Microplastics and Tire Wear Particles in Urban Stormwater: Abundance, Characteristics, and Potential Mitigation Strategies

Author

Ziajahromi, Shima, Lu, Hsuan-Cheng, Drapper, Darren, Hornbuckle, Andy, Leusch, Frederic DL

Published

2023

Journal Title

Environmental Science & Technology

Version

Accepted Manuscript (AM)

DOI

10.1021/acs.est.3c03949

Rights statement

Downloaded from

Griffith Research Online

Microplastics and tyre wear particles in urban stormwater: Abundance, characteristics and potential mitigation strategies

Shima Ziajahromi*[1], Hsuan-Cheng Lu[1], Darren Drapper[2], Andy Hornbuckle[3], and Frederic D.L. Leusch[1]

[1]Australian Rivers Institute, School of Environment and Science, Griffith University, Southport Qld 4222, Australia

[2]Drapper Environmental Consultants, 4/54 Quilton Place, Crestmead, QLD 4132, Australia

[3]SPEL Stormwater, Carole Park, QLD 4300, Australia

Submitted to:

Environmental Science & Technology

Date of re-submission

July 2023

* Corresponding author: Shima Ziajahromi (s.ziajahromi@griffith.edu.au)

Abstract:

Stormwater has been identified as a pathway for microplastics (MPs) including tyre wear particles (TWPs) into aquatic habitats. Our knowledge of the abundance of MPs in urban stormwater and potential strategies to control MPs in stormwater is still limited. In this study, stormwater samples were collected from micro-litter capture devices (inlet and outlet), during rain events. Sediment samples were collected from material captured in the device, and from the inlet and outlet of a constructed stormwater wetland. MP (>25 μm) concentration in stormwater varied across different locations ranging from 3.8 to 59 MPs/L in raw and 1.8 to 32 MPs/L in treated stormwater, demonstrating a decrease after passage through the device (35-88% removal). TWPs comprised ~95% of all particles followed by polypropylene (PP) and polyethylene terephthalate (PET). The concentration of TWPs ranged from 2.5 to 58 TWPs/L and 1450 to 4740 TWPs/kg in stormwater and sediment, respectively. A higher abundance of MPs was found in sediment at the inlet of the constructed wetland compared to the outlet, indicating a potential role of wetlands to remove MPs from stormwater. These findings suggest that both constructed wetlands and micro-litter capture devices can mitigate the transport of MPs from stormwater to the receiving waterways.

Keywords: Microplastics; Mitigation strategy; Stormwater; Tyre wear particles

Synopsis: Limited research exists on microplastics (MPs) and tyre wear particles (TWPs) in stormwater. This study reports on abundance of MPs and TWPs in stormwater in Australia and mitigation strategies to reduce MP pollution.

1. Introduction

The fast accumulation of plastics in the environment is occurring due to inadequate recycling and disposal, as well as mismanagement of plastic waste. In 2021, the global production of plastic was 390 million tons, of which only 9% was recycled, 12% was incinerated, and the rest was directed to landfills and the environment [1]. A considerable amount of plastic waste is released into aquatic and terrestrial environments, and the management of plastic pollution has been highlighted as a key environmental challenge of the 21st century [2].

Ubiquitous pollution of water bodies by microplastics (MPs; plastic particles <5 mm in size) has become an emerging environmental concern due to their persistence and accumulation in aquatic ecosystems [3]. The uptake of MPs by a variety of aquatic organisms at different trophic levels (from zooplankton to marine mammals) has been widely reported [4]. MPs can pose threat to exposed biota both physically (e.g., clogging and internal abrasion) and chemically (e.g., lethal and sub-lethal effects through leaching of absorbed chemicals) depending on the physicochemical properties of plastics [5].

Stormwater runoff has been considered a critical pathway for MPs to enter aquatic ecosystems from land sources [6]. Stormwater is a mixture of sediment, chemical, organic and physical pollutants, including MPs, that are washed off from urban landscapes during rain events and discharged to local receiving waterways [7]. Urban stormwater runoff typically requires treatment for the removal of suspended solids, and nutrients such as nitrogen and phosphorus in many jurisdictions in Australia and internationally. Some legislation also requires removal of gross pollutants, but regulations are lagging behind current research regarding MPs. Stormwater can contain various MPs depending on the type of land use (residential, industrial and commercial) as well as degraded road paint and tyre wear particles (TWPs) from vehicles [8]. MPs that enter the stormwater drainage system may be removed from stormwater and settle in sediment through sedimentation and formation of biofilm [9] leading to accumulation of MPs in sediment over time. Thus, attention must be paid to input of MPs in urban drainage systems and solutions to reduce the amount of MPs entering waterbodies.

Previous studies have usually reported a high abundance of MPs in urban stormwater runoff. For example, Liu et al. [10] reported 0.49 to 23 MPs/L in urban and highway stormwater in Denmark with higher concentration found in industrial and commercial catchments. A Canadian study reported 0.70 to 200 MPs/L in the stormwater runoff samples [11].

Road wear particles and TWPs are assumed to be one of the dominant land-based MPs entering into the aquatic environment mainly through the stormwater system [7, 12, 13] and have received increased attention over the past few years. Although the mass of TWPs ending up in aquatic environments depends on the treatment level of road runoff, which is greatly variable, previous research has suggested that TWPs could contribute to approximately 30% of all MPs entering aquatic environments [12, 14]. In addition, the wet deposition of suspended atmospheric MPs and TWPs can significantly contribute to stormwater MP pollution [15-17].

It has been shown that TWPs can cause toxic effects on various aquatic organisms through the ingestion of particles themselves as well as leachate [18]. For example, Cunningham et al. [18] reported a higher mortality rate in daphnia and zebrafish after exposure to nano-sized TWPs. A previous study has shown that tyre rubber contains up to 2,500 chemicals (such as, PAHs, phthalates, antioxidants, benzothiazole etc) with leachates from tyre more toxic to bacteria and microalgae compared to other polymers (polyethylene, polyethylene terephthalate, and polypropylene)[19].

In a recent review study, Wang et al. [20] showed a much higher abundance of MPs (mean 676 MPs/L from 25 studies) in stormwater runoff compared to other important land-based MP sources such as wastewater effluent (mean 12 MPs/L from 76 studies). This highlights the need to better understand the abundance of MPs in stormwater and to control this potentially important source of land-based MPs. One important limitation of most of the research done on

MPs in stormwater to date is that it often lacks information about the actual number of TWPs in the samples due to analytical challenges [16]. This quantitative information is crucial to enhance our understanding of the concentration and amount of TWPs in stormwater, assess the risk of emission to the environment, and inform management and mitigation strategies [21, 22]. Mennekes et al. [21] highlighted the urgent need for country-based TWP emission studies based on reliable measurement rather than theoretical estimation.

To the best of our knowledge, no previous study has quantified TWPs in urban stormwater and drainage sediment in Australia. In this paper we aimed to 1) quantify and characterise MPs and TWPs in both stormwater runoff and sediment of stormwater drainage systems in Queensland, Australia, 2) assess the effectiveness of a stormwater treatment device (micro-litter capture device) to capture and remove MPs and TWPs from stormwater, and 3) evaluate the role of a constructed stormwater wetland in retaining MPs in sediment from urban stormwater.

2. Materials and Methods

2.1. Sample collection

Stormwater samples were collected during eleven storm events (March to September 2020) from the inlet and outlet of a gross pollutant capture device installed in the drainage pit in the centre of a carpark located on the Griffith University Gold Coast campus (Figure S1 in the Supporting Information). The device consists of a 200 µm mesh bag supported by an aluminium frame that is inserted within the existing drainage pit to provide ongoing stormwater treatment. The inlet and treated (outlet) stormwater samples were collected in 9 L glass bottles using ISCO GLS autosampler installed on-site. The sampler automatically collects the stormwater when the rain starts with minimum rainfall of 2 mm over 30 min (and when flow measurement registers >0.5 L/s). The litter capture device design and the autosampler set up are provided in Figure S3.

Between 2.4 to 4 litres of stormwater was collected at each sampling event from two sites (carpark and road sites). The stormwater samples were not collected from townhouse site due to unavailability of a stormwater autosampler at this site. In total, 25 stormwater samples were collected. Details of stormwater sample collection dates and sampled volumes are provided in Table S1.

The sediment samples (1 kg) were collected during 2020 from the sediment captured in the litter capture devices from different catchments located at different sites (road, carpark, and townhouse sites) across Queensland. Information about the type of land use and catchment areas for each site is provided in Table S2. The samples were collected using a metal shovel and transferred to pre-cleaned glass jars with metal lids. The samples were collected in two replicates with a total of 6 sediment samples. The sediment sampling was also performed at the inlet and outlet of a floating stormwater treatment wetland located at the Gold Coast with two replicates each (n=4) (Figure S4). To minimise background contamination during sampling, the sample jars were kept closed at all times and no plastic material was used to collect the samples. A field control sample (an open glass jar) was also set up during sampling to monitor possible MP contamination from atmosphere *(e.g.,* airborne MPs) and other sampling procedures.

2.2.Sample processing

Sediment sample processing was performed as previously described [23, 24]. In brief, this includes drying and homogenising of the samples, wet peroxide oxidation (WPO) using hydrogen peroxide (H_2O_2 30%) in conjunction with ferrous sulfate ($FeSO_4$) solution, a two-step density separation using MiliQ water to separate low density material and sodium iodide (NaI, 1.8 g/cm^3) to separate a range of higher density plastics and filtration over 25 μm stainless-steel filters.

The collected stormwater samples from each sampling point (inlet, outlet) were filtered through 25 μm stainless-steel filters and processed according to a previously validated methodology [23, 24]. Briefly, this includes digestion using 30% hydrogen peroxide (H_2O_2), density separation using sodium iodide (NaI, 1.8 g/cm^3), filtration, staining using Rose-Bengal solution and drying at 40°C. The details of the sediment and water sample processing procedures are provided in Supporting Information Section S1.

2.3.Quantification and characterisation

Suspected MPs (>25 μm) from each sample were inspected under a stereo microscope (Olympus SZX10) equipped with a digital camera (Olympus DP74). All suspected MPs were counted using the point counting tool in the CellSens Standard image analysis software (Version 13.1 Olympus). In addition, MPs were classified according to their morphology (*e.g.,* fibre, fragment, and bead) and color. The suspected MPs extracted from all stormwater and sediment samples were analysed using a PerkinElmer Spotlight 400 μ-FTIR Imaging System with an MCT detector cooled in liquid nitrogen, operating in reflectance mode and with a wavenumber resolution of 4 cm^{-1}. A total of 64 scans were collected across a wavenumber range from 4000 to 650 cm^{-1}. Spectra were subjected to a library search using the search routine of the Nicolet Omnic 9.2 software using a library set that included the Nicolet polymer, forensics and common materials set in addition to the Hummel polymer library. The search routine produced a score out of 100 for goodness of match. Any match above 70% was considered acceptable after carefully checking the spectra. FTIR was applied to all suspected MPs in water samples and 20-50% of total particles extracted from sediment [25].

Due to the limitations of common spectroscopy techniques to detect TWPs because of the strong effect of filler components in tyre wear [26], the suspected tyre (black rubbery) particles were further identified using pyrolysis GC-MS. This technique can provide data on complex polymer mixtures (TWPs) due to the chromatographic separation and mass spectrometry detection [27]. Black particles were first examined using tweezers under the stereo microscope. If the particles presented a rubbery texture (soft and bouncy) they were considered as suspected TWPs. The suspected TWPs (up to six particles) were combined as composite samples for inlet and outlet stormwater and sediment from the townhouse, road, and carpark sites, separately. Then duplicate subsamples (0.5-1 mg) of each composite sample were transferred to a stainless-steel sample cup (Eco-Cup LF, Frontier Lab) and analysed using double-shot pyrolysis GC-MS (GCMS-QP2020 NX, Shimadzu, Japan) and they were all identified as styrene-butadiene rubber. Additionally, samples of known virgin TW fragments were analysed as reference particles. The samples first underwent thermal desorption (first shot), which was conducted with a starting temperature of 100°C, increased to 300°C at rate of 20°C/min and held at 300°C for 2 min. Subsequently, pyrolysis (second shot) was conducted at 550°C for 1 min. The pyrolyzer interface and GC injection port temperatures were set at 300°C. The samples were injected with a split of 100:1 on an Ultra Alloy® 5 capillary column (30 m, 0.25 mm I.D., 0.25 μm film thickness). The GC column temperature program was as held at 40°C for 1 min, then increased to 300°C at 20°C min^{-1}, and held for 10 min. Helium was used as the carrier gas at 1.0 mL/min with a constant column flow. The ion source temperature was kept at 230°C with an ionization voltage of 70 eV. Scan mode was used with a mass range from 29 to 800 m/z. Obtained chromatograms were then compared against library reference and the known tyre particles.

To better understand the surface morphology of TWPs, the particles were further examined using a scanning electron microscopy (SEM, ZEISS). This was performed by comparing virgin TWPs obtained from new car tyre and TWPs extracted from the environmental samples in this study. To ensure that any changes to the particle surface were not due to the effects of chemical used for sample processing, the virgin TWPs were also put through the same sample processing described in section 2.2 above.

The samples were coated with 3 nm thickness of Pt to minimise the charging issue. The morphology was inspected using Zeiss Sigma Variable Pressure (VP) Field Emission Scanning Electron Microscope (SEM). The acceleration voltage was set at 15 kV and chamber pressure was 45 Pa.

2.4.Quality assurance/quality control (QA/QC)

Recent review articles highlighted the importance of including QA/QC at every step of MP analysis to produce reliable data and to ensure the reproducibility of research output [28, 29]. Thus, a QA/QC protocol suggested in previous studies was implemented during the sampling, sample processing, and analysis steps. This included the use of field blanks (empty sampling container), laboratory procedural blanks (negative controls) processed in parallel with the samples, method validation and a series of contamination prevention measures such as wearing a cotton lab coat, minimising the use of plastic material, keeping samples covered all the time, rinsing and cleaning equipment and glassware, performing sample analysis in clean air (clean fume hood) and filtration of chemicals. Details of applied QA/QC activities are provided in Section S2.

2.5. Statistical analysis

Normality of the data was tested using Shapiro-Wilk test. When normality test was satisfied, a t-test was used to compare two data sets (e.g., inlet and outlet). All data were recorded using Excel and statistical analysis were performed using GraphPad Prism (v9.5.1). The statistically significance level set to $\alpha = 0.05$. All graphs were produced using GraphPad Prism and excel.

3. Results and Discussion

3.1. Field and lab blanks

A total of 16 laboratory blanks were set up and processed on different dates during laboratory sample processing of stormwater and sediment samples. Between 0 to 7 particles were found in the lab blanks with an average of 2.5 particles/blank (80% fibres, 20% fragments). The majority (85%) of the total fibres detected in the lab blanks were natural cellulose fibres and the remaining 15% were PET (total of 5 particles). Sixty percent of fragments in the blanks were also identified as plastic (total of 4 polypropylene; PP, and 1 polyvinyl chloride; PVC). The potential source of particles found in the blank could be airborne particles deposited during handling. Therefore, a blank correction was performed by subtracting the total amount of each particle type (polymer and non-polymer) from number of particles in each sample for each individual sample batch [30]. It should be mentioned that inclusion of field blanks was not practical for stormwater samples due to installation of the autosampler in an enclosed cabinet. One field blank was set up for each sampling location during sediment sampling, and between 5 to 18 particles were found across field blanks (total of 29 particles) with >93% of those fibres. The majority were PET (80%, total of 21 particles) were PET fibres, with the remainder (20%) identified as cellulose fibres. Thus, field blank correction for each sediment sample batch was performed as described for the stormwater lab blanks above.

3.2.Stormwater and efficacy of the litter capture device

The majority of the total suspected MPs in stormwater samples (85%, i.e., 1444 out of 1696 particles) were identified as plastic polymer, i.e. as MP. The bulk of MPs across all stormwater samples (>94%) were fragments (Figure 1), and most of those (92%) were black rubbery particles identified as TWPs using pyrolysis GC-MS. The major components detected in the TWP samples was polybutadiene rubber and styrene-butadiene rubber (SBR), which are mainly used in car tyre treads [13, 31]. This was expected, particularly in the car park runoff samples, as vehicles are likely to be the primary source of MPs in the carpark and the majority of MPs washed off by stormwater can be related to traffic. Previous studies also showed that urban stormwater is major source of tyre and road wear particles to urban waterways [7, 12]. Only 4.3 and 6.0% of MPs in the inlet and outlet, respectively, were fibres. Bead-shaped MPs were not found in any stormwater samples (Figure 1). FTIR analysis identified the MP fibres as polyethylene terephthalate (PET) and the remaining MP fragments primarily as polypropylene (PP).

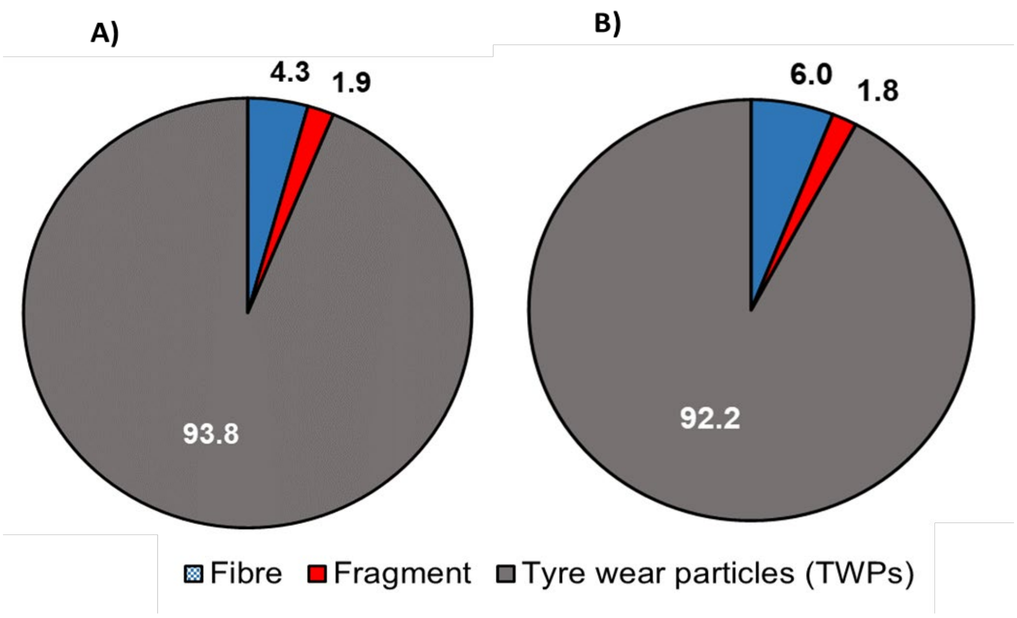

Figure 1. Different morphology of MPs found in (A) inlet stormwater samples and (B) outlet stormwater samples.

The abundance of MPs in stormwater samples ranged from 3.8 to 59 particles/L in the inlet (Figure 2) with TWPs alone accounting for 2.5 to 58 particle/L of total MPs, equivalent to the mass of 0.4 to 4 mg/L TWPs. Jarlskog et al. [12] reported up to 4500 MPs/L in street wash water, mostly rubber and bitumen MPs likely from car tyre and the road surface.

The abundance of MPs detected in the present study is comparable with previous studies. For example, MP concentration detected in urban stormwater runoff ranged from 1.1 to 24.6 MPs/L in the USA [7], 0.5 to 22.9 MPs/L in Denmark [32], 66 to 192 MPs/L in Mexico [33], 54 to 639 MPs/L in South Korea [34] and an average concentration of 15.4 MPs/L in Canada [35]. The mass of TWPs in stormwater is within the range of TWPs previously reported by Parker-Jurd et al. [36] (2.5 mg/L TWPs) in untreated surface runoff in the UK. Jarlskog et al. [22] reported higher concentration of 130 mg/L TWPs in untreated stormwater from roadside gully pots in Sweden. It should be noted that several factors, such as precipitation, catchment size, type of land use, and analysis methodology (e.g., sampling volume and size of collected MPs) can influence the reported MP abundance in stormwater [20, 37]. Jarlskog et al. [12] reported only 3 MPs/L of ≥ 100 µm in stormwater samples, however, this increased to 5,900 MPs/L when analysing smaller MPs (>20 µm). There is a clear relationship negative between size and abundance of MPs in various matrices.[38] Kooi et al. [39]also analysed size distribution reported by different studies and found a decreasing MP concentration with increasing size and highlighted that overlooking small MPs can easily lead to an analysis bias and underestimation of MP abundance. This emphasises the importance of using a harmonised methodology in MP research (especially smallest size cut off) that allows better comparability between studies [28].

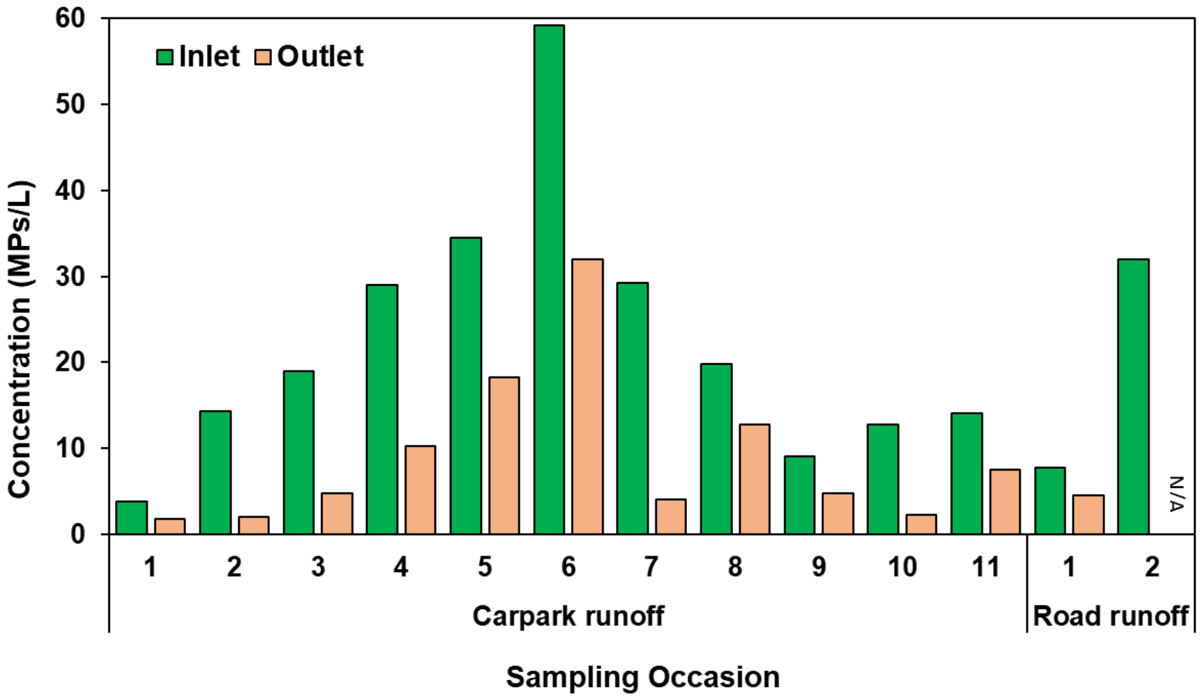

Figure 2. Number of MPs per L of stormwater samples collected from inlet and outlet of micro-litter capture devices at a carpark and road during 2020. N/A: not available

Interestingly, variations in MPs abundance (particularly for TWPs) were observed between different sampling occasions (Figure 2). For example, significantly lower MPs (t-test; $p = 0.03$) were found during Queensland Covid-19 restrictions in the carpark samples (Figure 2, sampling occasions 1,2,3, 8, and 9) as a result of change in traffic pattern that most likely reduced traffic-related MPs emission. Rodland et al. [13] also reported highly variable abundance of Tyre and road wear particles (76.0–14,500 mg/L meltwater) in roadside snow in Norway. The variability was attributed to variability in road surface and traffic density.

Clearly these results indicate that stormwater runoff can contribute a significant number of MPs to the receiving water and that some mitigation strategy is necessary. The litter capture device significantly reduced (t-test; $p < 0.001$) the abundance of MPs in all samples, with removal varied between different locations ranging from 35 to 88%. The concentration of MPs significantly decreased in treated stormwater (outlet) samples ranging from 1.8 to 32 MPs/L with TWPs accounting for 1.3 to 32 TWPs/L which is equivalent to 0.2 to 1.1 mg/L TWPs.

(Figure 2). Previous studies have also shown the role of other conventional mitigation strategies such as bioretention cells and gross pollutant traps to control MP pollution in stormwater runoff [6, 40]. Werbowski et al. [7] demonstrated that rain gardens can effectively retain between 84 to 94% of smaller MPs (0.5-3.5 mm) and 98 to 100% of larger MPs (3.5- 5 mm) in urban stormwater.

SEM was performed for surface analysis of TWPs. SEM images (Figure 3) show various surface roughness (e.g., cracked, damaged and porous) in different TWPs samples compared to virgin tyre particles. TWPs extracted from the samples had rougher and uneven surface with multiple wear marks, which suggest a high likelihood of further break down to smaller pieces, highlighting the importance of detecting smaller MPs in the environment. This decreased integrity is most likely due to the weathering process and physical and mechanical abrasion. It also increases the particle's surface area due to increased number of cracks and wrinkles on the surface. The alteration of surface properties can ultimately impact the toxicity of MP particles and can increase their capacity to sorb environmental pollutants [41]. In addition, weathered MPs are more likely to release additives and sorbed chemicals into the environment, increasing their toxicity and potentially causing greater risk to the exposed organisms [41]. This is particularly important for TWPs as they contain a wide range of hazardous organic and inorganic chemicals[19].

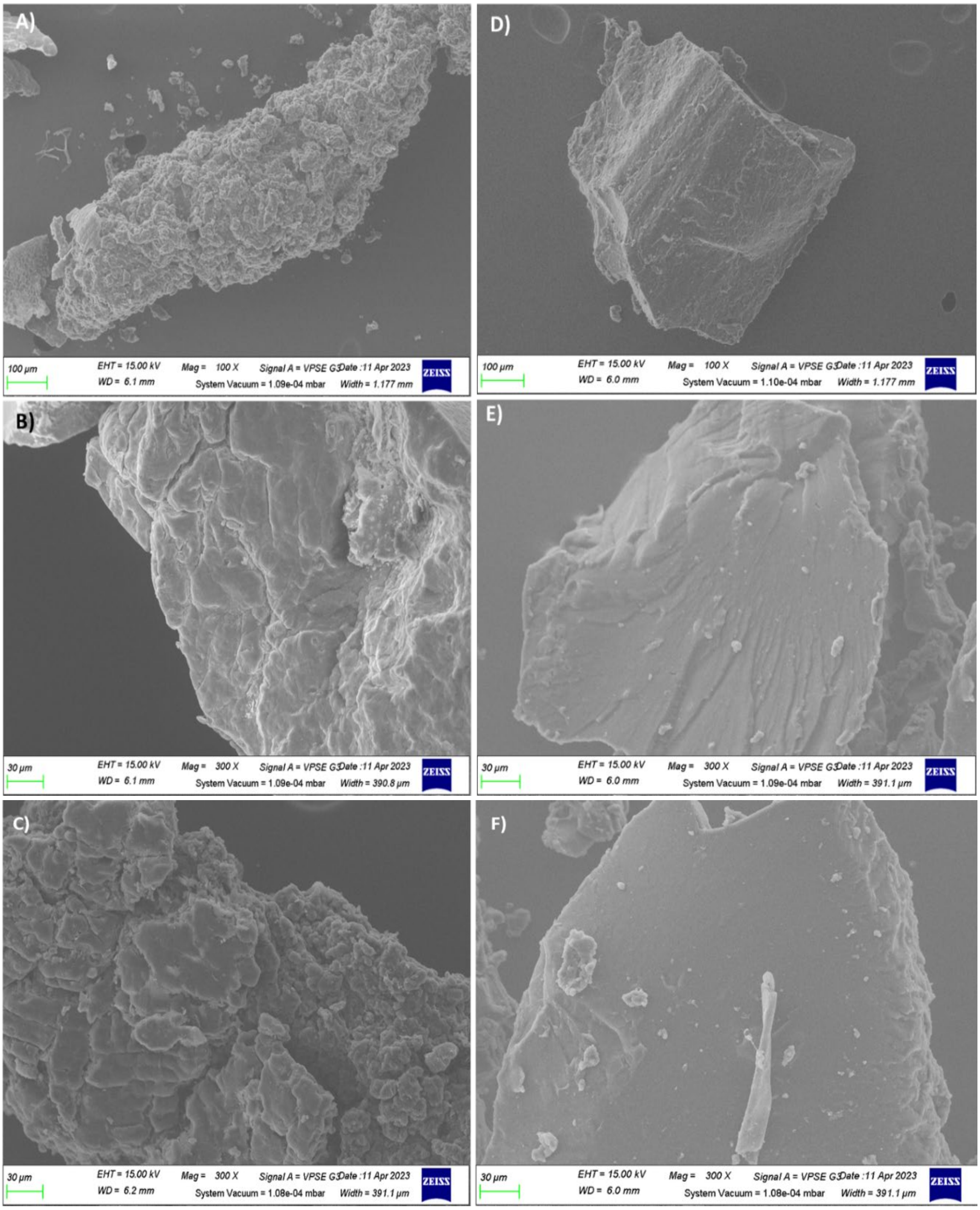

Figure 3. SEM images of TWPs. (A), (B) and (C) TWPs detected in the stormwater samples; (D), (E) and (F) virgin TWPs. The surface of particles extracted from stormwater shows rough, damaged and cracked surface compared to virgin particles.

3.3. Sediment from a constructed wetland and retained in the litter capture device

Wetland and retention ponds have been suggested as potential mitigation strategy to reduce the release of MPs to waterways [6]. A total of 385 particles were found across all sediment samples with >70% identified as plastic. Our analysis of sediment in a constructed wetland shows an average of 1810±410 MPs/kg in sediment samples collected from the inlet of the constructed wetland, significantly reduced (t-test; $p = 0.02$) to an average of 315±190 MPs/kg in outlet samples (Figure 4A). Fragments were the dominant MPs in inlet (average of 73%) and outlet (average of 63%) samples followed by fibres with average of 44% and 52% in inlet and outlet, respectively. A small number of beads (total of 12 particles; 0.5%) was also detected in the inlet sediment samples but no bead was found in the outlet samples. The plastic polymers detected in both inlet and outlet sediment were PP, PE, polyamide (PA), PET and TWPs, followed by polystyrene (PS) and PVC. Information about the number of different MP polymers in inlet and outlet samples is provided in Figure S4.

These results are consistent with our previous study, which showed a decreasing trend for MP abundance in sediment in the same stormwater floating wetland [23]. This suggests that the removal of MP from stormwater by the constructed wetland is likely due to settling of MP particles with the sediment during the passage of contaminated water through the constructed wetland, and that constructed wetlands can reduce MP pollution in aquatic environments by retaining MPs from stormwater before they enter receiving waterways. A microcosm study by Chen et al. [42] investigated the efficiency of surface flow and horizontal subsurface flow constructed wetlands to remove different morphotypes (fibres, fragments, film) and sizes (500 to 4000 μm) of PP, PE and PET MPs. The results showed that 100% of all MPs were retained in the horizontal subsurface flow wetland, while the surface flow wetland retained 81.6% of total MPs. The retention of lower density MPs (such as PP and PE) was related to biofilm attachment, which can increase the density of MPs.

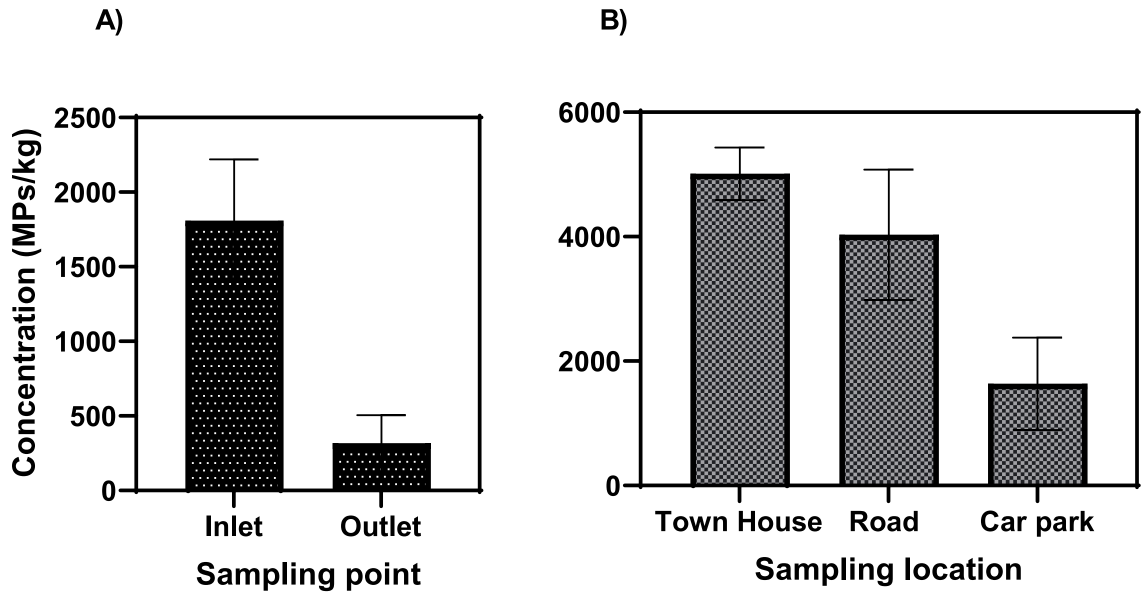

Figure 4. Number of MPs per kg dry of sediment collected from (A) stormwater constructed wetland (B) Litter capture device.

In the sediment samples collected from the litter capture devices, MPs abundance varied across the sites, and were also quite variable between sampling events. An average of 1630 ± 740 MPs/kg of dry sediment were recorded at the carpark samples while significantly higher (t-test; $P = 0.04$) abundance was observed at the other two sites with 4030 ± 1050 MPs/kg at road and 5010 ± 420 MPs/kg at townhouse samples (Figure 4B). A variety of polymer types (8 polymer types) was identified (Figure 5). Similar to stormwater samples, butadiene rubber (BR), from car tyre wear, were predominantly detected across three sites (46 to 89 %). This corresponds to 1450 TWPs/Kg/dry sediment in the carpark and 4510 and 4740 TWPs/Kg dry sediment at road and townhouse sites which is equivalent to 241, 751 and 790 mg/Kg TWPs, respectively. Mengistu et al. [43] has quantified TWPs in gully pot sediments in Norway and found between 1 to 150 mg TWPs/g sediment that were mainly related to the traffic density with site that had higher traffic densities showed greater concentrations. Observations of this study support this research, with lower traffic densities at the townhouse site producing a lower proportion of

TWPs in the overall MPs. However, in contrast, the townhouse site had higher TWPs compared with the sediment mass captured. This could be related to a longer maintenance cycle at the townhouse site, or a lower sediment loading produced from the catchment. Moreover, higher abundance of MPs at road and townhouse sites could be attributed to the larger catchment size compared to the carpark. Other dominant polymers detected in sediment include PP and polyethylene (PE). For the townhouse site, significantly higher concentration of PP was detected compared to other sites (Road and Carpark) (t-test; $p=0.02$), which could be related to the sources such as litter and industrial activities. Polymers such as PET, PVC, and PS were found in lower numbers. The FTIR spectra and GC-MS pyrogram of the extracted MPs and TWPs are shown in Figure S5.

The concentration observed in the stormwater sediment in this study are higher than the concentrations reported in sediment samples from freshwater environments (e.g., river, lakes and wetlands), which usually range from 20 to 2000 MPs/kg [37], indicating high abundance of MPs in stormwater drains. In a recent study, Lutz et al. [9] quantified MPs in stormwater drainage system in Western Australia (Perth) and found up to 3500 MP/kg of dry sediment in urban drains, which is comparable with the present study. Likewise, Niu et al. [44] reported 80 to 2610 MPs/kg in sediments of urban rainwater drainage systems in China. However, our knowledge of MPs abundance in urban areas is still limited.

The high abundance of MPs reported across the three sites demonstrated that stormwater without proper treatment can contribute significant amounts of MPs to the aquatic environments.

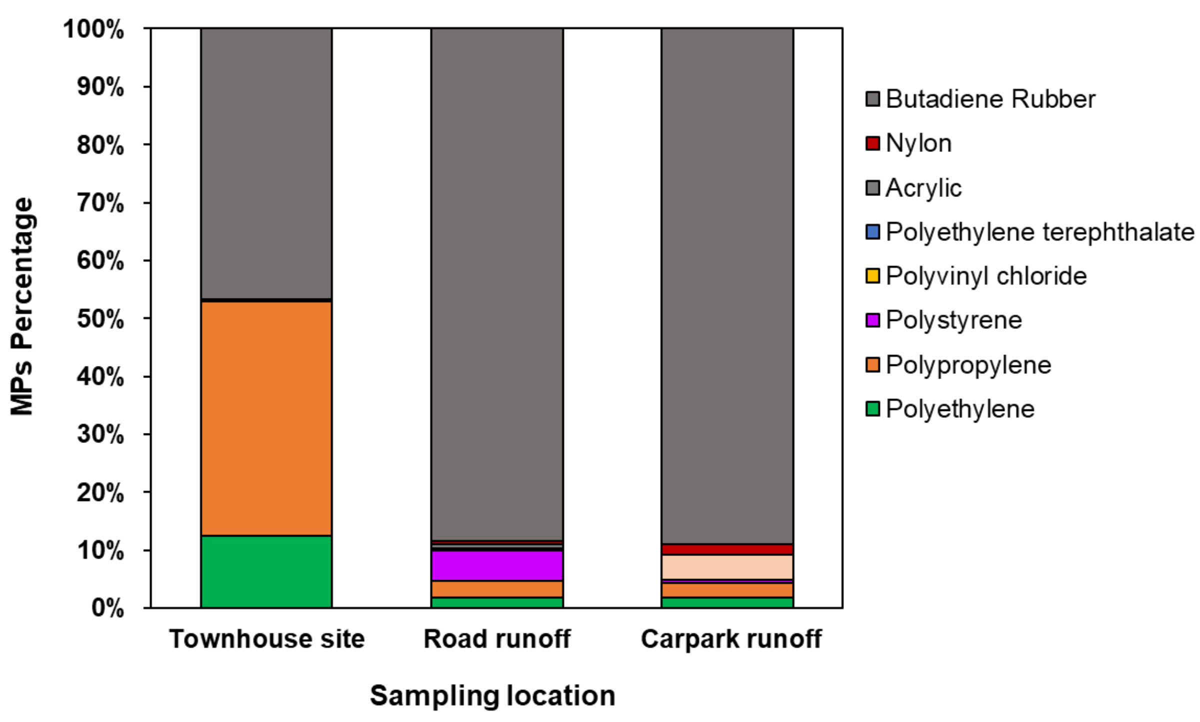

Figure 5. Chemical composition of MPs detected in the sediment samples using FTIR and pyrolysis GC-MS.

While black fragments are frequently found to be a major contributor of MPs in urban road runoff, many previous studies have been unable to confirm their identity as TWP due to analytical limitations of common techniques (e.g., FTIR and Raman), instead reporting them as "black rubbery fragment", "synthetic rubber" [7], or providing limited results about TWPs [34]. Other studies have used visual analysis techniques such as scanning electron microscopy (SEM), which cannot confirm the chemical composition of particles [45]. Studies that have only used pyrolysis GC-MS to identify and quantify TWPs usually report concentrations on a mass basis (e.g., mg/L), making it challenging to compare the abundance of TWP with other MPs, which are usually reported in particles/L, kg. In our study, MPs and TWPs were extracted and quantified so as to provide consistent information on their abundance in particles/L, which is a most common unit for MPs reporting in the literature [37]. We used pyrolysis GC-MS to confirm the composition of suspected TWPs already extracted (and counted) from stormwater and sediment. Studies that rely solely on pyrolysis GC-MS to identify MPs/TWPs use a different sample processing compared to the methods used in the current study, and express their results in mg/L. By using our methodology, we are able to express our results in particles/L and still benefit from the pyrolysis GC-MS confirmation of chemical composition. However, this makes it difficult to compare our results with those from studies that have used pyrolysis GC-MS alone, as they are expressed in a different unit. However, our result about other dominant MPs (PP and PE) is consistent with previous studies reporting MPs in stormwater sediment [9, 24].

This study has quantified and identified various MPs in urban stormwater and sediment of stormwater drainage systems from different sites in Queensland, Australia. The most common MP found across all samples (water and sediment) were TWPs, mainly butadiene rubber, from vehicle tyres. These results demonstrate that stormwater runoff acts as an important source of MPs, with TWPs the major type of MPs entering waterways. This information is critical to accurately estimate the total amount of TWPs released to the aquatic environments through road runoff, and highlights the need to provide appropriate treatment (particularly for litter capture) on roads, hardstands and highways at their discharge points to receiving waterways. Further work is required to better understand the abundance of TWPs in stormwater in different urban landscapes and seasons.

TWPs detected in this study had rougher surfaces than virgin tyre particles, highlighting the importance of using weathered MPs/TWPs in future ecotoxicology studies as the roughness and surface structure of particles can influence their toxicity and fate. This also highlights their potential for further breakdown into smaller particles.

MPs concentrations in stormwater were decreased by 35 to 88% after passing through a stormwater treatment device, demonstrating that a simple filtration strategy can effectively reduce the release of MPs from stormwater runoff. Thus, the MP quality of road runoff can be improved through the installation of end-of-line stormwater treatment systems. A constructed wetland also retained MPs from stormwater in the wetland's sediment, thus reducing the discharge of MPs to the downstream aquatic environment. More research is required to further investigate the fate and degradation of MPs in the wetland's sediment.

Despite the building body of knowledge surrounding MPs and TWPs in stormwater, there is no uniform methodology to measure and prove the efficacy of devices for gross pollutant capture, as well as MP removal. This paper explored one process and identified some limitations that can be learnt from. Further work is proposed to refine and improve a methodology for removal of these ubiquitous pollutants especially for different size fractions.

Associated Content

Further information about the sampling dates, volume, locations, sample processing, QA/QC, litter capture device and particle composition (PDF).

Acknowledgment

This study was funded by SPEL Stormwater through the project "Analysis of microplastics in stormwater". The Pyrolysis GC-MS and SEM imaging were undertaken at the Central Analytical Research Facility (CARF) hosted by the Institute for Future Environments at Queensland University of Technology (QUT). The authors acknowledge Dr. Lan Chan and Dr Ming Li at QUT for assistance in analysis of tyre particles.

References

1. Kumar, R.; Verma, A.; Shome, A.; Sinha, R.; Sinha, S.; Jha, P. K.; Kumar, R.; Kumar, P.; Shubham; Das, S.; Sharma, P.; Vara Prasad, P. V., Impacts of Plastic Pollution on Ecosystem Services, Sustainable Development Goals, and Need to Focus on Circular Economy and Policy Interventions. *Sustainability* **2021,** *13*, (17), 9963.
2. UN Environment Programme Historic day in the campaign to beat plastic pollution: Nations commit to develop a legally binding agreement. https://www.unep.org/news-and-stories/press-release/historic-day-campaign-beat-plastic-pollution-nations-commit-develop. Accessed April 2023.
3. Yusuf, A.; Sodiq, A.; Giwa, A.; Eke, J.; Pikuda, O.; Eniola, J. O.; Ajiwokewu, B.; Sambudi, N. S.; Bilad, M. R., Updated review on microplastics in water, their occurrence, detection, measurement, environmental pollution, and the need for regulatory standards. *Environ Pollut* **2022,** *292*, (Pt B), 118421.
4. Ziajahromi, S.; Leusch, F. D. L., Ecotoxicity of Micro- and Nano-Sized Plastics. In *Plastic Pollution in the Global Ocean*, 2023; pp 205-232.
5. Xu, S.; Ma, J.; Ji, R.; Pan, K.; Miao, A. J., Microplastics in aquatic environments: Occurrence, accumulation, and biological effects. *Sci Total Environ* **2020,** *703*, 134699.
6. Stang, C.; Mohamed, B. A.; Li, L. Y., Microplastic removal from urban stormwater: Current treatments and research gaps. *J Environ Manage* **2022,** *317*, 115510.
7. Werbowski, L. M.; Gilbreath, A. N.; Munno, K.; Zhu, X.; Grbic, J.; Wu, T.; Sutton, R.; Sedlak, M. D.; Deshpande, A. D.; Rochman, C. M., Urban Stormwater Runoff: A Major Pathway for Anthropogenic Particles, Black Rubbery Fragments, and Other Types of Microplastics to Urban Receiving Waters. *ACS ES&T Water* **2021,** *1*, (6), 1420-1428.
8. Horton, A. A.; Dixon, S. J., Microplastics: An introduction to environmental transport processes. *WIREs Water* **2017,** *5*, (2), 1268.
9. Lutz, N.; Fogarty, J.; Rate, A., Accumulation and potential for transport of microplastics in stormwater drains into marine environments, Perth region, Western Australia. *Mar Pollut Bull* **2021,** *168*, 112362.
10. Liu, F.; Olesen, K. B.; Borregaard, A. R.; Vollertsen, J., Microplastics in urban and highway stormwater retention ponds. *Science of The Total Environment* **2019,** *671*, 992-1000.
11. Ross, M. S.; Loutan, A.; Groeneveld, T.; Molenaar, D.; Kroetch, K.; Bujaczek, T.; Kolter, S.; Moon, S.; Huynh, A.; Khayam, R.; Franczak, B. C.; Camm, E.; Arnold, V. I.; Ruecker, N. J., Estimated discharge of microplastics via urban stormwater during individual rain events. *Front Environ Sci* **2023,** *11*, 1090267.
12. Jarlskog, I.; Stromvall, A. M.; Magnusson, K.; Gustafsson, M.; Polukarova, M.; Galfi, H.; Aronsson, M.; Andersson-Skold, Y., Occurrence of tire and bitumen wear microplastics on urban streets and in sweepsand and washwater. *Sci Total Environ* **2020,** *729*, 138950.
13. Rodland, E. S.; Lind, O. C.; Reid, M. J.; Heier, L. S.; Okoffo, E. D.; Rauert, C.; Thomas, K. V.; Meland, S., Occurrence of tire and road wear particles in urban and peri-urban snowbanks, and their potential environmental implications. *Sci Total Environ* **2022,** *824*, 153785.
14. Wagner, S.; Huffer, T.; Klockner, P.; Wehrhahn, M.; Hofmann, T.; Reemtsma, T., Tire wear particles in the aquatic environment - A review on generation, analysis, occurrence, fate and effects. *Water Res* **2018,** *139*, 83-100.
15. Smyth, K.; Drake, J.; Li, Y.; Rochman, C.; Van Seters, T.; Passeport, E., Bioretention cells remove microplastics from urban stormwater. *Water Res* **2021,** *191*, 116785.
16. Kovochich, M.; Parker, J. A.; Oh, S. C.; Lee, J. P.; Wagner, S.; Reemtsma, T.; Unice, K. M., Characterization of Individual Tire and Road Wear Particles in Environmental Road Dust, Tunnel Dust, and Sediment. *ES&T Letters* **2021,** *8*, (12), 1057-1064.
17. Koutnik, V. S.; Leonard, J.; Glasman, J. B.; Brar, J.; Koydemir, H. C.; Novoselov, A.; Bertel, R.; Tseng, D.; Ozcan, A.; Ravi, S.; Mohanty, S. K., Microplastics retained in stormwater control measures: Where do they come from and where do they go? *Water Res* **2022,** *210*, 118008.

18. Cunningham, B.; Harper, B.; Brander, S.; Harper, S., Toxicity of micro and nano tire particles and leachate for model freshwater organisms. *J Hazard Mater* **2022,** *429*, 128319.

19. Sorensen, L.; Gomes, T.; Igartua, A.; Lyngstad, I. L.; Almeida, A. C.; Wagner, M.; Booth, A. M., Organic chemicals associated with rubber are more toxic to marine algae and bacteria than those of thermoplastics. *J Hazard Mater* **2023,** *458*, 131810.

20. Wang, J.; Bucci, K.; Helm, P. A.; Hoellein, T.; Hoffman, M. J.; Rooney, R.; Rochman, C. M.; Liu, Y., Runoff and discharge pathways of microplastics into freshwater ecosystems: A systematic review and meta-analysis. *Facets* **2022,** *7*, 1473-1492.

21. Mennekes, D.; Nowack, B., Tire wear particle emissions: Measurement data where are you? *Sci Total Environ* **2022,** *830*, 154655.

22. Jarlskog, I.; Jaramillo-Vogel, D.; Rausch, J.; Gustafsson, M.; Stromvall, A. M.; Andersson-Skold, Y., Concentrations of tire wear microplastics and other traffic-derived non-exhaust particles in the road environment. *Environ Int* **2022,** *170*, 107618.

23. Ziajahromi, S.; Drapper, D.; Hornbuckle, A.; Rintoul, L.; Leusch, F. D. L., Microplastic pollution in a stormwater floating treatment wetland: Detection of tyre particles in sediment. *Sci Total Environ* **2020,** *713*, 136356.

24. Lu, H. C.; Ziajahromi, S.; Locke, A.; Neale, P. A.; Leusch, F. D. L., Microplastics profile in constructed wetlands: Distribution, retention and implications. *Environ Pollut* **2022,** *313*, 120079.

25. Ziajahromi, S.; Neale, P. A.; Telles Silveira, I.; Chua, A.; Leusch, F. D. L., An audit of microplastic abundance throughout three Australian wastewater treatment plants. *Chemosphere* **2021,** *263*, 128294.

26. Eisentraut, P.; Dümichen, E.; Ruhl, A. S.; Jekel, M.; Albrecht, M.; Gehde, M.; Braun, U., Two Birds with One Stone—Fast and Simultaneous Analysis of Microplastics: Microparticles Derived from Thermoplastics and Tire Wear. *ES & Te Letters* **2018,** *5*, (10), 608-613.

27. Matsueda, M.; Mattonai, M.; Iwai, I.; Watanabe, A.; Teramae, N.; Robberson, W.; Ohtani, H.; Kim, Y.-M.; Watanabe, C., Preparation and test of a reference mixture of eleven polymers with deactivated inorganic diluent for microplastics analysis by pyrolysis-GC–MS. *J Anal Appl Pyrolysis* **2021,** *154*.

28. Ziajahromi, S.; Leusch, F. D. L., Systematic assessment of data quality and quality assurance/quality control (QA/QC) of current research on microplastics in biosolids and agricultural soils. *Environ Pollut* **2022,** *294*, 118629.

29. Koelmans, A. A.; Mohamed Nor, N. H.; Hermsen, E.; Kooi, M.; Mintenig, S. M.; De France, J., Microplastics in freshwaters and drinking water: Critical review and assessment of data quality. *Water Res* **2019,** *155*, 410-422.

30. Kirstein, I. V.; Hensel, F.; Gomiero, A.; Iordachescu, L.; Vianello, A.; Wittgren, H. B.; Vollertsen, J., Drinking plastics? - Quantification and qualification of microplastics in drinking water distribution systems by microFTIR and Py-GCMS. *Water Res* **2021,** *188*, 116519.

31. Fazli, A.; Rodrigue, D., Waste Rubber Recycling: A Review on the Evolution and Properties of Thermoplastic Elastomers. *Materials (Basel)* **2020,** *13*, (3).

32. Liu, F.; Olesen, K. B.; Borregaard, A. R.; Vollertsen, J., Microplastics in urban and highway stormwater retention ponds. *Sci Total Environ* **2019,** *671*, 992-1000.

33. Pinon-Colin, T. J.; Rodriguez-Jimenez, R.; Rogel-Hernandez, E.; Alvarez-Andrade, A.; Wakida, F. T., Microplastics in stormwater runoff in a semiarid region, Tijuana, Mexico. *Sci Total Environ* **2020,** *704*, 135411.

34. Cho, Y.; Shim, W. J.; Ha, S. Y.; Han, G. M.; Jang, M.; Hong, S. H., Microplastic emission characteristics of stormwater runoff in an urban area: Intra-event variability and influencing factors. *Sci Total Environ* **2023,** *866*, 161318.

35. Grbic, J.; Helm, P.; Athey, S.; Rochman, C. M., Microplastics entering northwestern Lake Ontario are diverse and linked to urban sources. *Water Res* **2020,** *174*, 115623.

36. Parker-Jurd, F. N. F.; Napper, I. E.; Abbott, G. D.; Hann, S.; Thompson, R. C., Quantifying the release of tyre wear particles to the marine environment via multiple pathways. *Mar Pollut Bull* **2021,** *172*, 112897.
37. Lu, H.-C.; Ziajahromi, S.; Neale, P. A.; Leusch, F. D. L., A systematic review of freshwater microplastics in water and sediments: Recommendations for harmonisation to enhance future study comparisons. *Sci Total Environ,* **2021,** *781*.
38. Leusch, F. D.; Lu, H. C.; Perera, K.; Neale, P. A.; Ziajahromi, S., Analysis of the literature shows a remarkably consistent relationship between size and abundance of microplastics across different environmental matrices. *Environ Pollut* **2023,** *319*, 120984.
39. Kooi, M.; Koelmans, A. A., Simplifying Microplastic via Continuous Probability Distributions for Size, Shape, and Density. *ES&TLetters* **2019,** *6*, (9), 551-557.
40. Lange, K.; Magnusson, K.; Viklander, M.; Blecken, G. T., Removal of rubber, bitumen and other microplastic particles from stormwater by a gross pollutant trap - bioretention treatment train. *Water Res* **2021,** *202*, 117457.
41. Liu, P.; Zhan, X.; Wu, X.; Li, J.; Wang, H.; Gao, S., Effect of weathering on environmental behavior of microplastics: Properties, sorption and potential risks. *Chemosphere* **2020,** *242*, 125193.
42. Chen, Y.; Li, T.; Hu, H.; Ao, H.; Xiong, X.; Shi, H.; Wu, C., Transport and fate of microplastics in constructed wetlands: A microcosm study. *J Hazard Mater* **2021,** *415*, 125615.
43. Mengistu, D.; Heistad, A.; Coutris, C., Tire wear particles concentrations in gully pot sediments. *Sci Total Environ* **2021,** *769*, 144785.
44. Niu, S.; Wang, T.; Xia, Y., Microplastic pollution in sediments of urban rainwater drainage system. *Sci Total Environ* **2023,** *868*, 161673.
45. Rauert, C.; Rødland, E. S.; Okoffo, E. D.; Reid, M. J.; Meland, S.; Thomas, K. V., Challenges with Quantifying Tire Road Wear Particles: Recognizing the Need for Further Refinement of the ISO Technical Specification. *ES&TLetters,* **2021,** *8*, (3), 231-236.