Features of the highway road network that generate or retain tyre wear particles

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Abstract

The environmental accumulation of microplastics poses a formidable global challenge, with tyre wear particles (TWPs) emerging as major, and potentially harmful contributors to this particulate pollution. A critical pathway for TWPs to aquatic environments is via road drainage. While drainage assets are employed worldwide their effectiveness in retaining microplastics of highly variable densities (TWP~1-2.5 g cm^3), remains unknown. This study examines their ability to impede the transfer of TWPs from the UK Strategic Road Network (SRN) to aquatic ecosystems. Samples were collected from the influent, effluent, and sediments of three retention ponds and three wetlands. The rate of TWP generation is known to vary in response to vehicle speed and direction. To ascertain the significance of this variability, we further compared the mass of TWPs in drainage from curved and straight sections of the SRN across eight drainage outfalls. Pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) was used to quantify tyre wear using benzothiazole as a molecular marker for TWPs (with an internal standard benzothiazole-D4). Tyre wear was present in drainage from the SRN at concentrations of 2.86 ± 6 mg/L and was found within every sample analysed. Drainage from curved sections of the SRN contained on average a 40% greater TWP mass than straight sections but this was not significant. The presence of wetlands and retention ponds generally led to a reduction in TWP mass (74.9% ± 8.2). This effect was significant for retention ponds, but not for wetlands; most probably due to variability among sites and sampling occasions. Similar drainage assets are used on a global scale; hence our results are of broad relevance to the management of TWP pollution.

Introduction

Road drainage has been identified as a major pathway for microplastic (MP) pollution to enter aquatic environments (Järlskog *et al*. 2020; Moruzzi *et al* 2020; Wang *et al*., 2020; Xu *et al*., 2020; Parker-Jurd *et al*., 2021). Concentrations of anthropogenic particle loading in stormwater tends to be higher than other pathways, such as effluent from wastewater treatment plants which undergoes substantial treatment prior to its discharge (Werbowski *et al*.2021; Parker-Jurd *et al*., 2021). Stormwater runoff from road networks can carry MPs originating from the breakdown of intentional or unintentional littering, sped up by mechanical action from passing vehicles or from roadside maintenance (e.g. mowing or strimming roadside vegetation) and from atmospheric pollution, however tyre wear particles (TWPs) are thought to represent the dominant share of the load (Overdahl *et al*., 2021).

Tyre tread is worn at the tyre-road interface due to friction (Dall'Osto *et al*., 2014) generating particles that are typically elongated in shape with varying amounts of amounts of mineral encrustation from the road surface. Consequently, the density of TWPs is highly variable, estimated between 1 and 2.5 g cm^3 (Verschoor *et al*., 2016; Sommer *et al*., 2018; Vogeslang *et al*., 2018; Unice *et al*., 2019; Kovochich *et al*. 2021). A typical passenger tyre weighs around 11.8 kg, lasting approximately 40,000 – 50,000 km during which it can wear 10–30% of its tread weight before reaching its safety limit (Grigoratos and Martini, 2014). TWPs could pose a risk to organisms as they contain a complex blend of chemical compounds (Peter *et al.* 2018), however information on specific ecological risks is largely lacking.

TWP pollution has previously been 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), and driving characteristics such as braking, accelerating and cornering (Dannis, 1974; Councell *et al.*, 2004; Knight *et al*., 2020; Mengistu *et al*., 2021). Weather and climate have also been documented to impact tyre wear pollution loads, TWPs accumulating during periods of dry weather and transported during wet weather and storm events (Su *et al*., 2020). However, road wetness, temperature, and seasonal effects are thought to be 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 have quantified TWPs within stormwater (Kumata *et al.* 1997; Reddy and Quinn 1997; Baumann and Ismeier 1998; Kumata *et al.* 2002; Parker-Jurd *et al*. 2021), none appear to have looked at the efficiency of drainage management systems such as wetlands or retention ponds. However, such assets are used in highways systems globally, particularly in countries with developed transport infrastructure, where they have been suggested as a potential preliminary barrier to reduce the pollution load reaching downstream natural habitats (Grbić *et al*., 2020; Moruzzi *et al*., 2020; Smyth *et al*., 2021; Mengistu *et al*., 2021).

Due to their carbon black content and colour, TWPs cannot be reliably identified using approaches typically used for other forms of MPs, where particles are individually identified using spectroscopy (e.g. by Fourier-transform infrared spectroscopy (FTIR)). TWPs can instead effectively quantified by mass using analytical pyrolysis coupled with gas chromatography-mass spectrometry (Py-GC-MS). Pyrolysis is a process that subjects a polymeric sample to elevated temperatures, resulting in the thermal fragmentation of the polymer into monomeric, dimeric and oligomeric components leading to the formation of characteristic units (Picó and Barceló, 2021). These units are then separated in a gas chromatograph (GC) and identified through mass spectrometry, either by utilizing mass spectral libraries, by selecting characteristic ions of indicator compounds, or by comparison of retention times and mass spectral properties of authentic samples (Picó and Barceló, 2022).

Aims and objectives

the main aim of this study was to quantify the amounts of TWPs entering aquatic environments via the SRN, further seeking to investigate if existing drainage management systems such as wetlands may be appropriate for the retention of TWPs. We also evaluated whether curvature in the road network, influenced TWP concentrations in surface drainage. Lastly the study makes approximations as to the relative importance to TWPs compared to other forms of microplastics (MPs) such as plastic fibres and fragments. The outcome of the work are intended to be of broad applicability informing approaches to minimise the transfer of TWPs from roads to natural aquatic environments. Hence, this study will provide novel data on the burden of TWPs from roadways and better inform the management of TWP pollution globally.

Methods

The efficiency of existing road runoff management strategies for the retention of TWPs and the influence of road curvature on the generation of TPWs were considered as principal factors in the experimental design. Retention ponds and wetlands were selected as drainage assets to examine due to their prevalence across the SRN and their likely use in the construction of new road layouts. Site selection ensured some geographic spread and representation of a range of traffic volumes. The sampling design is detailed in Figure 1.

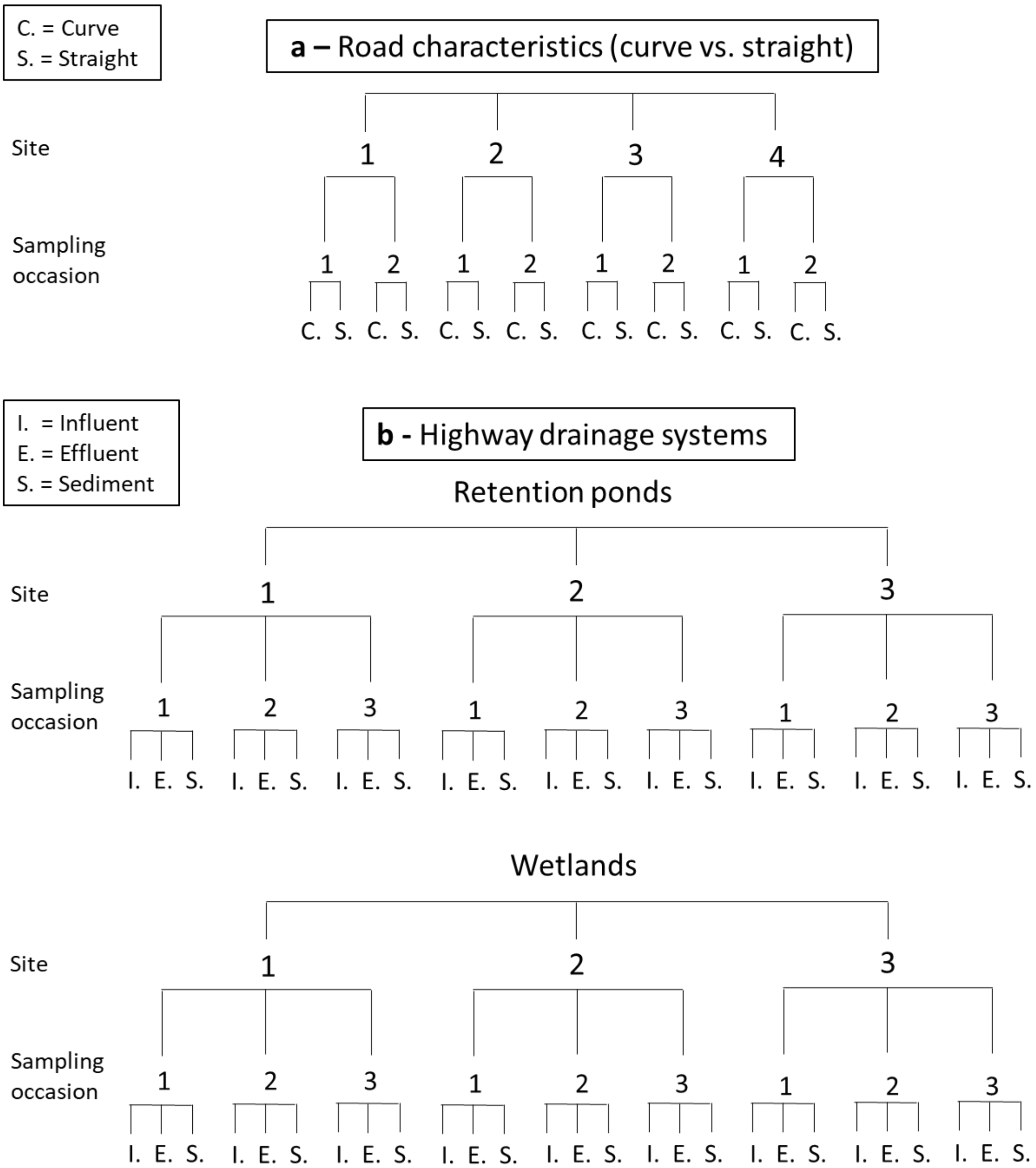

Fig. 1 *Sampling approach for a) drainage from curve and straight sections of the SRN, and b) influent, effluent and sediments from highway drainage systems, retention ponds and wetlands*

Site selection

Sites were selected according to their designation by the National Highways Drainage Data Management System (HADDMS) and/or National Highways drainage engineers for the region in which they were located. Site selection was further dictated by permission and ability to access and sample a safe distance from the live carriageway.

In order to compare particle generation between curved and straight section of the SRN (Figure 1a), pairs of drainage outfalls were located in close proximity to ensure characteristics such as annual average daily traffic loads (AADT) rainfall intensity and duration, were as comparable as possible. A 'curve' on the SRN was identified according to parameters in the National Highways Design Manual for Roads and Bridges (volume 6, section 1 CD109) (National Highways, 2020). Parameters state a bend on a road with a 70-mph speed limit should have a minimum radius of 1020m and minimum superelevation of 5%, superelevation being the transverse slope between the sides of the road, designed to counteract the effects of centrifugal force, reducing the chances of vehicles overturning or skidding when navigating into and through a bend. Curved sites were identified where the radius or superelevation fell short of the minimum requirements. Approximate superelevation and radius were calculated on Google Earth Pro. Each of the four paired sites were sampled over two precipitation events.

To test the efficiency of highway drainage systems for TWP retention, three wetlands and three retention ponds were sampled over three precipitation events (Figure 1b). According to the National Highways Design of Highways Drainage Systems the definition of a retention pond is '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.' While a wetland is defined 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). As highlighted, in addition to removing pollutants, ponds along the SRN are also designed to attenuate flow and prevent flooding.

Sampling was conducted over a 12-month period between October 2021 and September 2022. Water samples were collected during the onset of the rainfall event, with the aim of capturing the first flush of water liberated form the road surface, a change in colour and/or flow was used as an indication of when to commence sampling. When sampling pond influent, a minimum of 6L was collected over a period of approximately 20 minutes into prewashed 4 L glass containers. The same approach was applied to pond effluent which was collected once the waters levels reached the pond outlet, or once the normal baseflow of the effluent increased. In the event a pond had more than one inlet (wetlands 2 and 3), the same volume was collected from each inlet and the sample homogenised. The same approach was used for sampling outfalls from curve and straight sites, sampling at the point where the outfall began discharging, or when the normal baseflow increased and/or changed colour. Autosamplers (ISCO 6712) were employed in order to sample when manual sampling was not possible (i.e. at night) but were found to be of minimal use (used on 3 occasions) due to failures in the units to trigger sampling, or a lack of discrete locations to place the units. Autosampler units were attached to tipping rain gauges and programmed to trigger in excess of 2.5 mm hr^{-1} (estimated mobilisation threshold for tyre wear 2 – 2.5 mm d^{-1} (Brodie, 2007; Unice *et al*., 2019)) sampling 250 mL every minute in order to mimic manual sampling. On two sampling occasions, rainfall events did not generate enough runoff to fill retention pond 3 and allow the collection of effluent. Samples were instead collected as pooled water next to the outlet of the pond. This was considered a reasonable substitution as this is the first water to become displaced if enough rainfall occurred.

Sediment samples from wetlands and retention ponds were collected to depths of approximately 1.5cm into pre-washed containers at wetlands and retention ponds only. The very surface layer (1-2mm) was removed to allow quantification of TWP deposits, rather than TWP concentrations indicative only of the most recent rainfall event.. Access into ponds which held water was not permitted for health and safety reasons, therefore sediments were collected during dry weather periods where the ponds were either empty or water levels were lower to allow access as close to the central deepest part of the pond as possible. Sediments were collected from each of the six ponds on three occasions.

Across the fourteen study sites, the estimated impermeable drainage catchments ranged between 0.0064km^2 and 0.095km^2. Catchment area was calculated on HADDMS using assets drainage details and a digital terrain model contour (1m), the estimated catchment was further verified with a regional National Highways drainage engineer. Some sites took additional drainage from the permeable catchment, e.g. roadside banks, verges, or adjacent land. Eleven study sites were located in the Southwest of the UK, with a further two wetlands and one retention pond located in the Midlands (see the SI1 for site locations). Annual average daily traffic (AADT) at each site ranged between an estimated 17,500 and >100,000 vehicles a day. Key details for each site can be found in the supporting information (SI1) alongside detailed example site cards for wetland 1, retention pond 1 and curve vs. straight pair 4. Where the study makes reference to direct drainage, this refers to samples that had not passed a wetland or retention pond, i.e. collected from curved and straight sections of the network and from pond influent.

Sample processing and analysis

Water samples were first passed through 30µm and 15µm sieves in order to reduce the total volume, and backwashed with de-ionised water into a clean beaker before being vacuum filtered over one 1.6µm Whatman glass microfibre filter paper, and dried in a low temperature drying oven (≤30 °C). Mass (d.w.) was recorded once at a constant weight.

Sediment samples were dried at a low heat (≤30 °C) until they could be thoroughly homogenised. A sub-sample (~1.5g d.w.) was resuspended in deionised water and filtered over a 1.6µm Whatman glass microfibre filter paper. Dry mass was again recorded following drying to a constant weight.

Samples were analysed by pyrolysis coupled with gas chromatography-mass spectrometry (Py-GC-MS), using benzothiazole as a marker for TWPs. The analytical approach was adapted from the one detailed in Parker-Jurd *et al.* (2021). In brief: ~20 mg of sample was added with 30 µL of a stable isotope-labeled internal standard [4,5,6,7-$^2H_4$]benzothiazole (benzothiazole-D4) at a concentration of 5 ng/mL in dichloromethane and 30 µL of a recovery standard 5α-androstane (5 ng/mL in dichloromethane) to deactivated stainless steel pyrolysis cups (PY1-EC80F, Frontier Laboratories, Japan). Pyrolysis was performed with a micro-furnace pyrolyser 3030S combined with the auto-shot sampler (Frontier Laboratories, Japan). The pyrolysis unit was interfaced with an 7890A/5975C gas chromatograph/mass spectrometer detector (Agilent Technologies, USA). The pyrolyser temperature was held at 610 °C and the interface at 300 °C. Helium carrier gas was supplied to the gas chromatograph (GC) via the pyrolyzer. 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.) 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 voltage 70 eV. The mass analyser was operated in scan mode with mass range m/z 50 – 550.

To convert concentrations of benzothiazole to an estimated mass of tyre wear, benzothiazole was quantified from the pyrolysis products of fragments from seven common passenger tyre treads (Bridgestone, Continental, Goodyear, Michelin, Nokian, Pirelli and Vredestein), analysed in the same manner as described for the environmental samples. The response of the instrument was measured using a calibration curve of peak intensity versus the weight of an authentic standard of benzothiazole-D4 averaged over three runs ($R^2 > 0.99$). Data were then converted into a mass of tyre wear per sample and normalized by the volume or mass of sample collected (mg/L or mg/g). The limit of quantification (LOQ) for this approach was approximately 1ng per mg of sample.

Quality Assurance/Quality Control (QA/QC)

All samples were processed at the University of Plymouth in a two-chamber clean laboratory (ISO clean room classes 7 and 8, airways filtration to 0.5 µm). To ensure accurate and reliable analysis of TWPs by Py-GC-MS, nitrile gloves and cotton laboratory coats (100% cotton) were worn at all times. A thorough rinse with ultrapure water, methanol and dichloromethane was conducted on all glassware in order to avoid possible contamination. All solvents and procedural blank samples were analysed with Py-GC-MS to check for contamination during the processing of both water and sediment samples. In order to detect any instrumental drift, the analysis calibration standards (namely 5α-androstane and [4,5,6,7-$^2H_4$]benzothiazole (benzothiazole-D4)) was carried out daily.

The contribution of TWPs to total MP loads

Particles generated by the wear and tear of tyre tread are reported to represent a considerable proportion of MP emissions to the natural environment; Sundt *et al*. (2014), Lassen *et al*. (2015), Essel *et al*. (2015), Magnusson *et al.* (2016), Boucher and Friot (2017), and Eunomia (2018). However, due to analytical constraints, tyre wear is quantified by mass, and other forms of MPs by abundance, making direct comparisons on the relative importance of TWPs challenging. Therefore, the abundance of other forms of MPs were also recorded within each sample. In brief; prior to analysis for TWPs, samples were homogenised and 20% of the total volume of each sample was analysed for other MPs by FTIR. This was carried out using a Bruker Hyperion 1000 microscope coupled to a Vertex 70 spectrometer in transmission mode (400 – 6000 cm-1). While some studies (e.g. Frias *et al*., 2016; Gies *et al*., 2018; Neves *et al*., 2015; Peng *et al.*, 2018; Woodall *et al*., 2014) choose to include materials identified as viscose, cellulose, or rayon in their MP counts, due to the inability of the analytical approach to distinguish between the spectra of natural and synthetically altered natural materials (Lusher *et al*., 2014; Blumenröder *et al*., 2017; Martin *et al*., 2017), the present study did not. Using a similar approach to the one detailed in Parker-Jurd *et al.* (2021), the mass of other MPs was estimated based upon the density and estimated volume of each particle identified by FTIR as a synthetic polymer. This enabled some conclusion to be drawn about the relative importance of TWPs. A detailed description of the conversion from abundance to an estimated mass is provided in SI2.

Statistical analysis

Statistical analysis was performed in Minitab (V18). A mixed model analysis of variance (ANOVA) was used to perform three analyses comparing concentrations of TWPs in drainage between; the influent and effluent of wetland and retention ponds, the performance of two drainage asset types (wetlands vs. retention ponds) and the mass of TWPs between curved and straight sections of the SRN. In each instance factors; treatment (influent vs. effluent), asset type (wetland vs. retention pond), and road type (curve vs. straight) were fixed and nested within site which was random. Homogeneity of variance was assessed prior to ANOVA (Anderson-darling) and transformations applied if appropriate (log transformation). The influence of weather and site characteristics e.g. AADT, flow path, antecedent conditions (independent variable) on the quantity of TWPS (dependent variable) in direct runoff (curve vs straight or pond influent) was examined using a linear regression. 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 unless otherwise stated.

Results

TWPs were detected in every sample across the 14 study sites (70/70) and were present in drainage from the SRN at concentrations of 2.86 ± 6 mg/L. Summary data can be found in SI3.Benzothiazole was not detected in any of the procedural blanks. Drainage from curved sections of the SRN contained on average 0.77 mg/L of tyre wear ± 0.38, around 40% more than found in drainage from straight portions of the SRN, 0.47 mg/L ± 0.37, however this pattern was inconsistent between sites (see Figure 2) and was not significant (p=>0.05, df1).

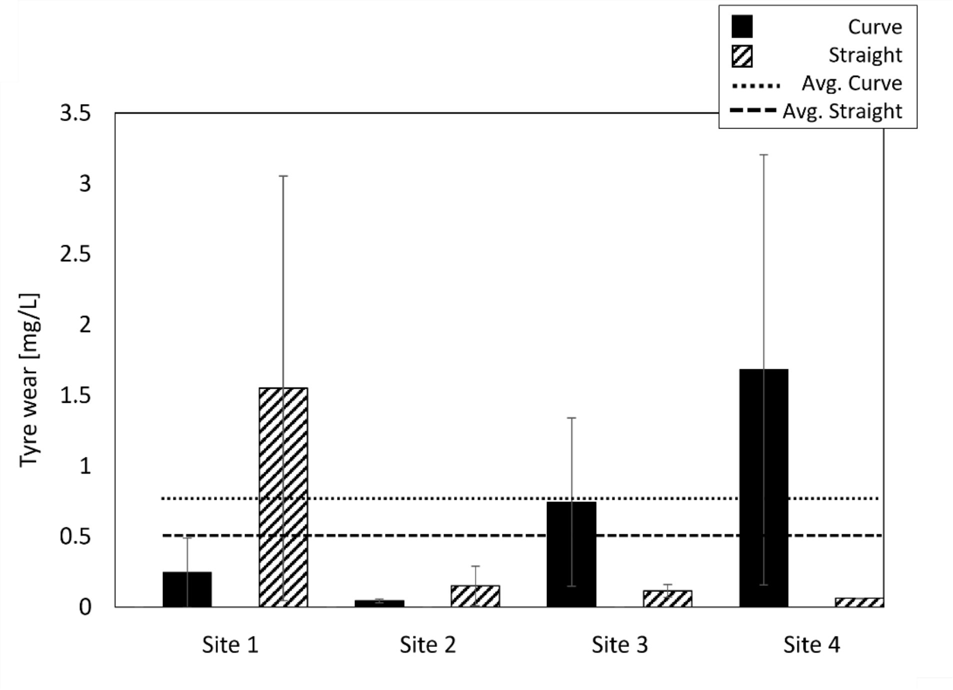

Fig. 2 *Concentrations of tyre wear in water collected from outfalls discharging from curved and straight sections of the SRN. Error bars represent variation over the two rainfall events sampled (SE), the dashed lines represent the average concentrations across the 4 study sites*

Wetlands removed between 13.6 and 99.7% (72.6% ± 14.5) of the mass of TWPs when comparing drainage entering and leaving. The concentration of TWPs was higher in effluent than influent on one occasion (at wetland 3, see SI3). Influent of wetlands contained on average 5.6 mg/L ± 1.92 of tyre wear (0.9 - 17.1 mg/L), while effluent contained on average 87% less at 0.71 mg/L ±0.38 (0.012 – 3.65 mg/L). However, because of between site variation this this was not statistically significant (p=≥0.05, df1, Figure 3a).

Influent at retention ponds contained on average 4.1 mg of tyre wear per litre ± 3.22 (0.17 – 29.8 mg/L), whereas effluent was in the range of 0.011 – 1.21 mg/L (average 0.22 ± 0.13), thus retention ponds removed on average 77.2% ± 7.4 (38.4 – 99.9%) of TWPs (Figure 3b), this effect was significant (p=<0.05, df1).

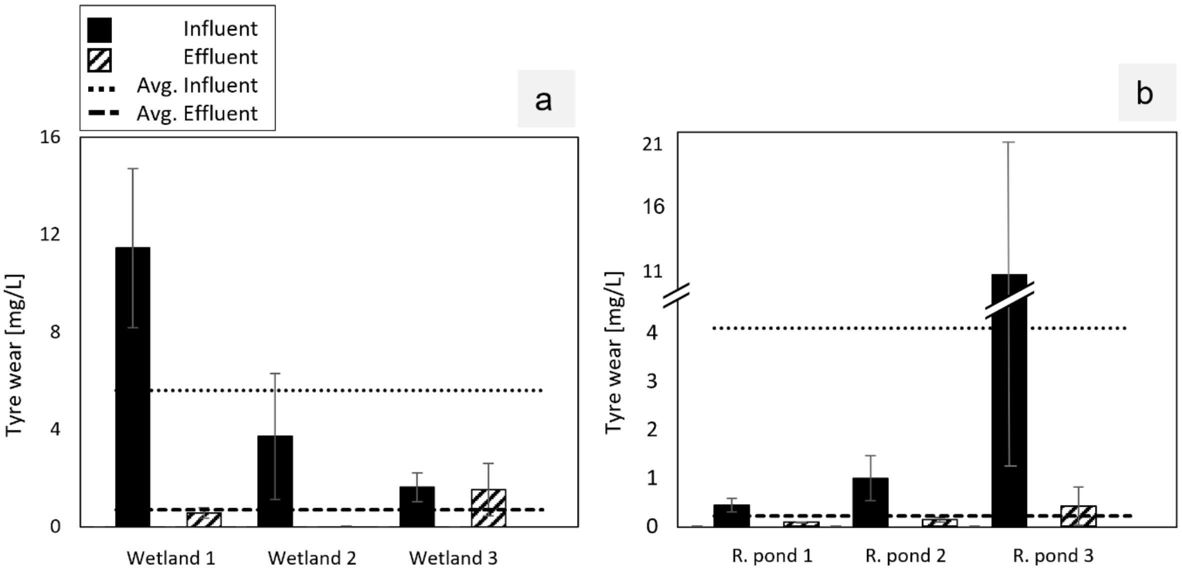

__Fig. 3__ Concentrations of tyre wear runoff in water collected from the influent and effluent of wetlands (a) and retention ponds (b). Error bars represent variation over the three rainfall events sampled (SE), the dashed lines represent the average concentrations across the three study sites

Sediments collected from wetlands and retention ponds contained between 0.21 and 11.32 tyre wear/g (3.83 tyre wear/g ± 0.89), see Figure 4.

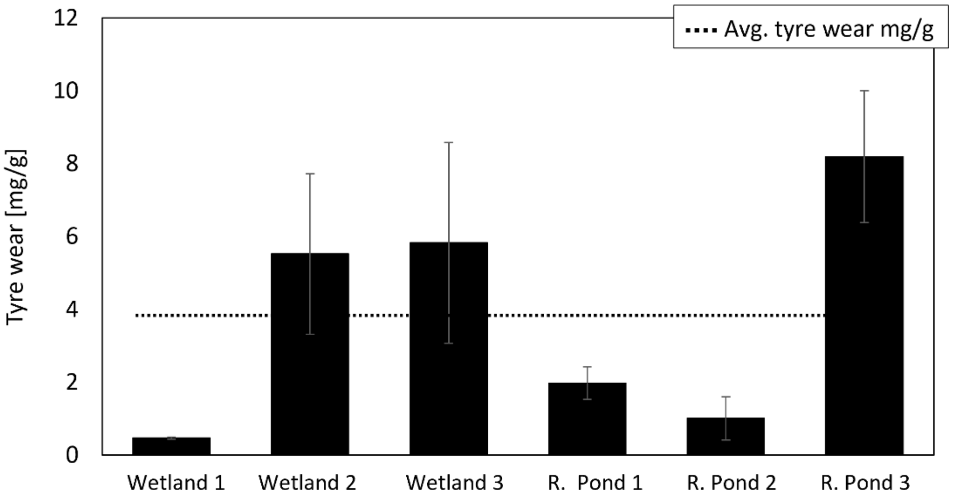

__Fig. 4__ Concentrations of tyre wear in the sediments from wetlands and retention ponds. Error bars represent variation over the three sampling occasions (SE), the dashed lines represent the average concentrations across the six study sites.

Concentrations of TWPs were positively correlated with the number of days of prior to sampling which did not exceed the estimated threshold at which TWPs are mobalised from road surfaces (2 – 2.5 mm/d (Brodie, 2007, Unice *et al.*, 2019)). Relationships between site characteristics (AADT, impermeable catchment area, and pond flow path) and concentrations of TWPs were examined but no significant correlations were found.

Other forms of MPs were found in 69/70 samples analysed, at concentrations in direct road runoff (wetland and retention pond influent and drainage from curve and straights) of 4.63 ± 4.83 MP/L, in pond effluent 2.32 ± 1.93 MP/L, and in pond sediment, 4.22 ± 3.84 MP/g. The individual estimated mass of MPs in the form of fibres was 0.0015 ± 0.000086 mg (n=312), and for MPs in the form of fragments 0.048 ± 0.016 mg (n=197) (see SI2). On average TWPs exceeded the estimated mass of other MPs in direct road runoff at 2.86 mg/L and ~0.6 mg/L respectively, and wetland and retention pond sediments, 3.83 mg/L and ~0.41 mg/L respectively. However, there was little difference in the estimated mass leaving wetlands and retention ponds as pond effluent, indicating that TWPs were more readily removed by highway drainage ponds that other forms of MPs.

Discussion

Here we show that TWPs are prevalent within drainage across the SRN (benzothiazole detected in 100% of samples). Agreeable with previous studies (e.g. Overdahl *et al*., 2021; Parker-Jurd *et al*. 2021), TWPs were also found to dominate the share of the anthropogenic particle load compared with other forms of MPs, highlighting the need for further research in the field of TWP mitigation.

Direct comparisons between concentrations of TWPs reported between the present and existing studies should be met with some caution due to the influence of; location and characteristics of the environment sampled, differences in the analytical approach e.g. chemical marker employed, or due sources of markers other than tyre tread to the environment. Masses of tyre wear reported in the present study were largely agreeable, though typically at the lower end of previous reports (see SI4), e.g. within direct road drainage the present study reported concentrations between 0.01 and 28.9 mg/L, compared with existing studies which ranged from 2.5 and up to 179 mg/L (Kumata *et al*. 1997; Reddy and Quinn, 1997; Baumann and Ismeier 1998; Kumata *et al.* 2002; Zeng *et al.* 2004; Parker-Jurd *et al.* 2021). Tyre wear loads are evidenced to be driven by characteristics of the drainage area e.g. traffic densities and driving behaviour; braking, accelerating, and cornering (Dannis, 1974; Councell *et al.*, 2004; Knight *et al*., 2020; Mengistu *et al*., 2021), often characteristic of urban environments. The location of studies with the highest reported concentrations are Rhode Island USA (Reddy and Quinn, 1997), urban Tokyo (Kumata *et al*., 2002), and a populous city in Germany (Klöckner *et al*., 2020). Notably sampling during the present study occurred exclusively along arterial road networks, not in populated or urbanised areas.

Despite concentrations of tyre wear being 40% greater in drainage from portions of the SRN that were curved compared with straight, this pattern was not consistent or significant. This was likely due to challenges in isolating the effects of road curvature from other influencing factors (e.g. road slope angle). Furthermore, curves on the SRN tend to be relatively gentle and driven without stopping, compared with bends on other road types e.g. roundabouts in urban settings which are more aggressive and typically involve braking and accelerating when stopping and starting at traffic lights or when giving way.

There are no previous published reports quantifying TWPs in effluent from highways pond, however Reddy and Quinn (1997) reported TWPs in water held within a motorway settling pond at concentrations of 2.3 mg/L, falling within the ranges reported for the present study (0.01 – 3.6 mg/L). Concentrations of tyre wear in the sediments of wetlands and retention ponds (0.2 – 12.5 g/kg) were agreeable with existing studies (0.35 – 20 g/kg), besides Klöckner *et al*. (2020) who reported concentrations far higher (360 - 480 g/kg) in a highway sediment basin. Of the three wetlands and three retention ponds sampled in the present study; three were preceded by oil separators, one by a pollution control tank, designed to intercept floating waste as well as removing solids from suspension, and the remaining two by catchpits (SI1), also designed to retain sediment. Sediment basins are typically located ahead of assets such as wetlands to reduce the sediment load reaching the drainage assets which may explain the higher concentration reported by Klöckner *et al*. (2020). A report by National Highways (2020) estimated particulate removal by pollution and flow control assets, estimating ponds and wetlands to remove 60% of total suspended solids (TSS). However, no estimates were provided for catchpits, oil separators, or pollution control tanks. A separate study by Moy *et al.* (2003) reported TSS removal by oil separators at 2 locations on the SRN to be between 37 and 56%. It is likely, providing these assets are maintained (sediment build up was observed inside the oil separator at retention pond 1 which may hinder efficiency), the presence of pre-treatments intercepted a portion of TWPs prior to drainage entering the ponds as influent.

It is worth noting the concentration of tyre wear in pond sediments was orders of magnitude greater than found in wetland and retention pond influent (3,833 mg/kg > 4.9 mg/L), further evidencing the accumulation of tyre wear. In the natural environment, tyre wear has been reported in river waters in the range of 0.5 to 3.6 mg/L (Reddy and Quinn, 1997; Kumata *et al*., 2000; Ni *et al*., 2008), in some instances exceeding concentrations found with road runoff. While diluted, the sampling locations where all located close to roads with considerable traffic flow in urban settings, likely explain the high concentrations.

Considerably variability in the removal of TWPs by wetlands and retention ponds was observed between sites and sampling occasions, notably at wetland 3 (Figure 3a) which removed on average just 26% of TWP mass. Wetland 3 was smallest pond (517 m^2) with the shortest flow path (16 m) giving rise to a shorter residence time than for example wetland 2 which was three times its size at 1567 m^2, had the longest flow path (100m), and removed on average 98.5% of TWP mass. However, no significant relationship was found between TWPs and flow path or wetland or retention pond size. A more targeted study exploring the influence of such site characteristics on performance is recommended. Notably, future work should examine the capture efficiency in other drainage assets.

A relationship between TWPs in road runoff and AADT might be expected. The absence of such an effect in the present study may in part be due to the influence of other variables e.g. preceding accumulation period or rainfall intensity, however it is also notable that many sites took drainage from areas in addition to the primary road network where AADT is recorded. For example at Wetland 2 which had the highest AADT (~100,000), in addition to the M1, slip roads and an A road where the AADT is lower also made up a considerable portion of the drainage.

According to the National highways Design Manual for Roads and Bridges (GM 701) standards, highways drainage assets such as ponds are maintained, for example by removal of sediments, on 5 to 10-year cycles. However, common practice has adapted to a reactive approach, maintaining assets as and when required. Maintenance of highway ponds entails de-silting and removal of material which may impair operations, though partial de-silting can occur more frequently. At the time of sampling the ponds studied were aged between 3 and 17 years old. Since construction, maintenance had not been reported at five of the six ponds, though a change in service provider may account for inaccurate maintenance records prior to 2016. The 6th had been maintained the year previous to the start of the sampling campaign, sediment accumulation periods therefore ranged between 1 and 17 years. Increasing the frequency of inspections and/or maintenance may result in improved TWP retention.

Parker-Jurd *et al.* (2021) conducted laboratory-based settling experiments which observed the majority of TWPs (~85%) to settle out of suspension within a settling column after a period of 1 hour, with similar observations after one week, further estimating TWPs to have a settling velocity between 0.00001 and 0.1 m/s. This is largely agreeable with the present study which saw on average 75% of TWP mass removed via sedimentation within wetlands and retention ponds. Inputs from atmospheric deposition, resuspension of previously captured particles, or insufficient residence time during intense or prolonged rainfall events may be attributable to occasions where removal rates were less efficient.

Over the course of the study, a number of organisms were observed ultilising wetlands and retention ponds. These included birds, mammals, invertebrates, vertebrates, and even protected species (*Triturus cristatus,* Great crested newts). While not a common or particularly widespread habitat, a study by Boisseaux *et al*. (in publication) showed at concentrations comparable to those in the present study (3 mg/L), that TWPs caused negative effects on reproduction of the freshwater crustacean *Daphnia magna*, and at higher concentrations, from 3 to 50 mg/L, effects on reproduction were more pronounced. Hence while providing protection for downstream habitats, wetland and retention ponds could therefore provide rare instances of possible high level of expose for an array of organisms.

Potential limitations, recommendations for further study

In addition to the impermeable catchment, highways drainage assets can take drainage from the permeable catchment (e.g. road verges) which may dilute or introduce variability in reported concentrations of tyre wear. Antecedent conditions, in particular the period of dry weather prior to the rainfall event, clearly has the potential to influence measured concentrations of micro particulates in runoff. While we endeavoured to collect samples after a minimum of 2 days of dry weather, due to unpredictable forecasting some rainfall occasionally occurred in the 48 hours preceding fieldwork. Further work to examine the relationship between antecedent conditions and measured concentrations of particulates in runoff would be of benefit to inform future sample campaigns. It should also be acknowledged that other sources of benzothiazole to the natural environment exist (e.g. biocides, herbicides, and antifreeze (Brownlee *et al*., 1992; Wik and Dave., 2009; He *et al*., 2011)) however no other sources can produce such large or continual emissions (Kumata *et al.* 2000) making benzothiazole an effective marker for TWPs. In the present study, the precision of TWP measurements was strengthened by the use of a microfurnace which facilitated larger sample sizes than other approaches such as a resistive pyrolyser (Miller *et al.* 2022). Additional QA/AC such as spiking artificial sediments and interlaboratory comparisons to assess the analytical accuracy (as has been done in studies of other microplastics) may enhance future TWP analyses.

The present study did not show significant effects of road curvature. However, curvature on the SRN tends to be gentle therefore it would be worth exploring the effects of tighter turning at lower speeds, for example at t-junctions and roundabouts away from major trunk roads. Further study of retention features would also benefit from increased information of site characteristics such as pond size, flow path, and maintenance cycles of the assets all of which could influence performance. Further exploration on the effect of rainfall intensity on the mobilisation of TWPs would also be advantageous.

From a highways management perspective it is important that any measures put in place regarding changes to pond design to mitigate the release of TWPs should not compromise ponds the ability to attenuate flow or mitigate flood risks. Routine monitoring of sediment depth within highway ponds in conjunction with more accurate record keeping of maintenance activities would also prove beneficial to better understanding TWP accumulation rates. Lastly, different tyres have been reported to wear at varying rates (Michelin, 2021), clearly signalling the potential for intervention at the design stage. Mitigation by better design is of key importance since it could reduce emissions to the natural environment via road drainage and via atmospheric transport.

Conclusion,

This study provides a much improved understanding on the extent and nature of TWP pollution originating from the SRN, confirming TWPs to be a substantial contributor of particle loading to aquatic waters, at a greater prevalence than other forms of MPs, with TWPs being detected in 100% of samples. While significant effects of road curvature along the SRN were not observed the study also concludes that the presence of wetlands or retention ponds typically lead to a reduction in the load of TWPs being discharged to aquatic waters, thus providing protection for downstream waters. Performance however was variable between sites. Notably, many drainage outlets across the SRN discharge directly to natural aquatic habitats without treatment and the performance of other drainage assets on the SRN for the retention of TWPs warrants further examination. Given the extent of TWP pollution originating from roads these results hold global significance in guiding the management of TWP pollution stemming from highways.

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Declarations

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Authors Contributions

Authors RCT and FPJ contributed to the conception of the work and formulation of the experimental design. Material preparation, field sampling/data collection and analysis were performed by GA, BG, FPJ and GPJ. The first draft of the manuscript was written by FPJ and RT. All authors commented on versions of the manuscript, and read, edited, and approved the final manuscript for publication.

Competing Interests

The authors declare no competing interests.

Ethical Approval

Not applicable.

Consent to Participate and Publish

Co-authors have seen and approved the manuscript for submission and subsequent publication.