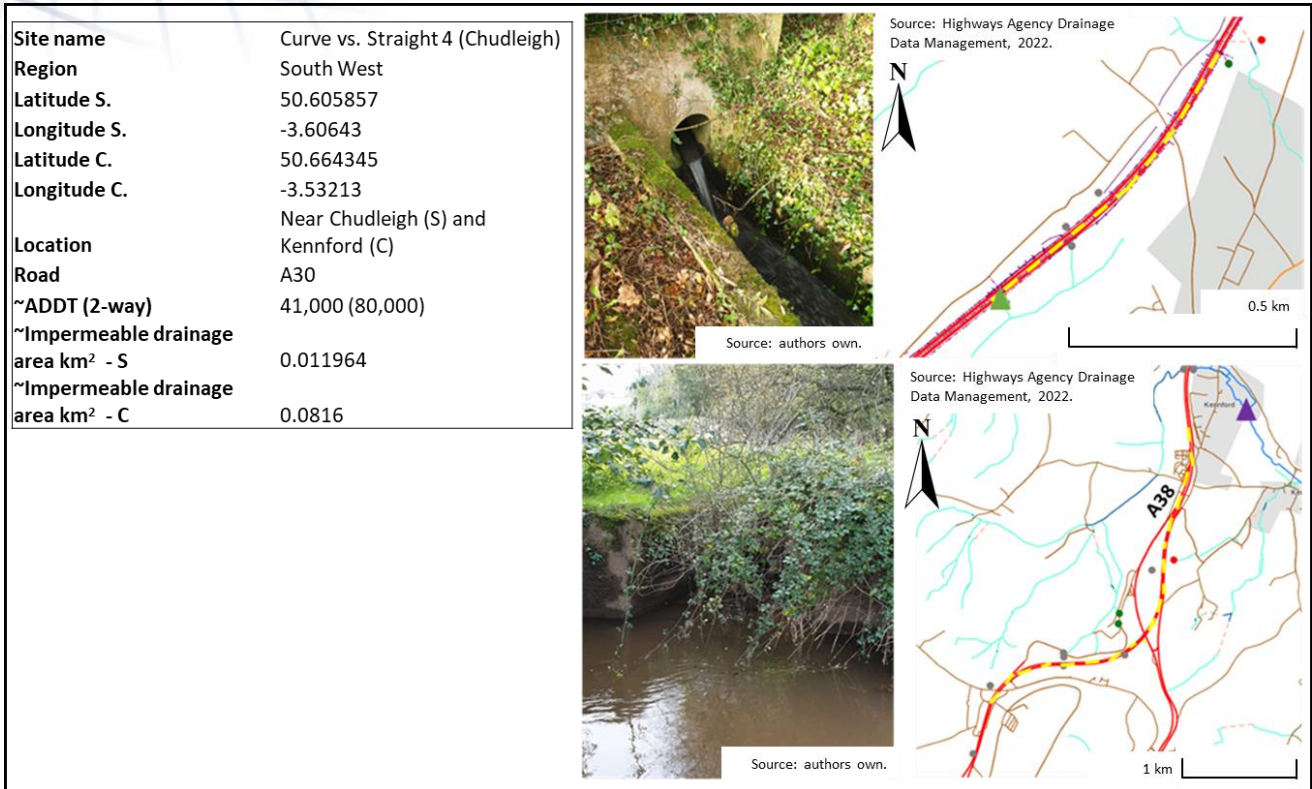












A.10.5. Estimating the relative importance of tyre wear vs. other microplastics

In order to draw a conclusion about whether tyre particles or microplastics discharging from the SRN are more prevalent, microplastic concentrations were converted from abundance to mass. This was done in preference of converting tyre wear from mass to abundance as the size and

density of tyre wear is highly variable and it was not possible to isolate and measure individual tyre wear particles at the smallest end of the spectrum, therefore not providing a representative sample.

Fibres and fragments were the most dominant form of microplastics, accounting for 98 % of all particles. Therefore, for the purposes of this comparison, the remaining 2 % of particles (films and spheres) were assumed to be fragments.

First the estimated volume of each particle was calculated using equation 1 where V = volume, r = radius and h = height (or length). To calculate the volume of fibres they were assumed to be cylindrical in shape. The length, or height, of each individual fibre was measured within the present study. Although length is variable, the radius of fibres tend to be more uniform. An average radius was taken from Cole *et al.* 2014 who reported the diameter of fibres from water samples in the English Channel to measure on average 28 μm .

Equation 1:

$$V = \pi r^2 h$$

To convert fragments from abundance to mass they were assumed to be equal in width and length, the width of each fragment having been recorded in the present study. Depth (or height) was measured from a smaller selection of the fragments ($n=30$) and were found to measure on average 79 μm . Volume was calculated using equation 2 where l = length, h = height and w = width.

Equation 2:

$$L \times h \times w$$

The calculated volume of each particle was multiplied by the density of the polymer each particle was identified as, allowing the calculation of mass using equation 3 where m = mass, ρ = density, and V = volume.

Equation 3:

$$m = \rho \times V$$

This enabled calculation of the average mass of a fibre, 0.0015 $\text{mg} \pm 0.00009$ ($\bar{x} \pm \sigma_M$), and the average mass of a fragment, 0.048 $\text{mg} \pm 0.016$ ($\bar{x} \pm \sigma_M$). The total mass of microplastics in each sample was determined based upon the ratio of fibres to fragment found within each sample, and compared with the mass of tyre wear. This comparison was based on a number of assumptions; therefore results will be presented qualitatively and should be met with some caution.

A.10.6. Raw data detailing concentrations of other microplastics and tyre wear in water and sediment samples

WETLANDS				
Site	Sample date	Tyre wear mg/L	Analytical SD	% efficiency of pond
1	Bodmin IN	11.4	1.2	98.6
	Bodmin OUT	0.15	0.012	
1	Bodmin IN	5.81	0.87	86.2
	Bodmin OUT	0.80	0.12	
	Bodmin IN	17.10	2.33	95.4
	Bodmin OUT	0.78	0.13	
	Kegworth IN	1.22	0.32	99
	Kegworth OUT	0.012	0.0024	
2	Kegworth IN	8.90	0.76	99.7
	Kegworth OUT	0.03	0.01	
	Kegworth IN	1.04	0.11	96.7
	Kegworth OUT	0.03	0.02	

WETLANDS				
Site	Sample date	Tyre wear mg/L	Analytical SD	% efficiency of pond
Don. Park IN	16/03/2022	2.80	1.38	-23.3
Don. Park OUT		3.65	1.43	
3 Don. Park IN	18/06/2022	1.21	1.11	87.5
Don. Park OUT		0.15	0.03	
Don. Park IN	11/05/2022	0.90	0.07	13.6
Don. Park OUT		0.78	0.05	

WETLANDS				
Site	Date	MPs/L	% efficiency of pond	
Bodmin IN	28/02/2022	3.3	25	
Bodmin OUT		2.5		
1 Bodmin IN	03/12/2021	6.3	93.3	
Bodmin OUT		0.4		
Bodmin IN	28/10/2021	10.8	61.5	
Bodmin OUT		4.2		
Kegworth IN	18/06/2022	5.4	76.9	
Kegworth OUT		1.3		
2 Kegworth IN	16/03/2022	8.7	84.9	
Kegworth OUT		1.3		
Kegworth IN	11/05/2022	2.9	46.4	
Kegworth OUT		1.6		
Don. Park IN	16/03/2022	5.6	-29	
Don. Park OUT		7.8		
3 Don. Park IN	18/06/2022	5.0	-14.3	
Don. Park OUT		5.8		
Don. Park IN	11/05/2022	2.1	-16.7	
Don. Park OUT		2.5		

RETENTION PONDS				
Site	Sample date	Tyre wear mg/L	Analytical SD	% efficiency of pond
1	Cornwall Serv. IN	28/10/2021	0.63	85.5
	Cornwall Serv. OUT		0.09	
	Cornwall Serv. IN	28/02/2022	0.51	81.2
	Cornwall Serv. OUT		0.10	
	Cornwall Serv. IN	09/03/2022	0.17	47.7
	Cornwall Serv. OUT		0.09	
2	Pond 12 IN	28/02/2022	1.91	93.7
	Pond 12 OUT		0.12	
	Pond 12 IN	28/10/2021	0.65	64
	Pond 12 OUT		0.23	
	Pond 12 IN	08/01/2022	0.42	85.3
	Pond 12 OUT		0.06	
3	P.B. North IN	16/08/2022	29.80	99.9
	P.B. North OUT		0.034	
	P.B. North IN	13/02/2022	1.97	38.4
	P.B. North OUT		1.21	
	P.B. North IN	30/09/2022	0.81	98.7
	P.B. North OUT		0.011	

RETENTION PONDS				
Site	Date	MPs/L	% efficiency of pond	
1	Cornwall Serv. IN	28/10/2021	5.7	50
	Cornwall Serv. OUT		2.9	
	Cornwall Serv. IN	28/02/2022	0.9	0
	Cornwall Serv. OUT		0.9	
	Cornwall Serv. IN	09/03/2022	0.9	-56.5
	Cornwall Serv. OUT		2.0	
2	Pond 12 IN	28/10/2021	4.0	42.9
	Pond 12 OUT		2.3	
	Pond 12 IN	28/02/2022	1.4	66.7
	Pond 12 OUT		0.5	
	Pond 12 IN	08/01/2022	8.9	87.5
	Pond 12 OUT		1.1	
3	P.B. North IN	16/08/2022	22.5	98.1
	P.B. North OUT		0.4	
	P.B. North IN	13/02/2022	10.9	79.2
	P.B. North OUT		2.3	
	P.B. North IN	30/09/2022	2.5	16.7
	P.B. North OUT		2.1	

DRAINAGE FROM CURVES AND STRAIGHTS			
Site	Sample date	Tyre wear mg/L	Analytical SD
1	Okehampton Curve	06/01/2022	0.35
	Okehampton Straight		0.045
	Okehampton Curve	04/02/2022	0.84
	Okehampton Straight		3.05
2	Ash CURVE	07/12/2021	0.059
	Ash STRAIGHT		0.29
	Ashburton CURVE	08/03/2022	0.03
	Ashburton STRAIGHT		0.010
3	Newquay Curve	06/01/2022	0.15
	Newquay Straight		0.16
	Newquay Curve	19/02/2022	1.34
	Newquay Straight		0.069
4	Chudleigh CURVE	28/06/2022	0.16
	Chudleigh STRAIGHT		0.063
	Chudleigh CURVE	23/05/2022	3.21
	Chudleigh STRAIGHT		0.062

DRAINAGE FROM CURVES AND STRAIGHTS			
Site	Date	MPs/L	
1	Okehampton Curve	06/01/2022	1.0
	Okehampton Straight		2.1
	Okehampton Curve	04/02/2022	8.5
	Okehampton Straight		5.6
2	Ash CURVE	07/12/2021	0.7
	Ash STRAIGHT		5.0
	Ashburton CURVE	08/03/2022	0.7
	Ashburton STRAIGHT		1.6
3	Newquay Curve	06/01/2022	1.8
	Newquay Straight		3.0
	Newquay Curve	19/02/2022	5.6
	Newquay Straight		1.1
4	Chudleigh CURVE	28/06/2022	3.3
	Chudleigh STRAIGHT		0.8
	Chudleigh CURVE	23/05/2022	7.9
	Chudleigh STRAIGHT		0.8

SEDIMENTS			
Site	Sample date	Tyre wear mg/g	Analytical SD

Wetland	1	Bodmin	02/02/2022	0.41	0.10
			28/10/2021	0.49	0.06
			03/12/2021	0.51	0.11
	2	Kegworth	30/03/2022	8.54	1.03
			16/03/2022	6.78	1.48
			11/05/2022	1.24	0.02
	3	Don. Park	30/03/2022	2.71	0.26
			11/05/2022	11.32	1.01
			16/03/2021	3.45	0.79
Retention Pond	1	Cornwall serv.	14/07/2022	2.86	0.50
			02/02/2022	1.62	0.04
			28/10/2021	1.45	0.16
	2	Pond 12	28/10/2021	0.64	0.36
			14/07/2022	2.17	0.16
			02/02/2022	0.21	0.01
	3	P.B. North	18/07/2022	9.00	0.98
			14/07/2022	10.84	0.36
			16/08/2022	4.74	0.66

SEDIMENTS

Site	Date	MPs per g		
Wetland	1	Bodmin	02/02/2022	0.49
			28/10/2021	1.27
			03/12/2021	2.20
	2	Kegworth	16/03/2022	3.28
			30/03/2022	14.29
			11/05/2022	4.62
	3	Don. Park	30/03/2022	0.00
			16/03/2022	3.27
			11/05/2022	1.52
Retention Pond	1	Cornwall serv.	28/10/2021	1.79
			02/02/2022	6.12
			28/02/2022	2.72
	2	Pond 12	28/10/2021	3.57
			02/02/2022	4.76
			24/08/2022	2.08
	3	P.B. North	16/08/2022	3.39
			18/02/2022	11.76
			14/07/2022	8.80

ATKINS **Jacobs**