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

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11 **Abstract**

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

25 **Key words:** Tire wear, Vehicle emissions, Microplastics, Surface runoff, Atmospheric
26 deposition, Wastewater treatment, Marine pollution

27 **1.0 Introduction**

28 Plastics are durable, versatile, inexpensive materials that bring societal benefits in a wide
29 range of applications, across all aspects of everyday life¹⁻³. Fragments of plastic generated
30 from deterioration of macroplastics, or small manufactured particles (<5 mm), termed
31 microplastics, have been recognised as a widespread contaminant in the environment since
32 2004⁴. Tyre wear particles are frequently regarded as microplastics, being small^{1,3,5,6,7,8},
33 solid in state⁸, comprised primarily of synthetic polymer^{3,8}, insoluble in water³, and durable in
34 the environment^{3,9-11}. The formation of tyre wear particles occurs at the tyre-road interface
35 due to frictional energy, producing microparticles, often referred to as tyre-road wear
36 particles (TRWPs)¹² due to the potential incorporation of road surface wear. They are
37 characteristically thin and cylindrical with tapered ends and are black in colour¹³.

38 Despite having been described as environmental contaminants since the 1970s^{14,15} the
39 contribution of tyre wear to microplastic contamination has only recently been
40 highlighted^{6,8,11,16}. These studies^{6,8,11,16} take a top-down desk-based approach, indicating tyre
41 wear contributes a substantial quantity to the total microplastic load; yet reliable empirical
42 data are lacking. These studies have provided the foundation for broader extrapolative
43 reports^{17,18}.that estimate emissions of tyre particles to be similar, and in some cases greater,
44 than other types of microplastic such as synthetic fibres, that are known to be widespread in
45 the environment.

46 In contrast to desk-based estimates, the frequency with which tyre wear particles are
47 reported in environmental samples is low¹⁹. This could be attributable to an inability to
48 confidently isolate and quantify tyre wear using methods typically utilised for microplastic
49 analysis such as density separation and spectroscopy²⁰. Alternatively it has been
50 demonstrated that the analytical flash pyrolysis of tyre wear can be a useful tool for

51 quantification in the environment^{14,21}. The presence of styrene, isoprene and dipentene in
52 flash pyrolysates have all been used as markers for tyre tread components styrene-
53 butadiene, isoprene and natural rubber^{14,15,22, 23}, however these markers have limitations if
54 other major sources to the environment exist. Benzothiazole however is not common in
55 natural products²⁴ and so despite a small number of applications (some biocides, antifreeze,
56 or anti algal agents)²⁵⁻²⁷ these sources do not produce substantial or continual emissions of
57 benzothiazole to the environment²⁶⁻²⁸ compared to its use as vulcanisation accelerators in
58 tyre tread (approx. 0.5 – 2 %)^{26,29,30}. This approach of using the molecules bound into the
59 synthetic rubber polymers has not been widely used to measure prevalence of tyre wear with
60 respect to emissions to the marine environment.

61 Evidence suggests that tyre wear is generated in considerable quantities, with tyres
62 shedding 10 – 50 % of their tread weight to the environment during life in service
63 (approximately 40,000 to 50,000 km)^{29,31-33}, equating to ~0.8 kg yr⁻¹ per capita globally³⁴.
64 This is important when considered in conjunction with the number of vehicles on the road
65 globally, estimated over 1 billion and expected to exceed 2 billion by 2040³⁵. Generation of
66 tyre particles is also thought to vary considerably between road types¹⁹; and driving
67 behaviour³⁶.

68 Tyre wear has been reported in ambient air (in proximity to roadways) in the range of 0.5 to
69 11 µg m⁻³^{14,15,37,22,23,26,28,38} however data on atmospheric deposition is lacking. Tyre wear
70 within road dust has been reported between 0.7 and 210 g kg⁻¹^{39,40,37,28,41,42,43}. While textured
71 road surfaces can retain particles⁴⁴, a sizeable portion of tyre wear deposited on roads may
72 be mobilised by wind, or during precipitation events^{45,46,20}. Upon mobilisation by surface
73 water particles will either run to nearby soils or into surface drains and combined sewers.
74 Once within combined systems surface flow is passed into storm water tanks and treated,
75 and discharged as final effluent. One study reported the mass of tyre wear discharged in
76 combined wastewater treatment effluent at 1 mg L⁻¹⁴⁷. Whereas tyre wear within road
77 surface runoff has been reported in the range of 12 to 179 mg L⁻¹^{26,28,42,43,47,48,49} and may

78 pass directly into aquatic environments without treatment. It is worth noting tyre wear
79 retained in the sludge fraction may also be returned to land as fertilizer which could be
80 mobilised during rainfall events into waterways²⁰.

81 If tyre particles enter aquatic environments, their distribution within the water column and
82 transport potential remains largely unknown. Recipient waters such as rivers and estuaries
83 may act as a pathway of tyre wear to the marine environment. Conversely, they could also
84 provide a sink via sedimentation²⁰. Using chemical markers to quantify tyre wear, previous
85 studies have reported greater concentrations within sediments than surface waters^{30,50,51}.

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

95 **2.0 Materials and methods**

96 *2.1 Quantification of tyre particles at their points of entry to the marine environment*

97 Three principal routes for tyre wear particles to enter the marine environment were
98 considered: two point sources, treated wastewater effluent and surface runoff via storm
99 water drainage, and one diffuse source, deposition from the atmosphere. We examined
100 quantities arriving into marine and estuarine conditions, hereafter referred to simply as
101 marine. Samples were collected from each pathway directly as they passed to receiving
102 waters. Sampling was undertaken in and around two British cities (Plymouth and Bristol), in
103 order to provide generality to the results, rather than to draw comparison between these

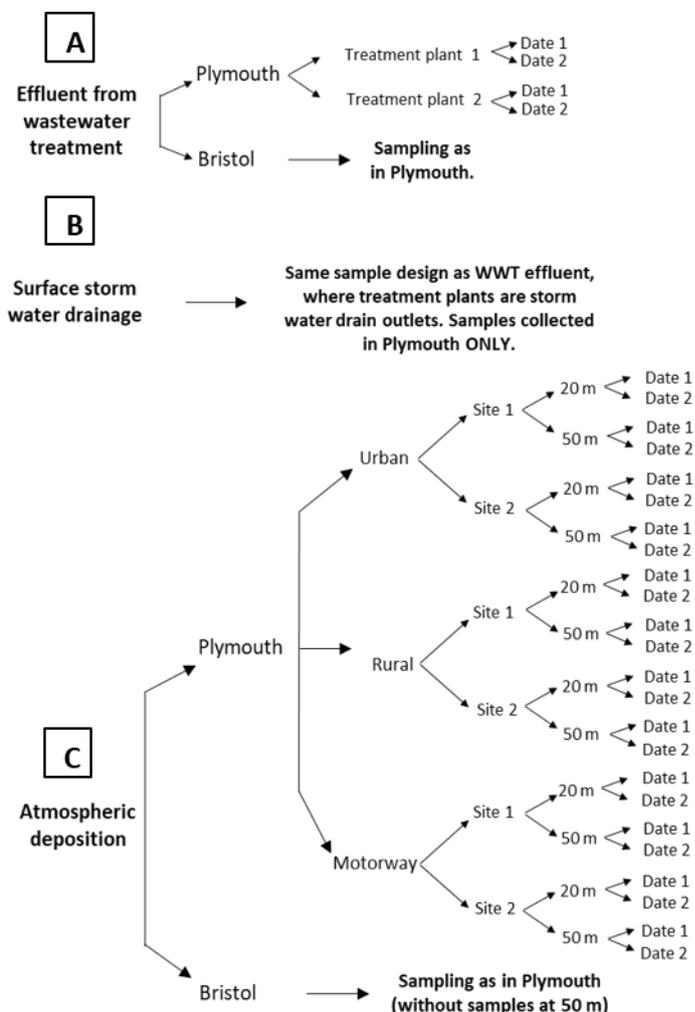
104 locations. Cities were selected based upon their accessibility from the University of
105 Plymouth, whilst being sufficiently spatially distinct from one another.

106 To assess the mass of tyre particles released from wastewater treatment plants, two
107 replicate 10 L final effluent samples were collected from two treatment plants in Plymouth
108 and two in Bristol (sampling conducted over ~ 45 minutes). Each treatment plant was
109 sampled on two separate occasions, stratified over wet and dry weather conditions (Figure
110 1A). Note, in the UK during rainfall events combined wastewater plants receive drainage
111 directly from road surface runoff *in addition* to foul water²⁰. The treatment plants served
112 populations of between 3,000 and 65,000 and catchment areas between 1 to 22 km².
113 Treatment varied between secondary and tertiary, and primarily served residential areas
114 (see SI for further details).

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

121 To quantify the deposition of tyre wear from the atmosphere, straight-sided glass dishes
122 (177 cm²) were filled (~ 1 L) 2.5 cm from the surface with deionised water, deployed at
123 ground level for 24 hours 20 m from roadsides during periods of dry weather, capturing
124 atmospheric fallout on the meniscus. Road type was considered an additional factor;
125 samples were collected beside two urban, two rural, and two motorway sites. Sites were
126 selected based primarily upon access and isolation from other roads (sufficient distance
127 between nearby roads), and classified according to the Eurostat Transport Glossary into;
128 motorways, roads inside built up areas (urban) and roads outside built up areas (considered
129 rural), see SI for specific site details. Samples were collected in replicates of two from each
130 sample site on two separate occasions. Following deployment, samples were transferred

131 into glass Duran bottles, the glass dishes were rinsed three times with deionised water and
 132 added to the sample to minimise any loss of material. This process was replicated in both
 133 Plymouth and Bristol. In Plymouth only, the same procedure was also carried out at 50 m
 134 from the roadside. The experimental design is detailed in Figure 1.



135
 136 **Figure 1** Breakdown of the experimental design, for treated wastewater effluent (A), for surface storm water
 137 drainage (B), and for atmospheric deposition (C). On each date, two replicate samples were collected in each
 138 case.

139 To minimise potential interference with the Py-GC-MS analysis glassware was used in place
 140 of plastic wherever possible and always prepared in the following manner; washed with
 141 detergent, rinsed x 3 with deionised water, soaked in nitric acid (2 %, minimum of 6 hours),
 142 rinsed (x 3) in deionised water, covered with aluminium foil and dried. Blank cellulose nitrate
 143 membrane filter papers and procedural field blanks were also subject to Py-GC-MS.

144 Laboratory procedures were undertaken in a limited access laboratory with restricted airflow.
145 Whenever samples were potentially exposed (e.g. during filtration) they were covered with
146 aluminium foil.

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

152 Benzothiazole, a pyrolysis product from benzothiazole derivatives²⁸ was selected as a
153 molecular marker for tyre wear during the analytical flash pyrolysis of environmental
154 samples. The conventional approach²⁸ has been to Soxhlet extract the target molecules e.g.
155 *N*-(1,3-benzothiazol-2-ylsulfanyl)cyclohexanamine). Such compounds are present in the
156 “free” solvent-extractable fraction and are consequently susceptible to leaching and
157 weathering. The present study focuses on target molecules that are bound into a polymer
158 which is cross-linked with sulphur into the elastomeric materials based on isoprene,
159 butadiene and styrene-butadiene. When using Py-GC-MS benzothiazole is effective as a
160 single marker for tyres because it arises during pyrolysis from the cleavage of the N-S and
161 C-S bonds of the specific benzothiazolic accelerants that are grafted into the synthetic tyre
162 rubber during the vulcanization process, therefore it is very difficult for them to be leached off
163 and weathered.

164 Py-GC-MS was carried out using a pulsed-mode system with a model 1000 pyroprobe (CDS
165 Analytical, Oxford, PA, USA) attached via a CDS1500 valved interface (320 °C) to a 6890
166 GC (Agilent, Santa Clara, CA, USA) that was linked to an Agilent 5973 MSD GC (Agilent,
167 Santa Clara, CA, USA) (ionization energy 70 eV) in full scan mode over the range *m/z* 50 –
168 650. From the centre of region of each filter paper, three 1 x 10 mm strips were cut with a
169 clean scalpel and placed in a quartz pyrolysis tube. The sample was pyrolysed for 10
170 seconds at 610 °C. A fused silica capillary column (60 m x 0.25 mm i.d) coated with 0.25 µm

171 5 % phenyl methyl silicone (ZB-5MS) was used to perform separation with helium as the
172 carrier gas. The gas chromatograph was held at 50 °C for 5 minutes and the temperature
173 was increased at a rate of 5 °C/minute to 320 °C where it was held isothermally for 15
174 minutes.

175 In order to relate the mass spectral response to tyre wear present in the samples,
176 benzothiazole was quantified from the pyrolysates of fragments of known tyre tread (0.26
177 mg), analysed in the same manner as described above. The instrument response was
178 measured using a calibration curve of peak intensity versus the weight of an authentic
179 standard of benzothiazole averaged over three pyrolysis runs ($R^2 > 0.99$, method as above).
180 Data were then converted to give a mass of tyre particles per sample. The detection limit of
181 benzothiazole using this method was 1 ng. Some peaks were eluted from the blank cellulose
182 nitrate membrane filter papers, however, these did not yield any detectable concentrations of
183 benzothiazole.

184 For the atmospheric data, a linear mixed model (R package lme4) was used to test effects
185 road type (fixed factor), with site and date as random factors. After inspection of fits and
186 residuals, data were transformed ($\log(X+1)$) to correct skewed residuals. The two random
187 factors were removed from the model based upon DAIC ($DAIC > 2$) and lack of change in C^2
188 log-likelihood ($p > 0.1$). Pair-wise planned contrasts were used to compare road types
189 following Hector⁵² The same model was also used to test effects of road type and distance
190 (fixed factors) at Plymouth only, with site retained as a random factor; p-values for the fixed
191 factors were derived from type III SS chi-square tests. Data were transformed in the same
192 manner as above and pair-wise contrasts were used to compare distances within and across
193 road types.

194 Analysis of variance (ANOVA, in GMav for Windows) was used to compare emissions
195 between wastewater treatment plants, each sampled on 2 independent dates where date
196 and city were random factors. Homogeneity of variance was assessed prior to ANOVA and
197 transformations applied if appropriate. The same process was applied to compare emissions

198 between surface water sites within Plymouth only. Standard error of the mean was used for
199 all analysis.

200 *2.2 Evaluation of the relative pathways of tyre wear to the marine environment.*

201 By necessity different approaches and hence metrics were used to quantify diffuse aerial
202 deposition ($\text{mg m}^2 \text{d}^{-1}$), and point source treated wastewater effluent (continuous discharge
203 in mg L^{-1}) and surface runoff drainage (intermittent discharge in mg L^{-1}) and consequently
204 direct comparisons were not possible. In order to *broadly* evaluate the relative importance of
205 each pathway examined, average emissions from each pathway were scaled up to an
206 estimated annual output in the regions in which sampling took place (mg yr^{-1}). To calculate
207 emissions of tyre wear deposited from the atmosphere, the surface area of marine waters
208 within 50 m of roadsides (and therefore vulnerable to atmospheric contamination) were
209 quantified for the region sampled using ArcGIS 10.7, and scaled to an estimated annual
210 atmospheric deposition load. Annual emissions from storm water drains were estimated
211 based upon the intensity, duration, and frequency of rainfall events that exceeded the
212 predicted total flush out threshold of tyre wear from road surfaces (5 mm d^{-1})⁵³, calculated
213 from precipitation data recorded in Plymouth and Bristol (for 2017)⁵⁴. On average, such
214 precipitation events lasted 1.5 hours and occurred 44 times a year. It is worth noting that
215 discharge of tyre wear from this pathway will vary further with flow rate (flow rate of surface
216 runoff samples between $0.17 - 25 \text{ L s}^{-1}$), gradient, land use, and surface area of the
217 drainage network served. Furthermore, it is not known at what point in the storm event tyre
218 wear will be 'flushed out', or if emissions are continual for the entire event. The preceding
219 period of weather will also be indicative of particle load⁵⁵. Annual effluent emissions (L yr^{-1})
220 of wastewater treatment plants were calculated from effluent flow data from each plant
221 sampled (averaged over the summer and winter period). The ratio of surface drains to
222 wastewater treatment plants was calculated based upon the distribution at which they were
223 located along waterways in the regions sampled within Plymouth and Bristol, on average
224 every 350 m.

225 Lastly, given that microplastics are typically reported by abundance and tyre wear by mass
226 due to necessary analytical approaches, further calculations were required in order to
227 evaluate the relative importance of tyre wear. This was achieved by calculating particle mass
228 (based upon particle volume and density, assuming particles to be a capsule shape, and
229 with a density of 1.8 g cm^3 ,⁵⁶) of each individual particle measured in image J (see Section
230 2.3, n=977). The average estimated mass was used to estimate the abundance of tyre
231 particles present in each sample which were compared with emissions of synthetic fibres via
232 the same three pathways. See SI (S7) for further information.

233 *2.3 Evaluation of aquatic transport potential for tyre wear particles.*

234 An evaluation of the transport potential and distribution of tyre particles was used to aid our
235 understating of behaviour once released to marine environments. A series of settling tests
236 were conducted on tyre wear particles harnessed from additional atmospheric samples and
237 from road surface dust (the latter collected from urban road surfaces, 2 g per replicate).

238 Samples were left to settle for periods of 1 minute, 1 hour, and 1 week (over 20 cm). Each
239 test was conducted in replicates of 3. Tyre wear from the surface, middle, and bottom of the
240 settling column (representing the surface, water column, and sedimented particles
241 respectively), were gently separated and vacuum filtered (Whatman glass microfibre filter,
242 $1.2 \mu\text{m}$). Around 50 tyre particles were recorded within each replicate. These tests were
243 undertaken in a system with no energy, in the environment wind, waves, and currents may
244 disturb and influence settling behaviour differently to a laboratory setting. They were also
245 conducted in fresh water ($0.2 \mu\text{m}$ ion exchanged), providing a more conservative settling
246 estimate. It is not possible to identify and characterise individual particles by chemical
247 analysis as the process is destructive, and most particles would fall below the limit of
248 detection. Therefore, particles were photographed using a LEICA M205C light microscope
249 and identified by visual examination, based upon their physical and morphological
250 characteristics (size $<500 \mu\text{m}$, shape - elongated typically with tapered ends, colour - black).

251 This approach is limited to particles $\geq 15 \mu\text{m}$, below which they were excluded from the

252 analysis. Consequently, any particles identified only by visual means should be considered
253 probable or suspect tyre wear. Tyre wear particles were counted, and measured using
254 Image J. In conjunction a desk-based exercise, calculation of settling velocity (using Stoke's
255 law), was used to further aid our evaluation of the distribution and transport potential of tyre
256 wear. Settling velocity was calculated for the lowest (1.2 g cm^3), highest (2.5 g cm^3)⁴⁶ and
257 central (1.8 g cm^3)⁵⁶ reported density estimates of tyre wear, across the size distribution
258 according to Kreider *et al.*¹³ (4 – 350 μm , where particles were generated on a road
259 simulator in a laboratory). The calculation was repeated for fresh and saline water density (1
260 g cm^3 and 1.027 g cm^3 respectively). A further assumption of Stoke's Law is that all particles
261 as spherical. This was then applied to the sample region of Plymouth with the caveat of a
262 uniform water depth, direction, and flow rate.

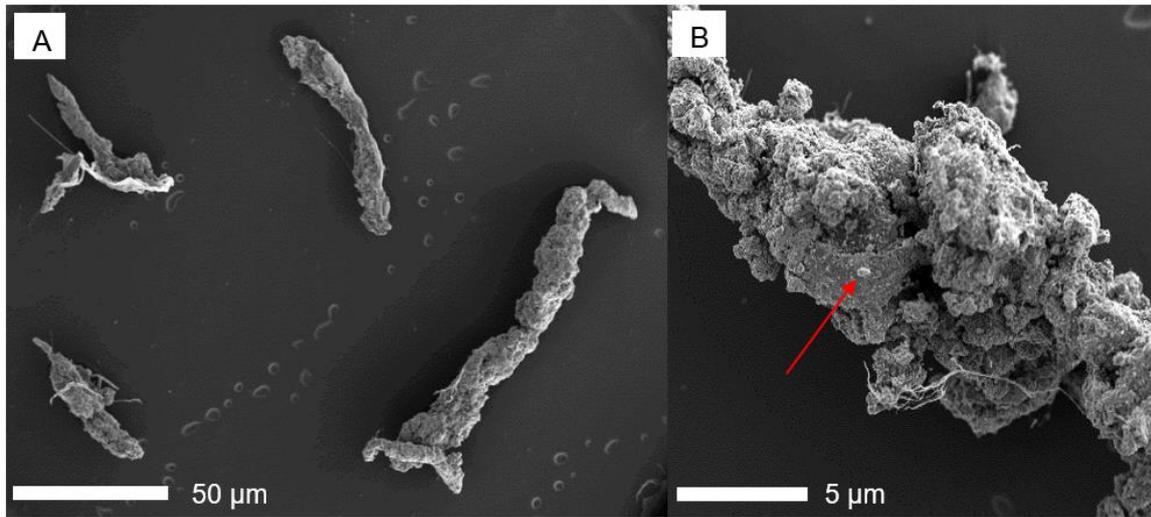
263 A small number of tyre particles (~ $n = 23$, harnessed from additional environmental
264 samples) isolated (visually as described above) from each pathway to the environment were
265 imaged by scanning electron microscopy. A greater selection of particles (photographed
266 prior to Py-GC-MS, $n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

269 **3.0 Results.**

270 *3.1 Quantification of tyre particles at their points of entry to the environment*

271 Particles recovered from the environment (Figure 2A) appeared highly heterogeneous in
272 their size, shape and proportion of tyre wear to road surface materials (the latter visible in
273 Figure 2B). Particles recovered from atmospheric deposition, treated wastewater effluent,
274 and from surface drainage measured between 15 μm (the smallest detectable length) and
275 415 μm , with an average length of 43 μm , and a mode centred around 20 μm . The average
276 aspect ratio was 0.4:1. Differences in particle dimensions were notable between pathways;

277 on average longest within surface runoff (42 μm), followed by deposition from the
278 atmosphere (36 μm), and treated wastewater effluent (21 μm).



279

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

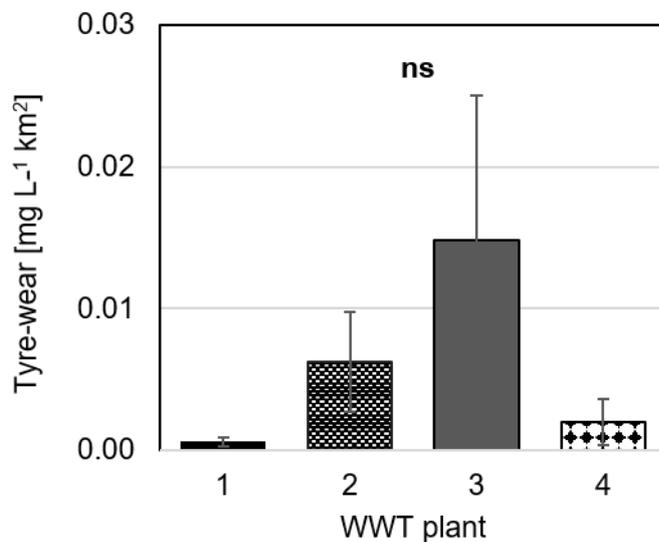
283 Benzothiazole (the molecular marker chosen for tyre wear) was detected by Py-GC-MS
284 during the pyrolysis of particles isolated from each pathway examined. Benzothiazole is not
285 the vulcanizer *per se* but is a predominant pyrolysis product of the primary vulcanization
286 accelerators used in tyre production. Vulcanization accelerators make up 1.2 % in relative
287 content of scrap tyres and include the thiazoles, sulfonamides, thiurams and guanidine⁵⁷.
288 Aside from guanidine all of these compounds will generate benzothiazole during pyrolysis.
289 The reference car tyre was analysed in triplicate and benzothiazole was equal to 0.9 % of
290 the total pyrolysate. Data for the 'average tyre' in the UK is not published so we can only
291 compare with Pan *et al.*⁵⁷ which indicates that the relative amount of components likely to
292 generate benzothiazoles in the reference tyre is analogous with their content in the global
293 scrap tyre repository.

294 Within wastewater effluent 50 % of the samples contained measurable concentrations of
295 benzothiazole (above 1 ng LOD), compared to 88 % in surface runoff, and 98 % within aerial

296 fallout. Values below the LOD were included as zeros as they did not generate quantifiable
297 concentrations of benzothiazole, which is a conservative approach. Peaks corresponding to
298 benzothiazole were not detected in the procedural field blanks analysed by Py-GC-MS.

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

302 The presence of tyre wear was significantly greater at wastewater treatment plant 2
303 (ANOVA. $p < 0.05$, $df = 3$), where the highest concentration was detected (0.3 mg L^{-1}), than
304 at plants 1, 3 and 4. However, when the mass was normalised by the population served (per
305 10,000 people), significant effects were no longer observed (ANOVA $df = 3$, $p > 0.05$). The
306 same was true when mass was normalised by catchment area served (km^2), see Figure 3
307 (ANOVA $df = 3$, $p > 0.05$).

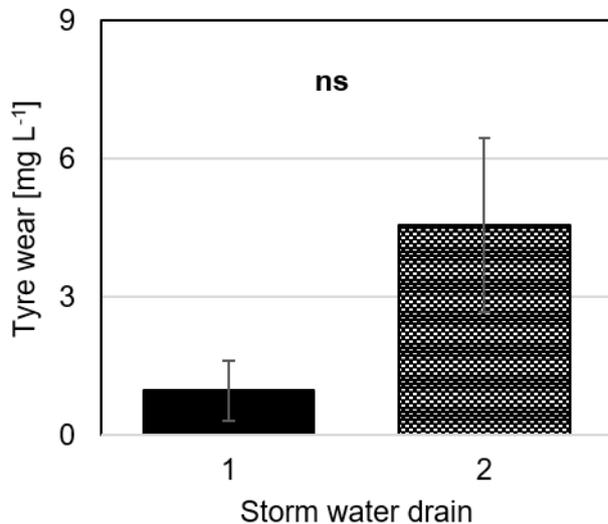


308

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

312 Variability in the mass of tyre wear recorded between storm water drains was observed
313 (Figure 4), but was not found to be significant (ANOVA $df = 1$, $p > 0.05$). The highest mass

314 was recorded at outfall 2, at 8.2 mg L⁻¹. It was not possible to confidently assess the area
315 served by the storm water drains sampled and therefore not possible to normalise the data
316 by catchment area.

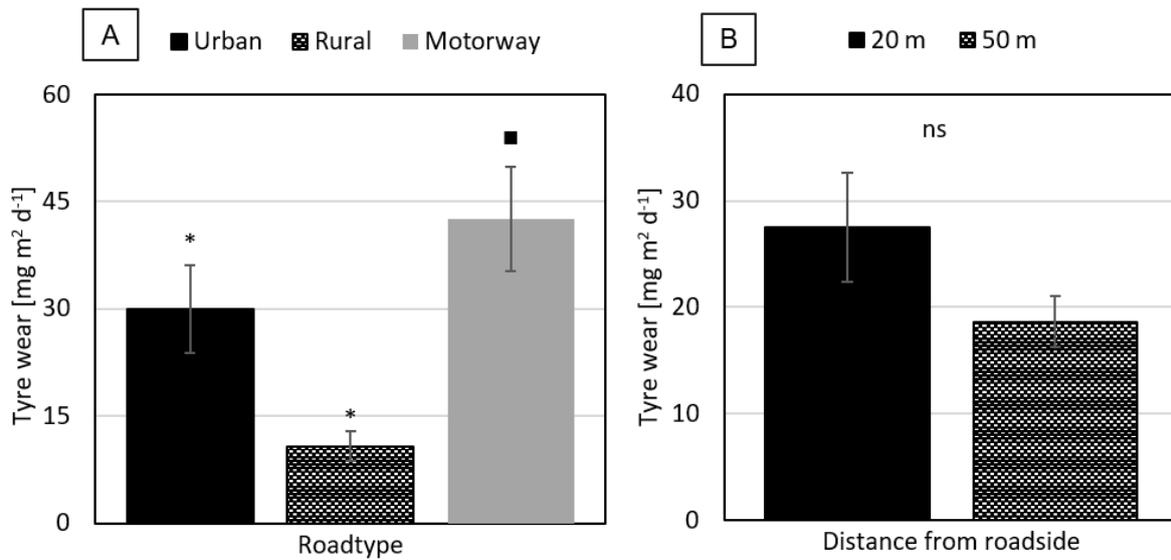


317

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

320 Within atmospheric fallout, the average mass of tyre particles deposited 20 m from urban,
321 rural, and motorways were 29.9 ± 6.1 mg m² d⁻¹ ($\bar{x} \pm SE$), 10.8 ± 2 mg m² d⁻¹ ($\bar{x} \pm SE$), and
322 42.6 ± 7.4 mg m² d⁻¹ ($\bar{x} \pm SE$) respectively (Figure 5A). The highest mass was recorded 20 m
323 besides a motorway site at 97.04 mg m². The mass of tyre wear beside motorways was
324 significantly greater than urban and rural emissions (ANOVA, Satterthwaites method, p
325 <0.05, df = 18). On average, tyre wear deposited beside urban roadsides was more than
326 twofold that of rural, but was not found to be significant (planned contrast, $p > 0.05$, df = 18).

327 Tyre wear was recorded at an average mass of 27.5 ± 5.1 mg m² d⁻¹ ($\bar{x} \pm SE$) 20 m from
328 roadsides, and 18.6 ± 2.4 mg m² d⁻¹ ($\bar{x} \pm SE$) 50 m from roadsides (Figure 5B). The highest
329 masses recorded at a site 20 m and 50 m from roadsides were 97.04 mg m² and 36.64 mg
330 m² respectively. Despite the presence of tyre wear typically declining (on average by 1/3rd) at
331 the distances examined in this study, the difference between samples collected at 20 m and
332 50 m was not significant (ANOVA. Satterthwaites method, $p > 0.05$, df = 18).



334

335 **Figure 5** Average concentrations of tyre wear (mg m² d⁻¹) deposited from the atmosphere, (A) collected 20 m
 336 from urban, rural, and motorway roadsides, and (B) 20 m and 50 m from roadsides urban, rural, and motorway
 337 roadsides. Different symbols denote bars that are statistically different, 'ns' indicates no significant differences.
 338 Analysis conducted on data prior to scaling. Error bars represent standard error.

339 3.2 Transport potential and distribution of tyre wear particles.

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

343 The estimated settling velocities of tyre particles between 4 and 350 μm according to Stoke's
 344 law ranged from 0.1 to 0.00001 m s⁻¹. Particles measuring less than 15 μm in length, that
 345 account for a large percentage of the total size distribution according to Kreider *et al.*¹³ are
 346 estimated to settle at a rate between 0.00001 and 0.0001 m s⁻¹, whereas those on the larger
 347 end of the spectrum (that account for a smaller percentage of total abundance¹³ are
 348 estimated to settle much quicker (0.1 to 0.01 m s⁻¹), see S5 and S6 for further details.

349 4.0 Discussion

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

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

364 Previous studies suggest the generation of tyre wear particles is influenced by: vehicle
365 operation^{29,58}, tyre and road characteristics, climate, road type and traffic
366 density^{3,19,30,34,36,55,59,60,61}. Although they account for a small portion of total mileage, driving
367 on urban networks is subject to amplified cornering, braking, and accelerating^{62,63}, resulting a
368 greater rate of wear than rural roads or motorways^{31,36}. The present study indicated that
369 motorway traffic released the greatest mass of tyre wear. In the absence of traffic count data
370 (preventing estimates of tyre wear emissions per vehicle), it is not possible to ascertain if this
371 is attributable to the traffic load, or speed of driving typical of motorways. Increased vehicle
372 speed has previously been evidenced to increase particle generation by Dahl *et al.*⁵⁸.

373 Atmospheric fallout of tyre wear was typically greater closer to the roadside but this effect
374 was short of statistical significance ($p < 0.05$). This suggests that a portion of tyre wear
375 released to the atmosphere settles close to the point of emission, previous reports
376 suggesting particles in excess of 10 μm ³⁴ are deposited on, or in close proximity to the road

377 surface. This is in agreement with earlier studies that report tyre wear concentrations to
378 decrease with distance from the source²⁰ within ambient air³⁸ soils⁶⁵ and road dust⁴⁰.
379 However, the data also indicates some tyre wear has the potential to travel at least 50 m
380 from the roadside, indicating it to be a key pathway for tyre wear pollution to aquatic
381 environments. Once released into the atmosphere, the transport potential of these particles
382 remains largely unknown and empirical evidence beyond the tests in this study is lacking. It
383 has been suggested that airborne tyre particles in the range of 1 - 10 μm have residence
384 times from minutes to hours, while those in the smallest size range of tyre wear ($<1 \mu\text{m}$), are
385 potentially analogous with $\text{PM}_{2.5}$, and could remain in the atmosphere for days to weeks,
386 traveling 1000's of kilometres³⁴.

387 While plant 2 emitted significantly greater tyre wear than plants 1, 3 and 4, normalising the
388 mass of tyre wear within wastewater effluent by catchment area and the serving population
389 removed significant differences between treatment plants. This could indicate that the
390 environment in which the plant is located (e.g. catchment size and local population) could in
391 part be explained as drivers in the extent of tyre wear contamination released in treated
392 wastewater effluent. The mass of tyre wear within wastewater effluent (0.02 mg L^{-1}) was
393 lower compared with a previous study (1 mg L^{-1} ⁴⁷).

394 Brodie⁶⁶ estimated that tyre particles remain on the road surface until a critical precipitation
395 intensity is reached; Unice *et al.*⁵⁶ predicts a total flush out of particles when rainfall exceeds
396 5 mm d^{-1} . Drain sumps (pits at the bottom of surface drains) are designed to capture solids
397 in runoff. However, retention of particles $<50 \mu\text{m}$ is thought to be poor even during slow flow
398 rates⁵⁵ and retention could be further reduced if the sump is at capacity⁶⁷. The greatest
399 emissions of tyre wear from wastewater effluent was recorded at treatment plant 2 (0.15 mg
400 L^{-1}). This coincided with an intense rainfall event (9.6 mm d^{-1}) where the treatment plant
401 exceeded its treatment capacity, discharging effluent subject only to primary screening and
402 settling. Any benzothiazole detected being discharged during drier conditions may be
403 attributable to sources other than tyre tread, tyre wear being residual contaminant in the

404 system, or the exposed nature of wastewater treatment plants lending themselves to
405 contamination from the atmosphere.

406 The mass of tyre wear discharged on average from surface water drainage was lower, but
407 largely agreeable with previous estimates 12 to 179 mg L⁻¹ ^{26,28,42,43,47-49}. Emissions via this
408 pathway were also orders of magnitude greater than in treated wastewater effluent.
409 However, it is not possible to directly compare the emissions between the two as one emits
410 continually and one intermittently. It is also not possible to directly compare with atmospheric
411 deposition due to the units with which tyre wear was quantified. The calculations detailed in
412 Section 2.2 allow an estimation of emissions of tyre wear in a common unit (annually over
413 the sample region), providing a broad assessment of the relative importance of each
414 pathway examined within the study areas of Plymouth and Bristol.

415 In agreement with Sundt *et al.*⁶, the largest emissions of tyre wear to aquatic environments,
416 within the two regions and three pathways examined, were emitted from storm water drains,
417 2.5 and 4 times greater than emissions from wastewater effluent and atmospheric deposition
418 respectively, which occurred on average every 350 m along the waterways sampled in both
419 Bristol and Plymouth (agreeable in both locations), indicating a key point for intervention. For
420 example, Gilbreath *et al.*⁶⁸ indicated the retention of anthropogenic particles (including
421 synthetic rubber) in surface water treatment bioretention gardens. Secondary to surface
422 water discharge, despite only being detected in half of the samples analysed, the release of
423 tyre wear within wastewater effluent presents another considerable pathway, attributable to
424 the sheer volumes processed and constant emissions. Transport in the atmosphere does not
425 appear to be considered in previous modelled estimates^{6,8,11,16-18}. Our study indicates the
426 atmosphere does present a pathway for tyre wear to aquatic environments (4 times less than
427 stormwater and 1.5 times less than wastewater) but more work is needed to assess the
428 transport of tyre wear via this medium at greater distances from the source to ascertain its
429 overall importance in contamination of different habitats.

430 Our findings should also be considered in the context of transport within aquatic
431 environments. In agreement with Kooi *et al.*⁵¹ and Unice *et al.*⁵⁶ estimated settling velocities
432 indicate that particle size appears to be most influential in settling rate of tyre wear. Particles
433 at the larger end of the spectrum are likely to settle close to the point of emission, and as
434 particle size decreases, the transport potential is likely to increase considerably, as was also
435 evident from our laboratory experiment which saw 15 % of tyre wear particles still present at
436 the water's surface after periods of an hour and a week. This should be considered in
437 conjunction with the size distribution of tyre wear, which indicates that by abundance,
438 smaller particles make up the bulk of the particulates¹³. These initial findings broadly agree
439 with Unice *et al.*⁵⁶ who estimated in a mass balance modelling effort, considerable retention
440 of tyre wear within fresh water systems, but further noted a portion of particles (0.97 - 13 %)
441 could be exported. Furthermore, some emissions do not pass through fresh water systems
442 but are released directly to marine waters. Given the magnitude at which tyre wear is
443 generated, even a small fraction of the total mass equates to substantial loads. Alternatively,
444 for particles that are more dense, accumulation in relatively high concentrations close to
445 points of entry, could also pose environmental concern.

446 The units used to quantify tyre wear (mass) do not allow direct comparisons with other
447 microplastics sources known to be abundant in the marine environment (e.g. synthetic
448 fibres) that are typically quantified by numerical abundance. Following a crude conversion of
449 tyre mass to abundance (see S7), the presence of tyre wear within storm water, wastewater
450 effluent, and atmospheric deposition eclipsed that of synthetic fibre emissions by 6, 5 and 4
451 orders of magnitude respectively. Given their apparent prevalence and relative importance to
452 other sources, and results being comparable to limited existing reports suggests findings are
453 in agreement with top-down modelled estimates; tyre wear being a major, but notably an
454 *additional* contributor to microplastic emissions to the environment. This suggests the lack of
455 previous reporting of tyre wear in marine environmental samples is likely a consequence of
456 inappropriate methods for quantification, rather than a low environmental presence.

457 Transport potential of these particles once in the marine environment should form a key part
458 of further research. This could incorporate quantifying the presence of tyre wear in the
459 marine environment with increasing distance from their input and from remote or isolated
460 locations.

461 We propose future work should consider a mass balance approach, quantifying tyre wear
462 from their points of generation, to their entry, transport, and distribution in the marine
463 environment. Further work should also consider both the toxicity of the particles⁶⁹, and the
464 leachate^{28,68,69,70,71} and sample under different rainfall conditions. Rainfall could influence
465 tyre particle distribution via suspension in surface flow, but could also hinder generation due
466 to reduce friction at the tyre road interface. Furthermore, some factors examined here
467 (distance, road type – urban versus rural) were approaching statistical significance; greater
468 replication may prove insightful. Further work should also establish the potential for longer-
469 range transport within the atmosphere. To further findings from this study, sampling a wider
470 range of catchments both temporally and spatially may enable scaling of results to a national
471 level to better provide evidence for policy change.

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