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Quantifying the release of tyre wear particles to the marine environment via multiple pathways.


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Abstract

Desk-based studies have suggested tyre wear particles contribute a substantial portion of microplastic emissions to the environment, yet few empirical studies report finding tyre wear. Samples were collected from three pathways to the marine environment: atmospheric deposition, treated wastewater effluent, and untreated surface runoff. Pyrolysis coupled to gas chromatography-mass spectrometry was used to detect benzothiazole, a molecular marker for tyres. Benzothiazole was detected in each pathway, emitting tyre wear in addition to other sources of microplastics. Release via surface water drainage was the principle pathway in the regions examined. Laboratory tests indicated larger particles likely settle close to their entry points, whereas smaller particles have potential for longer-range transport and dispersal. The previous lack of reports are likely a consequence of inadequate methods of detection, rather than a low environmental presence. Further work is required to establish distribution, transport potential, and potential impacts once within the marine environment.
**Key words:** Tire wear, Vehicle emissions, Microplastics, Surface runoff, Atmospheric deposition, Wastewater treatment, Marine pollution

**1.0 Introduction**

Plastics are durable, versatile, inexpensive materials that bring societal benefits in a wide range of applications, across all aspects of everyday life. Fragments of plastic generated from deterioration of macroplastics, or small manufactured particles (<5 mm), termed microplastics, have been recognised as a widespread contaminant in the environment since 2004. Tyre wear particles are frequently regarded as microplastics, being small, solid in state, comprised primarily of synthetic polymer, insoluble in water, and durable in the environment. The formation of tyre wear particles occurs at the tyre-road interface due to frictional energy, producing microparticles, often referred to as tyre-road wear particles (TRWPs) due to the potential incorporation of road surface wear. They are characteristically thin and cylindrical with tapered ends and are black in colour.

Despite having been described as environmental contaminants since the 1970s, the contribution of tyre wear to microplastic contamination has only recently been highlighted. These studies take a top-down desk-based approach, indicating tyre wear contributes a substantial quantity to the total microplastic load; yet reliable empirical data are lacking. These studies have provided the foundation for broader extrapolative reports that estimate emissions of tyre particles to be similar, and in some cases greater, than other types of microplastic such as synthetic fibres, that are known to be widespread in the environment.

In contrast to desk-based estimates, the frequency with which tyre wear particles are reported in environmental samples is low. This could be attributable to an inability to confidently isolate and quantify tyre wear using methods typically utilised for microplastic analysis such as density separation and spectroscopy. Alternatively it has been demonstrated that the analytical flash pyrolysis of tyre wear can be a useful tool for
The presence of styrene, isoprene and dipentene in flash pyrolysates have all been used as markers for tyre tread components styrene-butadiene, isoprene and natural rubber\textsuperscript{14,15,22,23}, however these markers have limitations if other major sources to the environment exist. Benzothiazole however is not common in natural products\textsuperscript{24} and so despite a small number of applications (some biocides, antifreeze, or anti algal agents)\textsuperscript{25-27} these sources do not produce substantial or continual emissions of benzothiazole to the environment\textsuperscript{28-28} compared to its use as vulcanisation accelerators in tyre tread (approx. 0.5 – 2\%\textsuperscript{26,29,30}). This approach of using the molecules bound into the synthetic rubber polymers has not been widely used to measure prevalence of tyre wear with respect to emissions to the marine environment.

Evidence suggests that tyre wear is generated in considerable quantities, with tyres shedding 10 – 50\% of their tread weight to the environment during life in service (approximately 40,000 to 50,000 km)\textsuperscript{29,31-33}, equating to \~0.8 kg yr\textsuperscript{-1} per capita globally\textsuperscript{34}. This is important when considered in conjunction with the number of vehicles on the road globally, estimated over 1 billion and expected to exceed 2 billion by 2040\textsuperscript{35}. Generation of tyre particles is also thought to vary considerably between road types\textsuperscript{19}; and driving behaviour\textsuperscript{36}.

Tyre wear has been reported in ambient air (in proximity to roadways) in the range of 0.5 to 11 µg m\textsuperscript{-3}\textsuperscript{14,15,37,22,23,26,28,38} however data on atmospheric deposition is lacking. Tyre wear within road dust has been reported between 0.7 and 210 g kg\textsuperscript{-1}\textsuperscript{39,40,37,28,41,42,43}. While textured road surfaces can retain particles\textsuperscript{44}, a sizeable portion of tyre wear deposited on roads may be mobilised by wind, or during precipitation events\textsuperscript{45,46,20}. Upon mobilisation by surface water particles will either run to nearby soils or into surface drains and combined sewers. Once within combined systems surface flow is passed into storm water tanks and treated, and discharged as final effluent. One study reported the mass of tyre wear discharged in combined wastewater treatment effluent at 1 mg L\textsuperscript{-1}\textsuperscript{47}. Whereas tyre wear within road surface runoff has been reported in the range of 12 to 179 mg L\textsuperscript{-1}\textsuperscript{26,28,42,43,47,48,49} and may
pass directly into aquatic environments without treatment. It is worth noting tyre wear retained in the sludge fraction may also be returned to land as fertilizer which could be mobilised during rainfall events into waterways.\textsuperscript{20}

If tyre particles enter aquatic environments, their distribution within the water column and transport potential remains largely unknown. Recipient waters such as rivers and estuaries may act as a pathway of tyre wear to the marine environment. Conversely, they could also provide a sink via sedimentation.\textsuperscript{20} Using chemical markers to quantify tyre wear, previous studies have reported greater concentrations within sediments than surface waters.\textsuperscript{30,50,51}

Despite evidence that tyre wear is generated in vast quantities, empirical confirmatory data on the presence and distribution of tyre wear in the environment is sparse. To the best of our knowledge, there are no studies outlining primary field data on the pathways of tyre wear particles to the environment or emissions relative to other microplastic sources; notably an understanding of the transfer to marine environment is lacking.\textsuperscript{6,11,16,30} Therefore, the principal aim of the present study was to quantify tyre wear in the environment while providing some examination of the relative emissions between different road types, and between pathways. A secondary aim, evaluated the transport potential and behaviour of tyre particles in aquatic environments.

\textbf{2.0 Materials and methods}

\textit{2.1 Quantification of tyre particles at their points of entry to the marine environment}

Three principal routes for tyre wear particles to enter the marine environment were considered: two point sources, treated wastewater effluent and surface runoff via storm water drainage, and one diffuse source, deposition from the atmosphere. We examined quantities arriving into marine and estuarine conditions, hereafter referred to simply as marine. Samples were collected from each pathway directly as they passed to receiving waters. Sampling was undertaken in and around two British cities (Plymouth and Bristol), in order to provide generality to the results, rather than to draw comparison between these
locations. Cities were selected based upon their accessibility from the University of Plymouth, whilst being sufficiently spatially distinct from one another.

To assess the mass of tyre particles released from wastewater treatment plants, two replicate 10 L final effluent samples were collected from two treatment plants in Plymouth and two in Bristol (sampling conducted over ~ 45 minutes). Each treatment plant was sampled on two separate occasions, stratified over wet and dry weather conditions (Figure 1A). Note, in the UK during rainfall events combined wastewater plants receive drainage directly from road surface runoff in addition to foul water. The treatment plants served populations of between 3,000 and 65,000 and catchment areas between 1 to 22 km². Treatment varied between secondary and tertiary, and primarily served residential areas (see SI for further details).

The mass of tyre wear within storm water effluent was assessed in a similar manner, but in Plymouth only. Here two replicate 5 L samples were collected in glass Duran jars, as discharge from two surface storm water drains located in urban environments (~0.3 m in diameter, conducted over ~ 30 minutes within the first hour of the rainfall event) that flowed directly into marine waters. Each drain was sampled on two separate occasions (Figure 1B). Sites were selected according to their access and relative geographic spread.

To quantify the deposition of tyre wear from the atmosphere, straight-sided glass dishes (177 cm²) were filled (~ 1 L) 2.5 cm from the surface with deionised water, deployed at ground level for 24 hours 20 m from roadsides during periods of dry weather, capturing atmospheric fallout on the meniscus. Road type was considered an additional factor; samples were collected beside two urban, two rural, and two motorway sites. Sites were selected based primarily upon access and isolation from other roads (sufficient distance between nearby roads), and classified according to the Eurostat Transport Glossary into; motorways, roads inside built up areas (urban) and roads outside built up areas (considered rural), see SI for specific site details. Samples were collected in replicates of two from each sample site on two separate occasions. Following deployment, samples were transferred
into glass Duran bottles, the glass dishes were rinsed three times with deionised water and added to the sample to minimise any loss of material. This process was replicated in both Plymouth and Bristol. In Plymouth only, the same procedure was also carried out at 50 m from the roadside. The experimental design is detailed in Figure 1.

Figure 1 Breakdown of the experimental design, for treated wastewater effluent (A), for surface storm water drainage (B), and for atmospheric deposition (C). On each date, two replicate samples were collected in each case.

To minimise potential interference with the Py-GC-MS analysis glassware was used in place of plastic wherever possible and always prepared in the following manner; washed with detergent, rinsed x 3 with deionised water, soaked in nitric acid (2 %, minimum of 6 hours), rinsed (x 3) in deionised water, covered with aluminium foil and dried. Blank cellulose nitrate membrane filter papers and procedural field blanks were also subject to Py-GC-MS.
Laboratory procedures were undertaken in a limited access laboratory with restricted airflow. Whenever samples were potentially exposed (e.g. during filtration) they were covered with aluminium foil.

Following collection, samples were vacuum filtered through Whatman cellulose nitrate membrane filter papers. Aerial deposition samples were filtered through 0.45 µm. Due to the higher particulate content and larger volumes, wastewater and storm water samples were first passed through 30 µm (stainless steel) and 12 µm (nylon) meshes, and back washed into a beaker with deionised water. Samples were then vacuum pumped through 12 µm.

Benzothiazole, a pyrolysis product from benzothiazole derivatives was selected as a molecular marker for tyre wear during the analytical flash pyrolysis of environmental samples. The conventional approach has been to Soxhlet extract the target molecules e.g. \( N-(1,3\text{-benzothiazol-2-ylsulfanyl})\text{cyclohexanamine} \). Such compounds are present in the “free” solvent-extractable fraction and are consequently susceptible to leaching and weathering. The present study focuses on target molecules that are bound into a polymer which is cross-linked with sulphur into the elastomeric materials based on isoprene, butadiene and styrene-butadiene. When using Py-GC-MS benzothiazole is effective as a single marker for tyres because it arises during pyrolysis from the cleavage of the N-S and C-S bonds of the specific benzothiazolic accelerants that are grafted into the synthetic tyre rubber during the vulcanization process, therefore it is very difficult for them to be leached off and weathered.

Py-GC-MS was carried out using a pulsed-mode system with a model 1000 pyroprobe (CDS Analytical, Oxford, PA, USA) attached via a CDS1500 valved interface (320 °C) to a 6890 GC (Agilent, Santa Clara, CA, USA) that was linked to an Agilent 5973 MSD GC (Agilent, Santa Clara, CA, USA) (ionization energy 70 eV) in full scan mode over the range \( m/z \) 50 – 650. From the centre of region of each filter paper, three 1 x 10 mm strips were cut with a clean scalpel and placed in a quartz pyrolysis tube. The sample was pyrolysed for 10 seconds at 610 °C. A fused silica capillary column (60 m x 0.25 mm i.d) coated with 0.25 µm
5 % phenyl methyl silicone (ZB-5MS) was used to perform separation with helium as the carrier gas. The gas chromatograph was held at 50 °C for 5 minutes and the temperature was increased at a rate of 5 °C/minute to 320 °C where it was held isothermally for 15 minutes.

In order to relate the mass spectral response to tyre wear present in the samples, benzothiazole was quantified from the pyrolysates of fragments of known tyre tread (0.26 mg), analysed in the same manner as described above. The instrument response was measured using a calibration curve of peak intensity versus the weight of an authentic standard of benzothiazole averaged over three pyrolysis runs (R² > 0.99, method as above).

Data were then converted to give a mass of tyre particles per sample. The detection limit of benzothiazole using this method was 1 ng. Some peaks were eluted from the blank cellulose nitrate membrane filter papers, however, these did not yield any detectable concentrations of benzothiazole.

For the atmospheric data, a linear mixed model (R package lme4) was used to test effects road type (fixed factor), with site and date as random factors. After inspection of fits and residuals, data were transformed (log (X+1)) to correct skewed residuals. The two random factors were removed from the model based upon DAIC (DAIC > 2) and lack of change in C² log-likelihood (p > 0.1). Pair-wise planned contrasts were used to compare road types following Hector. The same model was also used to test effects of road type and distance (fixed factors) at Plymouth only, with site retained as a random factor; p-values for the fixed factors were derived from type III SS chi-square tests. Data were transformed in the same manner as above and pair-wise contrasts were used to compare distances within and across road types.

Analysis of variance (ANOVA, in GMav for Windows) was used to compare emissions between wastewater treatment plants, each sampled on 2 independent dates where date and city were random factors. Homogeneity of variance was assessed prior to ANOVA and transformations applied if appropriate. The same process was applied to compare emissions...
between surface water sites within Plymouth only. Standard error of the mean was used for all analysis.

2.2 Evaluation of the relative pathways of tyre wear to the marine environment.

By necessity different approaches and hence metrics were used to quantify diffuse aerial deposition (mg m² d⁻¹), and point source treated wastewater effluent (continuous discharge in mg L⁻¹) and surface runoff drainage (intermittent discharge in mg L⁻¹) and consequently direct comparisons were not possible. In order to broadly evaluate the relative importance of each pathway examined, average emissions from each pathway were scaled up to an estimated annual output in the regions in which sampling took place (mg yr⁻¹). To calculate emissions of tyre wear deposited from the atmosphere, the surface area of marine waters within 50 m of roadsides (and therefore vulnerable to atmospheric contamination) were quantified for the region sampled using ArcGIS 10.7, and scaled to an estimated annual atmospheric deposition load. Annual emissions from storm water drains were estimated based upon the intensity, duration, and frequency of rainfall events that exceeded the predicted total flush out threshold of tyre wear from road surfaces (5 mm d⁻¹)⁵³, calculated from precipitation data recorded in Plymouth and Bristol (for 2017)⁵⁴. On average, such precipitation events lasted 1.5 hours and occurred 44 times a year. It is worth noting that discharge of tyre wear from this pathway will vary further with flow rate (flow rate of surface runoff samples between 0.17 – 25 L s⁻¹), gradient, land use, and surface area of the drainage network served. Furthermore, it is not known at what point in the storm event tyre wear will be ‘flushed out’, or if emissions are continual for the entire event. The preceding period of weather will also be indicative of particle load⁵⁵. Annual effluent emissions (L yr⁻¹) of wastewater treatment plants were calculated from effluent flow data from each plant sampled (averaged over the summer and winter period). The ratio of surface drains to wastewater treatment plants was calculated based upon the distribution at which they were located along waterways in the regions sampled within Plymouth and Bristol, on average every 350 m.
Lastly, given that microplastics are typically reported by abundance and tyre wear by mass due to necessary analytical approaches, further calculations were required in order to evaluate the relative importance of tyre wear. This was achieved by calculating particle mass (based upon particle volume and density, assuming particles to be a capsule shape, and with a density of 1.8 g cm$^{-3}$) of each individual particle measured in image J (see Section 2.3, n=977). The average estimated mass was used to estimate the abundance of tyre particles present in each sample which were compared with emissions of synthetic fibres via the same three pathways. See SI (S7) for further information.

2.3 Evaluation of aquatic transport potential for tyre wear particles.

An evaluation of the transport potential and distribution of tyre particles was used to aid our understating of behaviour once released to marine environments. A series of settling tests were conducted on tyre wear particles harnessed from additional atmospheric samples and from road surface dust (the latter collected from urban road surfaces, 2 g per replicate). Samples were left to settle for periods of 1 minute, 1 hour, and 1 week (over 20 cm). Each test was conducted in replicates of 3. Tyre wear from the surface, middle, and bottom of the settling column (representing the surface, water column, and sedimented particles respectively), were gently separated and vacuum filtered (Whatman glass microfibre filter, 1.2 µm). Around 50 tyre particles were recorded within each replicate. These tests were undertaken in a system with no energy, in the environment wind, waves, and currents may disturb and influence settling behaviour differently to a laboratory setting. They were also conducted in fresh water (0.2 µm ion exchanged), providing a more conservative settling estimate. It is not possible to identify and characterise individual particles by chemical analysis as the process is destructive, and most particles would fall below the limit of detection. Therefore, particles were photographed using a LEICA M205C light microscope and identified by visual examination, based upon their physical and morphological characteristics (size <500 µm, shape - elongated typically with tapered ends, colour - black).

This approach is limited to particles ≥ 15 µm, below which they were excluded from the
analysis. Consequently, any particles identified only by visual means should be considered probable or suspect tyre wear. Tyre wear particles were counted, and measured using Image J. In conjunction a desk-based exercise, calculation of settling velocity (using Stoke’s law), was used to further aid our evaluation of the distribution and transport potential of tyre wear. Settling velocity was calculated for the lowest (1.2 g cm$^{-3}$), highest (2.5 g cm$^{-3}$) and central (1.8 g cm$^{-3}$) reported density estimates of tyre wear, across the size distribution according to Kreider et al.$^{13}$ (4 – 350 µm, where particles were generated on a road simulator in a laboratory). The calculation was repeated for fresh and saline water density (1 g cm$^{-3}$ and 1.027 g cm$^{-3}$ respectively). A further assumption of Stoke’s Law is that all particles as spherical. This was then applied to the sample region of Plymouth with the caveat of a uniform water depth, direction, and flow rate.

A small number of tyre particles (~ n = 23, harnessed from additional environmental samples) isolated (visually as described above) from each pathway to the environment were imaged by scanning electron microscopy. A greater selection of particles (photographed prior to Py-GC-MS, n = 977) were photographed on a LEICA M205C light microscope and identified and measured using Image J as described above, in order to characterise and compare dimensions of particles between pathways.

3.0 Results.

3.1 Quantification of tyre particles at their points of entry to the environment

Particles recovered from the environment (Figure 2A) appeared highly heterogeneous in their size, shape and proportion of tyre wear to road surface materials (the latter visible in Figure 2B). Particles recovered from atmospheric deposition, treated wastewater effluent, and from surface drainage measured between 15 µm (the smallest detectable length) and 415 µm, with an average length of 43 µm, and a mode centred around 20 µm. The average aspect ratio was 0.4:1. Differences in particle dimensions were notable between pathways;
on average longest within surface runoff (42 µm), followed by deposition from the atmosphere (36 µm), and treated wastewater effluent (21 µm).

Figure 2 Tyre wear particles isolated from storm water drain material (A), and at greater magnification to show a rough exterior and incorporation of road surface and other materials (B), an example highlighted with a red arrow. Plymouth Electron Microscopy Centre, 2019.

Benzothiazole (the molecular marker chosen for tyre wear) was detected by Py-GC-MS during the pyrolysis of particles isolated from each pathway examined. Benzothiazole is not the vulcanizer *per se* but is a predominant pyrolysis product of the primary vulcanization accelerators used in tyre production. Vulcanization accelerators make up 1.2 % in relative content of scrap tyres and include the thiazoles, sulfonamides, thiurams and guanidine\(^{57}\).

Aside from guanidine all of these compounds will generate benzothiazole during pyrolysis. The reference car tyre was analysed in triplicate and benzothiazole was equal to 0.9 % of the total pyrolysate. Data for the ‘average tyre’ in the UK is not published so we can only compare with Pan *et al.*\(^{57}\) which indicates that the relative amount of components likely to generate benzothiazoles in the reference tyre is analogous with their content in the global scrap tyre repository.

Within wastewater effluent 50 % of the samples contained measurable concentrations of benzothiazole (above 1 ng LOD), compared to 88 % in surface runoff, and 98 % within aerial
Values below the LOD were included as zeros as they did not generate quantifiable concentrations of benzothiazole, which is a conservative approach. Peaks corresponding to benzothiazole were not detected in the procedural field blanks analysed by Py-GC-MS.

Within treated wastewater effluent and storm water runoff tyre wear was detected on average at a mass of 0.02 ± 0.01 mg L\(^{-1}\) (\(\bar{x} \pm \text{SE}\)) and 2.5 ± 1 mg L\(^{-1}\) (\(\bar{x} \pm \text{SE}\)) respectively, and within aerial deposition at 24.7 ± 2.6 mg m\(^{2}\) d\(^{-1}\) (\(\bar{x} \pm \text{SE}\)).

The presence of tyre wear was significantly greater at wastewater treatment plant 2 (ANOVA, \(p<0.05, \text{df}=3\)), where the highest concentration was detected (0.3 mg L\(^{-1}\)), than at plants 1, 3 and 4. However, when the mass was normalised by the population served (per 10,000 people), significant effects were no longer observed (ANOVA df = 3, \(p>0.05\)). The same was true when mass was normalised by catchment area served (km\(^{2}\)), see Figure 3 (ANOVA df = 3, \(p>0.05\)).

![Figure 3](image)

**Figure 3** Average concentrations of tyre wear in final effluent collected from four wastewater treatment plants normalised by catchment areas in mg L\(^{-1}\) km\(^{2}\). 'ns' indicated no significant differences. Error bars represent standard error.

Variability in the mass of tyre wear recorded between storm water drains was observed (Figure 4), but was not found to be significant (ANOVA df= 1, \(p>0.05\)). The highest mass
was recorded at outfall 2, at 8.2 mg L\(^{-1}\). It was not possible to confidently assess the area served by the storm water drains sampled and therefore not possible to normalise the data by catchment area.

**Figure 4** Average concentrations of tyre wear in effluent from two storm water drains (mg L\(^{-1}\)), 'ns' indicates no significant differences. Error bars represent standard error.

Within atmospheric fallout, the average mass of tyre particles deposited 20 m from urban, rural, and motorways were 29.9 ± 6.1 mg m\(^2\) d\(^{-1}\) (\(\bar{x} \pm SE\)), 10.8 ± 2 mg m\(^2\) d\(^{-1}\) (\(\bar{x} \pm SE\)), and 42.6 ± 7.4 mg m\(^2\) d\(^{-1}\) (\(\bar{x} \pm SE\)) respectively (Figure 5A). The highest mass was recorded 20 m besides a motorway site at 97.04 mg m\(^2\). The mass of tyre wear beside motorways was significantly greater than urban and rural emissions (ANOVA, Satterthwaites method, \(p < 0.05\), df = 18). On average, tyre wear deposited beside urban roadsides was more than twofold that of rural, but was not found to be significant (planned contrast, \(p > 0.05\), df = 18).

Tyre wear was recorded at an average mass of 27.5 ± 5.1 mg m\(^2\) d\(^{-1}\) (\(\bar{x} \pm SE\)) 20 m from roadsides, and 18.6 ± 2.4 mg m\(^2\) d\(^{-1}\) (\(\bar{x} \pm SE\)) 50 m from roadsides (Figure 5B). The highest masses recorded at a site 20 m and 50 m from roadsides were 97.04 mg m\(^2\) and 36.64 mg m\(^2\) respectively. Despite the presence of tyre wear typically declining (on average by 1/3rd) at the distances examined in this study, the difference between samples collected at 20 m and 50 m was not significant (ANOVA. Satterthwaites method, \(p > 0.05\), df = 18).
Figure 5 Average concentrations of tyre wear (mg m\(^{-2}\) d\(^{-1}\)) deposited from the atmosphere, (A) collected 20 m from urban, rural, and motorway roadsides, and (B) 20 m and 50 m from roadsides urban, rural, and motorway roadsides. Different symbols denote bars that are statistically different, ‘ns’ indicates no significant differences.

Analysis conducted on data prior to scaling. Error bars represent standard error.

3.2 Transport potential and distribution of tyre wear particles.

The majority of particles (~ 80 ± 3.2 %) settled to the bottom of the chamber within the first minute. Little difference in the settling behaviour was observed between 1 hour and 1 week, after which approximately 85 % of particles had settled.

The estimated settling velocities of tyre particles between 4 and 350 \(\mu\)m according to Stoke’s law ranged from 0.1 to 0.00001 m s\(^{-1}\). Particles measuring less than 15 \(\mu\)m in length, that account for a large percentage of the total size distribution according to Kreider \textit{et al.}\(^{13}\) are estimated to settle at a rate between 0.00001 and 0.0001 m s\(^{-1}\), whereas those on the larger end of the spectrum (that account for a smaller percentage of total abundance\(^{13}\)) are estimated to settle much quicker (0.1 to 0.01 m s\(^{-1}\)), see S5 and S6 for further details.

4.0 Discussion
This study presents data evidencing treated wastewater effluent, surface runoff, and atmospheric fallout all serve as pathways for tyre wear to marine waters. While some data exist on the presence of tyre wear in different environmental mediums, this study provides novel empirical evidence of tyre wear particles explicitly entering the marine environment, and hence directly contributing to microplastic emissions. The proportion of samples containing measurable quantities of benzothiazole within these pathways (98 % within aerial deposition, 50 % within wastewater effluent, and 88 % within surface runoff) further suggests that tyre wear contamination was widespread. This study facilitates comparison of the primary data with existing desk-based modelled estimates e.g. by Sundt et al.6 Lassen et al.8 Essel et al.11 Magnusson et al.16 Boucher and Froit17 and Eunomia18.

The heterogeneous nature of the tyre particles recorded in this study is in agreement with previous reports suggesting tyre wear to be diverse in size (reported between 0.1 and 350 µm)13,14, density (0.94 and 2.5 g cm⁻³)3,4,6,13,51,53,55,56 and relative encrustment of tyre to road wear (0.1:1 to 0.5:1)46.

Previous studies suggest the generation of tyre wear particles is influenced by: vehicle operation29,58, tyre and road characteristics, climate, road type and traffic density3,19,30,34,36,55,59,60,61. Although they account for a small portion of total mileage, driving on urban networks is subject to amplified cornering, braking, and accelerating62,63, resulting a greater rate of wear than rural roads or motorways31,36. The present study indicated that motorway traffic released the greatest mass of tyre wear. In the absence of traffic count data (preventing estimates of tyre wear emissions per vehicle), it is not possible to ascertain if this is attributable to the traffic load, or speed of driving typical of motorways. Increased vehicle speed has previously been evidenced to increase particle generation by Dahl et al.58.

Atmospheric fallout of tyre wear was typically greater closer to the roadside but this effect was short of statistical significance (p <0.05). This suggests that a portion of tyre wear released to the atmosphere settles close to the point of emission, previous reports suggesting particles in excess of 10 µm34 are deposited on, or in close proximity to the road
This is in agreement with earlier studies that report tyre wear concentrations to decrease with distance from the source within ambient air soils and road dust. However, the data also indicates some tyre wear has the potential to travel at least 50 m from the roadside, indicating it to be a key pathway for tyre wear pollution to aquatic environments. Once released into the atmosphere, the transport potential of these particles remains largely unknown and empirical evidence beyond the tests in this study is lacking. It has been suggested that airborne tyre particles in the range of 1-10 μm have residence times from minutes to hours, while those in the smallest size range of tyre wear (<1 μm), are potentially analogous with PM$_{2.5}$, and could remain in the atmosphere for days to weeks, traveling 1000’s of kilometres.

While plant 2 emitted significantly greater tyre wear than plants 1, 3 and 4, normalising the mass of tyre wear within wastewater effluent by catchment area and the serving population removed significant differences between treatment plants. This could indicate that the environment in which the plant is located (e.g. catchment size and local population) could in part be explained as drivers in the extent of tyre wear contamination released in treated wastewater effluent. The mass of tyre wear within wastewater effluent (0.02 mg L$^{-1}$) was lower compared with a previous study (1 mg L$^{-1}$).

Brodie estimated that tyre particles remain on the road surface until a critical precipitation intensity is reached; Unice et al. predicts a total flush out of particles when rainfall exceeds 5 mm d$^{-1}$. Drain sumps (pits at the bottom of surface drains) are designed to capture solids in runoff. However, retention of particles <50 μm is thought to be poor even during slow flow rates and retention could be further reduced if the sump is at capacity. The greatest emissions of tyre wear from wastewater effluent was recorded at treatment plant 2 (0.15 mg L$^{-1}$). This coincided with an intense rainfall event (9.6 mm d$^{-1}$) where the treatment plant exceeded its treatment capacity, discharging effluent subject only to primary screening and settling. Any benzothiazole detected being discharged during drier conditions may be attributable to sources other than tyre tread, tyre wear being residual contaminant in the
system, or the exposed nature of wastewater treatment plants lending themselves to
contamination from the atmosphere.

The mass of tyre wear discharged on average from surface water drainage was lower, but
largely agreeable with previous estimates 12 to 179 mg L\(^{-1}\)\(^{26,28,42,43,47-49}\). Emissions via this
pathway were also orders of magnitude greater than in treated wastewater effluent.

However, it is not possible to directly compare the emissions between the two as one emits
continually and one intermittently. It is also not possible to directly compare with atmospheric
deposition due to the units with which tyre wear was quantified. The calculations detailed in
Section 2.2 allow an estimation of emissions of tyre wear in a common unit (annually over
the sample region), providing a broad assessment of the relative importance of each
pathway examined within the study areas of Plymouth and Bristol.

In agreement with Sundt \textit{et al.}\(^6\), the largest emissions of tyre wear to aquatic environments,
within the two regions and three pathways examined, were emitted from storm water drains,
2.5 and 4 times greater than emissions from wastewater effluent and atmospheric deposition
respectively, which occurred on average every 350 m along the waterways sampled in both
Bristol and Plymouth (agreeable in both locations), indicating a key point for intervention. For
example, Gilbreath \textit{et al.}\(^{68}\) indicated the retention of anthropogenic particles (including
synthetic rubber) in surface water treatment bioretention gardens. Secondary to surface
water discharge, despite only being detected in half of the samples analysed, the release of
tyre wear within wastewater effluent presents another considerable pathway, attributable to
the sheer volumes processed and constant emissions. Transport in the atmosphere does not
appear to be considered in previous modelled estimates\(^{6,8,11,16-18}\). Our study indicates the
atmosphere does present a pathway for tyre wear to aquatic environments (4 times less than
stormwater and 1.5 times less than wastewater) but more work is needed to assess the
transport of tyre wear via this medium at greater distances from the source to ascertain its
overall importance in contamination of different habitats.
Our findings should also be considered in the context of transport within aquatic environments. In agreement with Kooi et al.\textsuperscript{51} and Unice et al.\textsuperscript{56} estimated settling velocities indicate that particle size appears to be most influential in settling rate of tyre wear. Particles at the larger end of the spectrum are likely to settle close to the point of emission, and as particle size decreases, the transport potential is likely to increase considerably, as was also evident from our laboratory experiment which saw 15% of tyre wear particles still present at the water’s surface after periods of an hour and a week. This should be considered in conjunction with the size distribution of tyre wear, which indicates that by abundance, smaller particles make up the bulk of the particulates\textsuperscript{13}. These initial findings broadly agree with Unice et al.\textsuperscript{56} who estimated in a mass balance modelling effort, considerable retention of tyre wear within fresh water systems, but further noted a portion of particles (0.97 - 13%) could be exported. Furthermore, some emissions do not pass through fresh water systems but are released directly to marine waters. Given the magnitude at which tyre wear is generated, even a small fraction of the total mass equates to substantial loads. Alternatively, for particles that are more dense, accumulation in relatively high concentrations close to points of entry, could also pose environmental concern.

The units used to quantify tyre wear (mass) do not allow direct comparisons with other microplastics sources known to be abundant in the marine environment (e.g. synthetic fibres) that are typically quantified by numerical abundance. Following a crude conversion of tyre mass to abundance (see S7), the presence of tyre wear within storm water, wastewater effluent, and atmospheric deposition eclipsed that of synthetic fibre emissions by 6, 5 and 4 orders of magnitude respectively. Given their apparent prevalence and relative importance to other sources, and results being comparable to limited existing reports suggests findings are in agreement with top-down modelled estimates; tyre wear being a major, but notably an additional contributor to microplastic emissions to the environment. This suggests the lack of previous reporting of tyre wear in marine environmental samples is likely a consequence of inappropriate methods for quantification, rather than a low environmental presence.
Transport potential of these particles once in the marine environment should form a key part of further research. This could incorporate quantifying the presence of tyre wear in the marine environment with increasing distance from their input and from remote or isolated locations.

We propose future work should consider a mass balance approach, quantifying tyre wear from their points of generation, to their entry, transport, and distribution in the marine environment. Further work should also consider both the toxicity of the particles, and the leachate and sample under different rainfall conditions. Rainfall could influence tyre particle distribution via suspension in surface flow, but could also hinder generation due to reduce friction at the tyre road interface. Furthermore, some factors examined here (distance, road type – urban versus rural) were approaching statistical significance; greater replication may prove insightful. Further work should also establish the potential for longer-range transport within the atmosphere. To further findings from this study, sampling a wider range of catchments both temporally and spatially may enable scaling of results to a national level to better provide evidence for policy change.

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