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PHYSICAL AND CHEMICAL CHARACTERIZATION OF LABORATORY-GENERATED TYRE WEAR PARTICLES

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ABSTRACT

Tyre wear particles are generated by the frictional forces between a tyre and the road during driving. Tyre wear represents one of the biggest sources of synthetic polymer-based material released into the environment, significantly contributing to microplastic pollution and the associated ecological consequences. However, the extent of tyre particle pollution is not fully understood, and research and understanding are hindered by a lack of described chemical compounds that meet all the criteria for an effective marker of tyre particles. The aims of this study were to develop a methodology for generating tyre particles using a pin-on-disc tribometer; and to distinguish the chemical components in the particles – using two-dimensional gas chromatography-mass spectrometry – to propose a suite of potential markers. The results show that the morphology of the tyre particles reflected that of particles generated in previous literature and during driving. Additionally, the suggested markers were common across the three tyre brands studied here, thus meeting one of the criteria for a successful marker. Future research into measuring the concentration of tyre particles in environmental samples is necessary to understand further their distribution, and assessing the contribution of tyre particles to non-exhaust emissions can inform on future engineering strategies to minimise their release.

1. INTRODUCTION

Plastics are synthetic polymers that are not naturally occurring (Geyer, 2020). An early example of plastic was Parkesine, a thermoplastic nitrocellulose created by Alexander Parkes in the 1850s. However, Parkesine was not fully synthetic (Rasmussen, 2021). The first truly synthetic plastic was "Bakelite," which was introduced over a century ago and was used in a variety of household items such as radios (Napper & Thompson, 2020). Plastics were not produced on an industrial scale until after the Second World War, reaching a global annual production of two million tonnes by 1950 (Geyer, 2020). Since then the plastic industry has increased exponentially, with the global output now exceeding 350 million tons per annum (Geyer, 2020), 50% of which is disposed of after a single use (Xanthos & Walker, 2020). The growth of the plastics industry was fuelled by their desirable properties, including affordability, durability, malleability, and low weight (Wang et al., 2021), resulting in their rapid incorporation into every aspect of life, including packaging, clothing, electronics, furniture, vehicles, buildings, sports equipment, medical supplies, and agriculture (Geyer, 2020). Supplementary Table S1 shows the uses, properties, and greatest environmental sinks of common plastics.

Plastic debris is commonly classified based on particle size, as this eases comparison between different studies (Ramkumar et al., 2022). Microplastics are the size fraction that has received the most attention since evidence of their presence in oceans and marine sediments was first reported by Thompson et al. in 2004. The most agreed-upon definition for microplastics is "any synthetic solid particle or polymeric matrix of any shape and with size ranging from 1 µm to 5 mm, of either primary or secondary derivative/degraded material from the primary origin, which is insoluble in water", which was proposed by Frias & Nash in 2019. Plastic particles that are greater than 5 mm are referred to as "macroplastics", whereas those less than 1 µm are termed "nanoplastics" (Ramkumar et al., 2022). The term "primary microplastics" describes plastics that were manufactured to be between 1 µm and 5 mm in size for use in cosmetics, industrial cleaners, or as virgin plastic pellets, whereas secondary microplastics are formed from the physical abrasion and chemical breakdown of larger plastic fragments (Wang et al., 2021).

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Plastic's resistance to degradation means that it is present in every habitat on Earth (MacLeo et al., 2021), with soils and oceans being the first destination for 32% of discarded plastics (Machado et al., 2018). The ocean is currently considered to be the largest environmental sink for plastic waste (Wang et al., 2021), with land-originated plastics comprising 40-80% of marine litter (Barnes et al., 2009). Awareness of marine plastic waste began over 50 years ago when there were reports of plastic fragments being ingested by seabirds, and now plastic debris is distributed in oceans across the planet, along coastlines, in sea ice, at the surface and on the sea floor (Barnes et al., 2009). The latter is a major sink of ocean plastic, where it accumulates after breaking down into smaller particles, losing buoyancy and sinking (Abel et al., 2023). The remote nature of the deep-sea means that little is known about the extent of plastic pollution here, but a recent study discovered microplastics at depths of over 5000 m in the Kuril-Kamchatka Trench of the Pacific Ocean (Fischer et al., 2015). Plastic pollution differs from other pollutants in that it can induce three types of toxic effects: physical, chemical, and biological (Leistenschneider et al., 2023), which are detailed in Table 1.

Although the oceans are considered to be the world's biggest plastic pollution sink, terrestrial soils – particularly agricultural soils – could harbour more microplastics (Machado et al., 2018). It is estimated that one third of all plastic waste reaches soils, breaking down into microplastics and nanoplastics (Tudor et al., 2019). Wastewater treatment plants (WWTPs) are one of the largest contributors to soil microplastics, as they release plastics from textile fibres, vehicle tyres, industrial processes and microplastic beads into the environment (Tudor et al., 2019). According to an estimate by Rochman et al. in 2015, 99% of microbeads in WWTPs settle into sludge, half of which is spread on agricultural land as fertiliser, adding 44,000-300,000 tons of microplastics to North American soils annually (Hurley & Nizzetto, 2018). The eight trillion microbeads remaining in the effluent are released into aquatic environments daily from WWTPs in the United States (US) (Rochman et al., 2015). Microbeads in cosmetic products have since been banned in many countries, including many European countries, the US, China, South Korea, Brazil, and New Zealand. In the UK, the Department for Environment, Food and Rural Affairs' (DEFRA) microbead ban covered "any water-insoluble solid plastic particle of less than or equal to 5 mm in dimension" and has been in place since 2018 (Anagnosti et al., 2021).

However, microbeads are not the only source of microplastics in sewage. The wear of vehicle tyres is one of the biggest sources of solid, water-insoluble, synthetic polymer-based material released into the environment (Knight et al., 2020; Sommer et al., 2018) Tyre wear particles are generated by the friction and shear forces that occur because of contact between a tyre and the road surface during driving (Baensch-Baltruschat et al., 2020). Many factors impact the properties of these particles, including the tyre material; vehicle characteristics (e.g. weight); driving style

TABLE 1: The physical, chemical, and biological toxic effects induced in marine organisms by exposure to microplastics.

Type of effects	Mechanism of interaction	Effects
Physical effects	• Macroplastic debris can trap and entangle marine mammals • Microplastics and nanoplastics can be ingested by marine organisms at all trophic levels via a variety of feeding techniques. • Plastic debris can sometimes be ingested due to being mistaken for a specific prey (e.g. green turtles mistaking plastic bags for jellyfish).	• Entrapment can cause death by starvation, blood-loss, or oxygen deprivation (Guzzetti et al., 2018). • Ingestion of microplastics results in digestive tract obstructions resulting in a pseudo-satiety sensation, dehydration, and poor nutrition (Guzzetti et al., 2018). • Ingestion also causes internal abrasions leading to physiological stress (Guzzetti et al., 2018). • Microplastics can translocate between body tissues (Leistenschneider et al., 2023). • Nanoplastics can pass up the food chain from low trophic levels (Leistenschneider et al., 2023).
Chemical effects	• Plastic additives (add useful properties to plastic) can leach out of plastic debris due to not being chemically bound. • Other environmental pollutants such as polychlorinated biphenyls (BCPs) and polycyclic aromatic hydrocarbons (PAHs) can adsorb onto the surface of microplastics causing additional toxic effects.	• Tanaka et al. found flame retardants in the tissues of Puffinus tenuirostris that had leached from ingested microplastics. Flame retardants are associated with a range of toxic effects, including reproductive toxicity, carcinogenicity, neurotoxicity and genotoxicity (Deng et al., 2018). • Causes endocrine disruption and cell cycle interruption, often leading to death (Hermabessiere et al., 2017).
Biological effects	• Surface of microplastic particles acts as a vector for pathogens, forming a biofilm. • Biofilms can decrease the buoyancy of plastic debris, increasing the availability of plastic toxicity throughout the water column.	• Pathogens can enter marine organisms upon ingestion of microplastic vectors (Leistenschneider et al., 2023). • Some species (e.g. copepods) have been observed being preferentially attracted to biofilm microplastics as opposed to pristine ones (Dahms et al., 2007). • Plastic debris may be accidentally ingested when a marine organism wants to ingest the biofilm (Dahms et al., 2007). • Reduction in fertility (Guzzetti et al., 2018)

(e.g. speed, acceleration, cornering); road material; and environmental conditions (Wagner et al., 2018).

Tyre particles in the environment are vastly different compared to the original tyre material. Firstly, shearing forces generate coarser particles which roll across the road surface in a "snowball" manner, collecting other road material to form a tyre and road wear particle (TRWP) complex. Moreover, heat from friction between the tyre and road surface changes the chemical composition of the particles compared to the original tyre material (Kreider et al., 2010). Harsher driving conditions, such as tyre slip, result in increased friction, generating a significantly higher proportion of ultrafine particles (≤ 100 nm) through evaporation and condensation of volatile organic compounds (VOCs) from the tyre tread (Liu et al., 2022).

It is estimated that almost six million tonnes of tyre wear particles are generated annually, around 12% of which end up in the atmosphere (Ding et al., 2023). Here, they can cause many effects upon inhalation, such as the release of inflammatory markers in human alveolar cells (Gualtieri et al., 2008). Another 6% of tyre wear particles end up in surface waters (Ding et al., 2023), the effects of which have been researched in depth (Kreider et al., 2010) despite this being a small sink of tyre particles. 15% of tyre wear particles end up in sewers, and the remaining 67% end up in soils, making soils the largest environmental sink of tyre-related microplastics. However, the consequences of tyre particles in soils have been researched far less compared to in aquatic environments (Ding et al., 2023). The ecological and health implications of tyre wear particles in various environmental compartments are shown in Table 2.

In the literature, tyre particles are described as being black in colour and elongated in shape, ranging from "sausage rolls" to rough spheres (Dannis, 1974), gathering road material as they roll across the road (Adachi & Tainosho, 2004). In previous studies tyre wear particles have been generated in the laboratory to study their physical and chemical characteristics, but there is a lack of a standardised methodology. For example, Kreider et al. (2010) generated tyre wear particles using a road stimulator laboratory at the German Federal Highway Research Institute, which mimics a variety of driving conditions. Nevertheless, whilst this method produces realistic tyre wear particles, it uses specialist, expensive equipment that is inaccessible for most researchers. In the study by Son & Choi (2022), tyre wear particles were mixed with microplastics to replicate real-world TRWP. However, precise replication of TRWP is time consuming and is unlikely to be representative of the particles in question. Conversely, Gualtieri et al. (2005) generated tyre wear particles by rotating a new vehicle tyre against a steel brush, resulting in particles with a similar morphology to those released during real driving conditions. However, using a new tyre means that it has not been exposed to weathering and friction with the road surface, meaning the chemical characteristics of the particles are unlikely to be comparable to those in the environment (Wagner et al., 2022).

A reliable chemical marker of tyre wear particles should be specific to the rubber polymer; comparable across different tyre brands; water-insoluble so it cannot leach out; stable under environmental conditions; and easily and precisely detectable (Baensch-Baltruschat et al., 2020). Previous studies have assessed the accuracy of different markers such as benzothiazole (Liao et al., 2018) and zinc (Zn) (Chae et al., 2021). However, the concentration of benzothiazole varies significantly across different tyre brands (Chae et al., 2021), and it is also highly polar and hence water-soluble (Wagner et al., 2018). Additionally, Zn

TABLE 2: The ecological and health impacts of tyre particles and their leachates including zinc (Zn), other metals and organic compounds (e.g. benzothiazoles and resin acids).

Impacts of airborne tyre particles on human health	Impacts of leachate on aquatic organisms	Impacts of tyre particles and leachate on soil organisms	Impacts of tyre particles on sediments and energy cycle
• Inhalation can cause alveolar irritation and inflammation (Gottipolu et al., 2008). • Smaller metal particles may migrate directly into the systemic circulation, directing cardiac changes (Gottipolu et al., 2008). • Oxidative stress inhibits mitochondrial enzymes (Gottipolu et al., 2008). • Cell mortality and DNA damage (Wik & Dave, 2009). • Modification of cell morphology (Wik & Dave, 2009). • Can induce reactive oxygen species (ROS), causing an inflammatory response (Wik & Dave, 2009).	• Lethal in concentrations ranging from 50-100,000 mg/l to organisms such as algae, water fleas, zebrafish, and frogs (Wik & Dave, 2009). • Reduced growth or growth inhibition (Ding et al., 2023). • Reduced number of offspring (Ding et al., 2023). • Delayed development (Camponelli et al., 2009) • Deformity (Camponelli et al., 2009). • Teratogenic (interferes with normal fetal development) (Wik & Dave, 2009). • Mutagenic (interferes with an organism's DNA, causing gene mutations) (Wik & Dave, 2009). • Endocrine disruption. • Induction of cytochrome P450 (involved in detoxification) (Camponelli et al., 2009).	• Zn increases soil pH, increasing rate of nitrification, leading to nitrate leaching from soils (Gualtieri et al., 2005). • Leachates such as bisphenol A and di-n-butyl phthalate affect hydrogen and methane production of waste active sludge (Ding et al., 2023). • Heavy metals, antibiotics and pathogens can adsorb to tyre wear particles, selecting for antibiotic resistance genes amongst soil microbiota and transferring pathogens (Ding et al., 2023). • Ingestion of tyre wear particles can damage earthworms' guts, and toxic compounds can leach out in the gut decreasing their reproductive rate and survival (Ding et al., 2023). • Smaller tyre wear particles can be up taken by plant roots, having a toxic effect (Ding et al., 2023). • Some leachates, e.g. PAHs, can inhibit plant growth (Ding et al., 2023).	• Tyre wear particles slowly settle in sediments, following their entry into water bodies (Ni et al., 2024) • Burrowing activity of sediment dwelling organisms might be affected (Ni et al., 2024). • Microbial community involved in ecological cycling of nitrogen and carbon can get affected, disturbing the ecosystem (Ni et al., 2024).

is released from other traffic-related sources such as brake wear (Baensch-Baltruschat et al., 2020), and hence neither of these markers is useful when identified alone. Oleamide is added to tyre materials to increase abrasion resistance and improve the compounding process, and it is not commonly found in other components of road dust (Chae et al., 2021). Furthermore, a previous study successfully identified oleamide in organic extracts of tyre wear particles using gas chromatography-mass spectrometry (GC-MS) (Chae et al., 2021). Additionally, liquid chromatography-MS (LC-MS) has been used to determine the concentrations of known tyre additives such as 1,4-benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl- (commonly known as 6-PPD) and benzothiazoles (Rauert et al., 2022). However, GC is the more commonly employed in the analysis of VOCs due to its greater selectivity, resolution and sensitivity compared to LC-MS (Pandey et al., 2011). When combined with detection techniques such as MS, GC provides a powerful tool for the identification of separated compounds from complex mixtures, with lower limits of detection (LOD) than GC alone (Braithwaite & Smith, 1999; Pandey et al., 2011). However, some chemical mixtures contain too many target analytes which can co-elute as part of an unresolved complex mixture (UCM), complicating identification and quantification of individual components. Two-dimensional (2D) GC mitigates this issue by utilising two separation columns with different stationary phases connected in series, which separate the components by volatility and polarity, resulting in a higher chromatographic resolution and greater selectivity of individual components. 2D GC is a powerful technique for separating large numbers of organic constituents, and hence it has often been applied to the analysis of complex environmental samples (Worton et al., 2012).

The first aim of this study was to develop and characterise a method for the generation of realistic tyre particles so the study can be repeated by other researchers. The objectives taken to achieve this aim were: (1) generating realistic tyre wear particles from samples of Michelin, Bridgestone, and Radial tyres in a tribometry laboratory; and (2) giving a comprehensive overview of the steps taken throughout this project, using accessible materials and equipment. The second aim was to assess the physical and chemical characteristics of tyre wear particles to propose a suite of characteristics that can be used to identify them in the environment. This was achieved by: (1) physically characterising the particles using an optical microscope and a scanning electron microscope (SEM); (2) employing 2D GC-MS to separate and identify the chemical components present in the tyre wear particles; and (3) evaluating the chemical composition of the different tyre brands in order to select the compounds most likely to be effective markers for tyre wear particles in environmental samples.

2. METHODS

2.1 Generation of the tyre wear particles in the laboratory

Used tyres of distinct brands (Michelin, Bridgestone and Radial) were supplied by a local vehicle repair garage (Southampton, UK). These tyre brands were readily accessible as used tyres from a local automotive workshop. Old tyres were selected because they have already been subjected to environmental factors such as wind, sunlight, and rain, making them environmentally relevant (Wagner et al., 2022).

Three samples were cut from each tyre using a bandsaw (Axminster Tools, Devon, UK) (Supplementary Figure S1). The samples were cut 120° apart to assess intra-tyre variability and to provide repeated measurements for each tyre brand. In a specialist tribometry laboratory each tyre sample was glued to a separate aluminium pin using a strong adhesive, allowing each sample to be attached to the pin-on-disc (PoD) tribometer (RJH Finishing Systems Ltd, West Yorkshire, UK).

Tyre wear particles from each tyre sample were generated using the PoD tribometer which consisted of the sample glued to an aluminium pin and a rough-textured stainless-steel disc (Supplementary Figure S2). The roughness of the disc, as measured by an Alicona G4 InfiniteFocus (Alicona, Raaba/Graz, Austria), was 160 µm. The tribometer was run under a vertical force of 38 N. It was observed that increasing the vertical force beyond 38 N elevated the contact pressure between the pin and the disc, potentially leading to wear of the disc due to rough texture of the disc. Therefore, a 38 N force was suitable to have a balance between effective particle generation and minimizing damage to the disc. The pin of the tribometer was positioned close to the central point of rotating disc. Each sample was run on the PoD tribometer for 20 mins (30 rpm, clockwise run direction) or until sufficient mass of tyre particles for physical and chemical characterisation was generated (200-300 mg). The PoD tribometer was run at 30 rpm as this speed generated sufficient particles without generating ultra-fine stainless-steel particulates that could contaminate the samples. The particles from each tyre sample were collected into separate petri dishes (Supplementary Figure S3) that had been pre-weighed using an analytical balance (Mettler-Toledo Ltd, Leicester, UK). The coarse and ultra-coarse particle fractions were collected from the disc using stainless-steel tweezers and the finer fraction was removed from the disc and into the petri dish using a plastic toothbrush in a sweeping motion. A magnet was swept over each particle sample to remove any potential contaminating stainless-steel particulates. The disc was cleaned between being run for different tyre samples using the toothbrush, and any remaining particulates on the brush were removed by nitrile-gloved hands. Generating tyre particles using the PoD was loud and hence 3M Peltor Optime III ear defenders (RS Components Ltd, Northamptonshire, UK) were worn as an item of personal protective equipment (PPE) in accordance with the risk assessment.

2.2 Physical characterisation of the tyre wear particles

Once the particles had been generated using the PoD tribometer, they were stored in their petri dishes in a standard laboratory refrigerator (4°C) until they were physically characterised. The particles were spread evenly in the petri

dishes and their sizes and morphologies were observed by placing each petri dish under the lens of a Leica M205C optical microscope (Leica Microsystems Ltd, Milton Keynes, UK). The Leica camera was used to capture a range of photographs, and the lengths of different particles were measured to assess the size range of the particles in each sample.

A JEOL JCM-6000 SEM (JEOL Ltd, Welwyn Garden City, UK) was used to conduct further analysis of the morphology of the tyre particles, including their microstructure. Particles were selected at random from each sample using aluminium tweezers and were stuck onto aluminium stubs using carbon tape. The particles on the stub were then coated with a thin layer of gold using a JEOL JFC-1300 sputter coater (JEOL Ltd, Welwyn Garden City, UK). Gold was used to sputter coat the samples due to its incredibly high conductivity, meaning it increases the signal-to-noise ratio during SEM imaging, producing better quality images. Tyre wear particles themselves are not conductive and their surface would function as an electron trap, charging the particles and creating bright-white regions on their surface on the produced image. Gold has a high secondary electron yield, and hence it is often used when examining surface morphology of samples (Heu et al., 2019). Magnification ranging from x20 to x1500 was used to analyse and measure the particles, their microstructure, and any irregularities in the tyre material.

2.3 2D GC-MS separation and identification of VOCs from the tyre wear particles

To analyse the chemical composition of the tyre particles, a single particle from each tyre brand underwent thermal desorption at 240°C and 500°C to extract the VOCs. The VOCs released at each thermal desorption temperature were then concentrated and injected into a Pegasus BT 4D GC x GC TOF MS (LECO Corp., St. Joseph, Michigan, US) in turn. For each run, the GC column flow rate was 1 ml/min with a helium carrier gas, constant GC inlet and a transfer line temperature of 250°C. Split 200:1 1 µl injections were made onto an Rxi-5SilMS primary column (30 m length x 250 µm inlet diameter x 0.25 µm film thickness) coupled to an Rxi17SilMS secondary column (1 m length x 250 µm inlet diameter x 0.25 µm film thickness). The primary oven temperature was held at 40°C for 2 min, ramped 5°C/min to 300°C and held for 4 mins. The secondary oven temperature offset was +5°C relative to the primary oven. A modulation period of 8 secs with hot pulse duration of 2.4 secs and cooling time between stages of 1.6 secs was used for the data acquisition. The detector was on Maximum Sensitivity Mode. The modulator temperature was maintained +15°C relative to the secondary oven. The MS ion source temperature was 250°C and the MS data was collected at a spectral acquisition rate of 200 spectra/sec. Data acquisition with an m/z range of 35-550 started after a solvent delay of 250 secs.

2.4 Data handling and analysis

The data output from the 2D GC-MS was managed on Microsoft Excel. The total number of identified organic compounds in each tyre particle sample was recorded before filtering the data so that only organic compounds with a chromatogram peak similarity to the MS database of ≥ 900 were included in the analysis. Conditional formatting was used to highlight any compounds that were found in all three tyre brands at each thermal desorption temperature, and these compounds were then sorted into a table based on their chemical categories (aliphatic; aromatic; polycyclic aromatic; hydrocarbons; and sulphur-, nitrogen- and silicon-containing) (Supplementary Tables S2 and S3). A literature search of each compound along with "tyres;" "rubber;" "industrial uses" and "sources in environmental samples" was performed using Google Scholar and Web of Science in order to identify the compounds with distinct links to tyre manufacturing or the rubber industry.

3. RESULTS

3.1 Comparison of the morphology of tyre wear particles from the different tyre brands

Observation of the tyre particles from the three tyre brands using an optical microscope revealed that they were all black in colour and ranged from sausage-shaped to spherical. Many of the Michelin tyre particles were larger than the Bridgestone and Radial particles, with some reaching over 11.0 mm in length (Figure 1A). However, most tyre particles from the Michelin tyre ranged from approximately 1.0 mm to 5.0 mm in length (Figure 1B), and the larger tyre particles tended to be more sausage-shaped than the smaller ones, which were more spherical (Figure 1B). The optical microscope analysis of the Michelin tyre particles also revealed the presence of a colourless fibrous material interwoven with the tyre rubber polymer (Figure 1B). This material was much less abundant in the Bridgestone particles (Figures 1C and 1D) and in the Radial particles (Figures 1E and 1F).

Initial observation of the tyre particles from the Bridgestone tyre revealed that, on average, they were smaller than the Michelin particles (Supplementary Figure S4), with many measuring under 2.5 mm in length (Figure 2D). Although the smaller Bridgestone particles were more spherical as opposed to sausage-shaped, the larger Bridgestone particles displayed the characteristic sausage shape, and ranged from approximately 1.5 mm to 6.0 mm (Figure 2C).

The Radial tyre particles were a similar shape and size to the Bridgestone particles, and most were between 3.0 mm and 6.0 mm (Figure 1E), with the largest reaching approximately 9.0 mm in length (Figure 4F). Similarly to the Michelin and Bridgestone particles, the Radial particles were mostly sausage-shaped, although the smaller particles (≤ 2.0 mm) tended to be more spherical (Figures 1E and 1F).

Analysis of the microstructure of the tyre wear particles from the different tyre brands using the SEM revealed that there were few stark differences between them. However, the Michelin tyre particles appeared less dense than the other two brands, and the microstructure seemed porous and stretchy (Figure 2A). The colourless fibrous material seen with the optical microscope was also visible in the

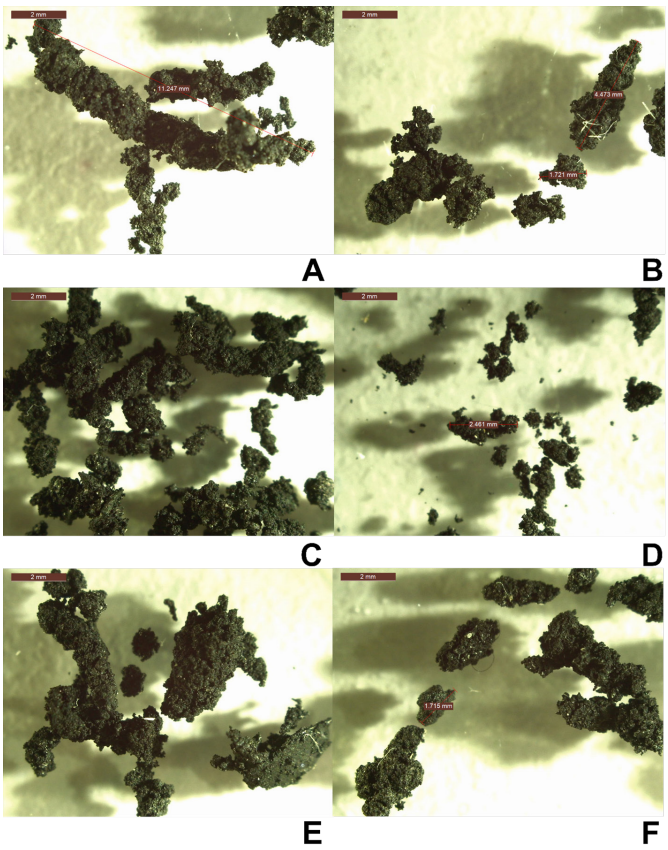

FIGURE 1: The optical microscope images of tyre wear particles from the three tyre brands (Michelin, Bridgestone and Radial).

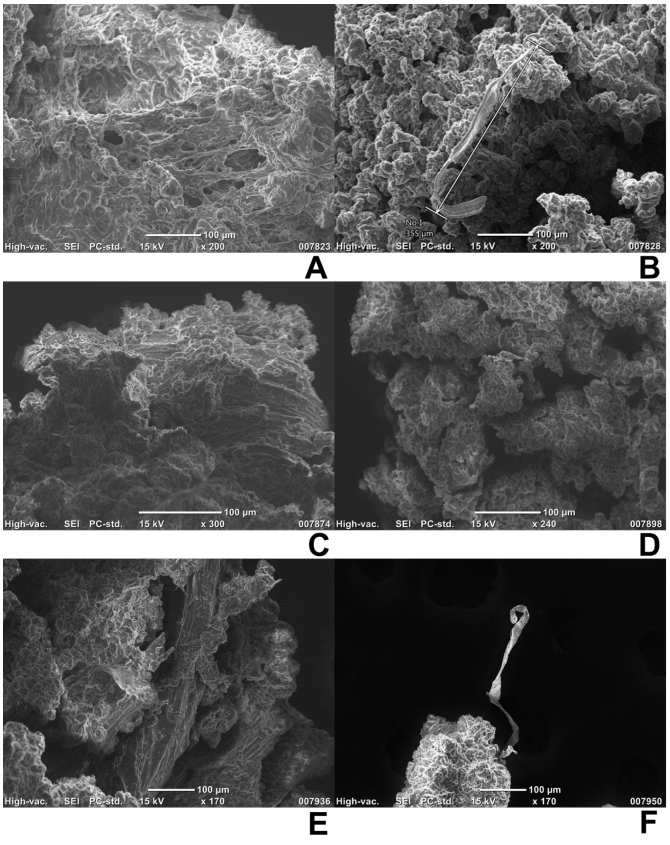

FIGURE 2: SEM images of tyre wear particles' microstructure.

SEM imaging, appearing as long, ribbon-shaped artefacts protruding from the rubber (Figure 2B).

In comparison, the Bridgestone tyre particles had a much denser microstructure with less visible porosity (Figure 2C) compared to the Michelin tyre particles. Furthermore, the surface of the particles appeared cracked (Figure 2D), indicating a potentially harder tyre composition.

Similarly to the Bridgestone tyre particles, the Radial tyre particles had a dense microstructure (Figure 2E). The ribbon-shaped artefacts were more sparsely distributed in the Radial particles compared to in the Michelin particles, but some were clearly visible extending from the rubber (Figure 2F).

3.2 Compounds detected in the different tyre brands after thermal desorption at 240°C

The chromatograms for the 2D GC-MS at a thermal desorption temperature of 240°C (Figure 3) showed that more compounds were released from the Michelin and Bridgestone tyre particles (Figures 3A and 3B) than from the Radial tyre particle (Figure 3C). Analysis of the 2D GC-MS output prior to filtering the data revealed that, in total, there were 146 identified compounds released from the Michelin tyre particle at 240°C; 159 from the Bridgestone tyre particle and only 116 from the Radial tyre particle.

After filtering data, there were most similarities between the chemical composition of the tyre particles from the Michelin and Radial tyres, whereby there were 37 compounds common to the Michelin and Radial tyre particles. Furthermore, there were 33 compounds common to the Michelin and Bridgestone particles, and only 23 compounds present in both the Bridgestone and Radial particles.

Nineteen compounds were present in all three tyre brands after thermal desorption at 240°C (Supplementary Table S2), 21% of which were straight chain alkanes (ranging from C_{18}-C_{25}) and 32% were other hydrocarbons, mainly fatty acids which are commonly used in the synthetic rubber industry (Hirata et al., 2014). Compounds linked to the tyre industry were p-xylene, a thermal desorption product of natural rubber (Han et al., 2023); and cyclohexanethiol and benzothiazole (and its derivative 2-mercaptobenzothiazole) which are a processing aid (Molanorouzi & Mo-

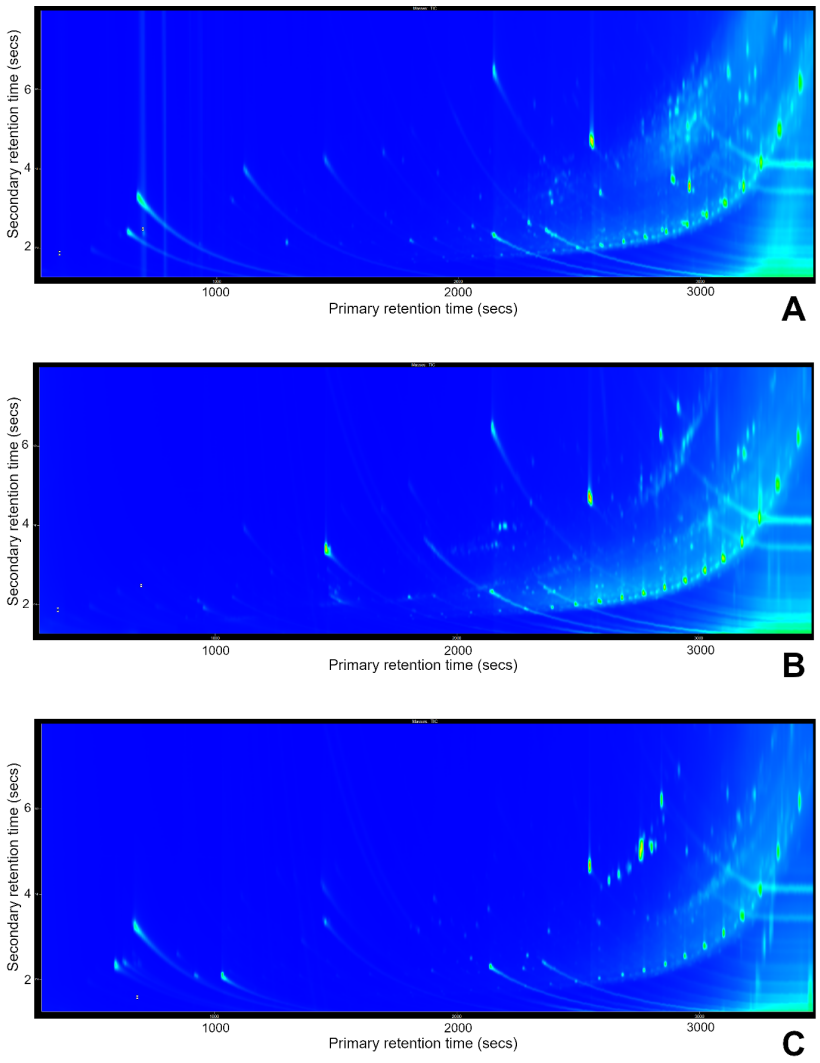

FIGURE 3: The chromatograms from the 2D GC-MS after thermal desorption at 240°C for the (A) Michelin; (B) Bridgestone and (C) Radial tyre particles.

haved, 2016) and a vulcanisation accelerator (Valdes et al., 2016) in synthetic rubber processing, respectively.

Styrene is used in the production of styrene-butadiene rubber (SBR) – the most common synthetic tyre rubber (Grieco et al., 2008) – yet at 240°C it was only present in the Michelin and Bridgestone tyre particles, but not in the Radial tyre particle until 500°C. α-methylstyrene is blended with styrene in synthetic rubber manufacturing to modify the viscoelastic properties of the tyre (Wolf et al., 2021). At 240°C it was present in the Radial tyre particle, but it was not present in the Michelin and Bridgestone tyre particles until 500°C.

6-PPD is an antioxidant and antiozonant widely used in rubber tyres to increase their resistance to weathering and thus extend their useful life (Chen et al., 2023). There was a peak on the chromatograms for the Michelin and Bridgestone tyre particles that was a close match to the MS database for 6-PPD. 6-PPD was also present in the Radial tyre after thermal desorption at 240°C, but with a peak similarity of 887. Nonetheless, it was included in these results because of its proven link to tyre particles in previous literature (Rauert et al., 2022).

Figure 4 is a hierarchy presenting the compounds with the strongest links to the tyre manufacturing industry. Although none of these compounds fulfil all the criteria for a suitable marker of tyre wear, they provide a strong indication of tyre wear particles in environmental samples when identified together. These compounds were common to all the tyre brands at 240°C (except styrene and α-methylstyrene), which is a key consideration when identifying a successful tyre wear marker (Baensch-Baltruschat et al., 2020).

3.3 Compounds detected in the different tyres after thermal desorption at 500°C

The chromatograms after thermal desorption at 500°C (Figure 5) showed that many more VOCs had vaporised from the tyre particles compared to after thermal desorption at 240°C. As with thermal desorption at 240°C, more compounds were released from the Michelin and Bridgestone particles (Figures 5A and 5B) than from the Radial particle (Figure 5C). There were 710 identified compounds in the Michelin particle; 790 in the Bridgestone particle; and only 504 in the Radial particle. However, once the data was filtered so that only compounds with a similarity to the MS database of ≥ 900 were included, the number of compounds in each tyre brand were within a range of 10: 148 in the Michelin particle; 158 in the Bridgestone particle and 150 in the Radial particle. Of these compounds, ninety were present in both the Michelin and Bridgestone tyre particles; 89 in both the Bridgestone and Radial tyre particles; and 92 in both the Michelin and Radial tyre particles.

There were seventy compounds present in all three tyre brands after thermal desorption at 500°C, a 268% increase from the number of compounds present in all three brands at 240°C. The majority of these compounds were aromatic, with 31% being single ring aromatics and 29% being polycyclic aromatic hydrocarbons (PAHs) with two to four aromatic rings. The remaining compounds were aliphatic compounds (straight chain alkanes and alkenes ranging from C_{10}-C_{24}); hydrocarbons (mainly non-aromatic cyclic compounds); sulphur compounds; nitrogen compounds (including benzothiazole); and CMS compounds (Supplementary Table S3).

The only compounds identified after thermal desorption at 240°C that were still present at 500°C were benzothiazole, tetracosane, styrene/α-methylstyrene and two CMSs. Benzothiazole is used as an antibacterial in hospitals and for the management of viral diseases in the agriculture sector (Zou et al., 2023). Similarly, styrene/α-methylstyrene is used as a raw material in the formulation of road paints (Hoppe et al., 2005), which may lead to overrepresentation of tyre wear particles on roads. Tetracosane is an alkane, and its presence is not indicative of tyre particles. CMSs

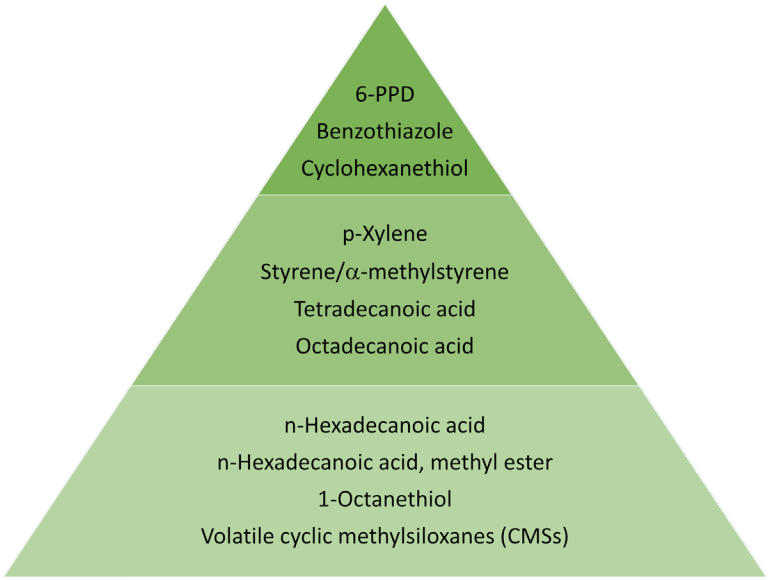

FIGURE 4: A hierarchy of the most useful compounds present in the tyre particles from the three tyre brands after thermal desorption at 240°C.

are widespread in the environment because they are used in personal care products and industrial processes related to silicon and rubber (Genualdi et al., 2011).

Other compounds present after thermal desorption at 500°C that have links to the rubber and tyre industry were aniline; cyclopentanone; and various PAHs, which were included in a hierarchy of potential markers (Figure 6). However, the increase in the proportion of PAHs to 29% at 500°C compared to just 5% at 240°C suggests that PAHs at 500°C are either by-products of degradation of larger compounds or are formed through reactions with other composites. For example, Richter & Howard (2000) found that PAHs react with single ring aromatic compounds, leading to successive growth of PAHs. Moreover, PAHs, as constituents of petrochemical fuels, are produced through combustion of fuel in engines (Dandajeh et al., 2019). Since PAHs are associated with burning of fuel and rank lower in hierarchy of potential markers (Figure 6), they might not be suitable indicators of tyre wear particles in the environment.

As with the hierarchy of potential markers at 240°C, these compounds were present in all three tyre brands (except styrene/α-methylstyrene), which is a key consideration when proposing a suitable marker compound (Baensch-Baltruschat et al., 2020). Compounds related to tyre manufacturing that were identified at 240°C, such as 6-PPD, cyclohexanethiol and p-xylene, were absent at 500°C.

4. DISCUSSION

Our study's first aim was to develop and characterise a method of generating tyre wear particles in the laboratory. Initial examination of the tyre particles' morphology using an optical microscope revealed that the particles from each tyre brand were black in colour and ranged from sausage-shaped to rough spheres, supporting observations made in previous literature (Adachi & Tainosho, 2004; Dannis, 1974; Gualtieri et al., 2005; Padovan et al., 1999). Tyre particles generated here ranged from approximately 200.0 µm to 11.0 mm in length, and were significantly larger than the tyre particles generated in previous research at the University of Southampton. Preceding studies similarly used

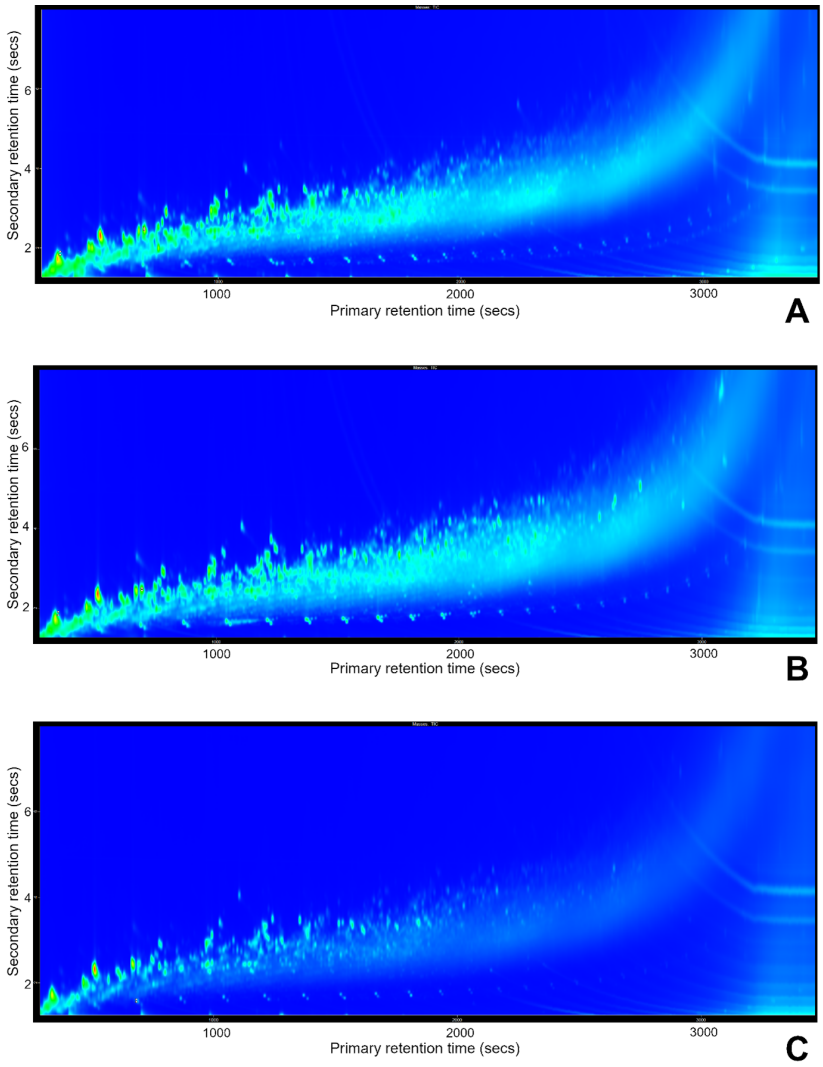

FIGURE 5: The chromatograms from the 2D GC-MS after thermal desorption at 500°C for the (A) Michelin; (B) Bridgestone and (C) Radial tyre particles.

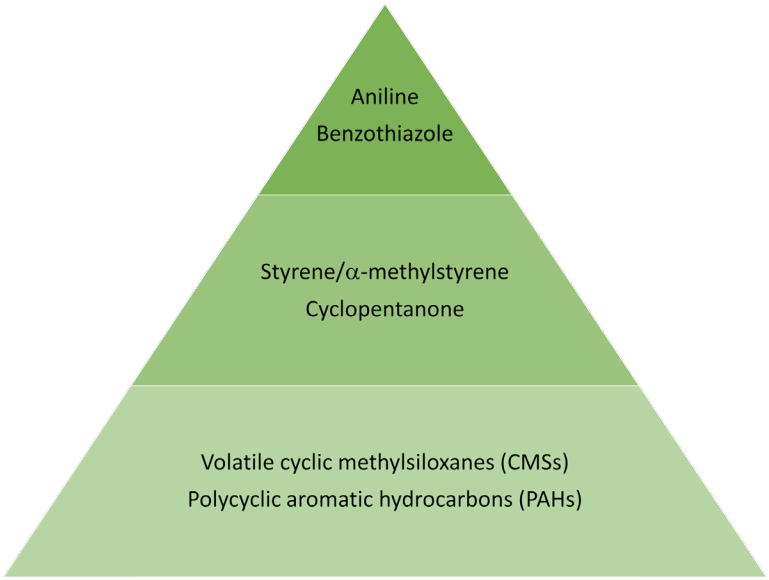

FIGURE 6: A hierarchy of the most useful compounds present in the tyre particles from the three tyre brands after thermal desorption at 500°C.

a PoD tribometer, but with a finer textured disc, producing tyre particles ranging from 120.0 µm to 3.0 mm in size. The texture of the disc used in this study was coarser, and consequently the tyre particles were larger in size. Subsequent analysis using an SEM revealed that the microstructure of the tyre particles was consistent in particles from the three brands. However, the Michelin particles were larger on average and their microstructure was less dense compared to the Bridgestone and Radial tyre particles. One potential explanation for the unique characteristics of the Michelin tyre particles is that the rubber polymer is softer and has a higher viscoelasticity, resulting in larger particles being formed during wear conditions (Cao et al., 2022). The higher viscoelasticity would also account for the porous appearance of the Michelin tyre particles' microstructure. Nonetheless, these differences were not pronounced enough to distinguish the Michelin tyre wear particles from other brands.

Our study's second aim was to propose a suite of chemical compounds that can be useful indicators for the presence of tyre wear particles in the environment. To address this aim, a 2D GC-MS was used to analyse the chemical composition of tyre particles from each tyre brand. No previous research was found evidencing the application of this technique to the chemical analysis of tyre particles, and hence its usage here is a novel approach to the study of tyre wear. Previous studies have often focused on a small number of potential marker compounds (Chae et al., 2021; Rauert et al., 2022), whereas this study provided a comprehensive overview of all the compounds in the tyre particles that have links to the tyre and rubber industries. Benzothiazole (Chae et al., 2021) and 6-PPD (Rauert et al., 2022) have been suggested as markers for tyre wear in previous literature and they were present here after thermal desorption at 240°C. There were nineteen compounds common to all three tyres after thermal desorption at 240°C, the majority of which were aliphatic compounds and other hydrocarbons. The compounds deemed to be the most indicative of tyre particles in environmental samples were those that are used as additives or processing aids in tyre manufacturing, or those that are thermal desorption products of natural and synthetic rubber. Styrene was not released from the Radial tyres until 500°C, whereas it was released from the Michelin and Bridgestone tyres at 240°C. α-methylstyrene on the other hand, was released from the Radial tyres at 240°C, but not from the other two brands until 500°C. Oleamide, used as a marker of tyre wear in a previous study quantifying tyre particles in road dust (Chae et al., 2021), was notably absent from all the tyres after thermal desorption at both 240°C and 500°C. A possible explanation for the absence of oleamide is that it is not used in the manufacturing processes for Michelin, Bridgestone or Radial tyres. Alternatively, it may be present in concentrations below the lower limit of detection for the 2D GC-MS. Future research would benefit from repeating this study with a wider range of tyre brands and assessing whether oleamide is a suitable marker compound for tyre particles.

The proportion of aromatic compounds released from the tyre particles increased after thermal desorption at 500°C, whereby 60% of the compounds present in all three tyre brands were either single ring aromatics or PAHs. This observation is explained by the fact that more aromatic rings contain higher numbers of delocalised electrons, resulting in increased intermolecular Van der Waals interactions (Achten & Andersson, 2015). To overcome these forces a higher energy input is required, meaning the PAHs were vaporised at 500°C and not at 240°C (Alonso et al., 2014). This accounts for the increased number of compounds present in the three tyre brands after thermal desorption at 500°C compared to at 240°C.

However, although there were more compounds common to all three tyre brands at 500°C, fewer were suggested as potential markers because many were not unique to

tyres. Benzothiazole and styrene/α-methylstyrene were the only marker compounds present at 240°C that remained at 500°C. Toluene and benzene (and its derivatives) are solvents used in tyre manufacturing (Nazarparvar-Noshadi et al., 2022), but they have many other industrial sources (Yu et al., 2022) and their presence in environmental samples does not conclusively indicate the presence of tyre wear. Additionally, petrogenic PAHs are found in crude oil and products such as plastics, rubber, and asphalt, whilst pyrogenic PAHs arise from incomplete combustion of organic compounds such as crude oil and wood (Saha et al., 2012). Consequently, PAHs are not a reliable indicator of tyre wear when identified alone, but they can provide extra evidence for the presence of tyre wear particles if other indicative compounds are also present, and hence they were included in the marker hierarchy (Figure 6). However, there are large variations in the PAH content of different tyres depending on when they were manufactured. The dominant source of PAHs in tyres produced before 2010 were the highly aromatic extender oils used as processing aids during tyre manufacturing. In 2010, the European Union (EU) banned the use of extender oils with a regulated PAH content of over 10 mg/kg, and thus tyres manufactured after this date have a lower PAH content (Alves et al., 2020). Furthermore, the internal temperature reached by a typical passenger tyre during normal driving conditions is between 20 and 60°C (Genovese & Timpone, 2022), and the tread temperature rarely exceeds 160°C (Mavros, 2019). For these reasons, future research would ideally focus on the compounds released at 240°C, which more accurately represents tyre temperatures experienced during driving.

The optical microscope analysis revealed an unexpected colourless material protruding from some of the tyre particles, particularly those from the Michelin tyre. Closer analysis using an SEM showed that this material was ribbon-shaped with jagged edges (Supplementary Figure S4F). Daniela Taverner – an undergraduate researcher at the University of Southampton – ground chunks of tyre tread to generate particles instead of using the PoD tribometer, resulting in colourless flakes separating from the Michelin tyre tread. Observation of these flakes using an optical microscope and an SEM (Supplementary Figures S4B-S4E) revealed similarities with the material in the Michelin tyre particles generated here. One hypothesis was that the material was silica, commonly used as a tyre filler to improve the wet tyre grip and decrease rolling resistance. Silica tyre filler was developed by Michelin in the 1990s as an alternative to carbon black (Veiga et al., 2017), a probable reason it was observed in higher quantities in the Michelin tyre particles compared to the other two brands.

A strength of this study was the specifications for the tyres used for particle generation compared to previous literature. For example, Gualtieri et al. (2005) used laboratory-generated tyre particles to assess the toxicity of tyre leachates. However, they generated particles using a single, unused vehicle tyre, whereas this study used three brands of tyres – Michelin, Bridgestone and Radial – allowing comparison of the physical and chemical characteristics of the particles from each brand. This was vital in ensuring that suggested markers were present in all the tyre brands, satisfying one of the criteria for a successful marker of tyre wear. Furthermore, there is evidence that the quantities of certain organic compounds in tyre tread change over the course of a tyre's life. For instance, the compounds 1-octanethiol, phenanthrene and anthracene have been found in higher proportions in new tyres compared to old tyres of the same brand and model (Wagner et al., 2022), reducing the reliability of the toxicity results from Gualtieri et al.'s study in 2005 which used only new tyres. The tyres used here were used/old and had been exposed to weathering and friction with the road during their use, meaning the chemical composition of the tyre particles was comparable to those present in the environment.

Although used tyres were selected here for particle generation, the exact history of each tyre was unknown, introducing an uncontrolled variable. Each tyre could have experienced significantly different driving conditions, leading to different alterations in their chemical compositions. Future work should attempt to minimise the variation in the tyres' history as much as possible, whilst acknowledging that this is a challenging aspect to control.

Several previous researchers have cryogenically milled tyre tread (Miller et al., 2022; Shin et al., 2023; Son & Choi, 2022) to generate large volumes of particles, for studying the chemical composition of tyres (Wagner et al., 2022). However, cryogenic milling generates larger tyre particles than those from road simulators and real-world driving, which are not the characteristic sausage-shape (Wagner et al., 2022). Contrastingly, the tyre particles were generated here by friction between samples of tyre tread and the rotating disc of a PoD tribometer, closely replicating the driving process and producing tyre particles with a similar morphology to those identified in environmental samples in previous literature (Klockner et al., 2021).

5. CONCLUSIONS

This study has established a reproducible methodology for generating tyre wear particles in the laboratory. Several factors should be considered for effective generation of wear particles. For instance, the disc of tribometer should be abrasive enough to generate particles. Future studies could evaluate particle generation with a disc of roughness greater than 160 µm. In this study, a vertical force of 38 N was most suitable for production of wear particles; horizontal forces could be reviewed in subsequent studies. Reducing the distance between the pin and the centre of rotating disc is essential to reduce the torque, as higher torque could reduce the functioning of tribometer.

The study has provided a comprehensive suite of potential marker compounds and physical characteristics that can be used to identify tyre wear particles in environmental samples. For example, 6PPD and benzothiazole - at the top of the hierarchy (Figure 4) and present in the tyres studied when analysed at 240°C - could be indicators for tyre wear particles in the environment, recognising that other potential sources of these compounds should be taken into consideration. Future research should focus on assessing the concentration of tyre wear particles in samples from

different environmental compartments to evaluate the relative significance of tyre particle pollution when compared to other, more researched pollutants, such as microplastics and airborne particulate matter (PM). The physical characteristics for tyre wear particles are important in this type of study. For example, if a study aims to evaluate the number of tyre wear particles in environmental samples, sausage-shaped assemblies of particles should be used, as this shape is unique to tyre wear particles. Since section 3.1 of this paper outlines that the generated tyre wear particles ranged from sausage-shaped to spherical, spiking experiments should be carried out to assess the underrepresentation of particles other than sausage-shaped. For the determination of tyre wear particle mass, 6PPD along with benzothiazole could be used.

More work is necessary to understand the factors that impact the emission of tyre wear particles, and how these factors may change. For instance, the average electric vehicle weighs ~20% more than a similarly sized internal combustion engine vehicle (Liang et al., 2021), with their growing usage increasing the emissions of tyre wear particles. It is important to assess the contribution of tyre wear particles to non-exhaust emissions, which can inform future engineering strategies to minimise the release of tyre particles into the environment.

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