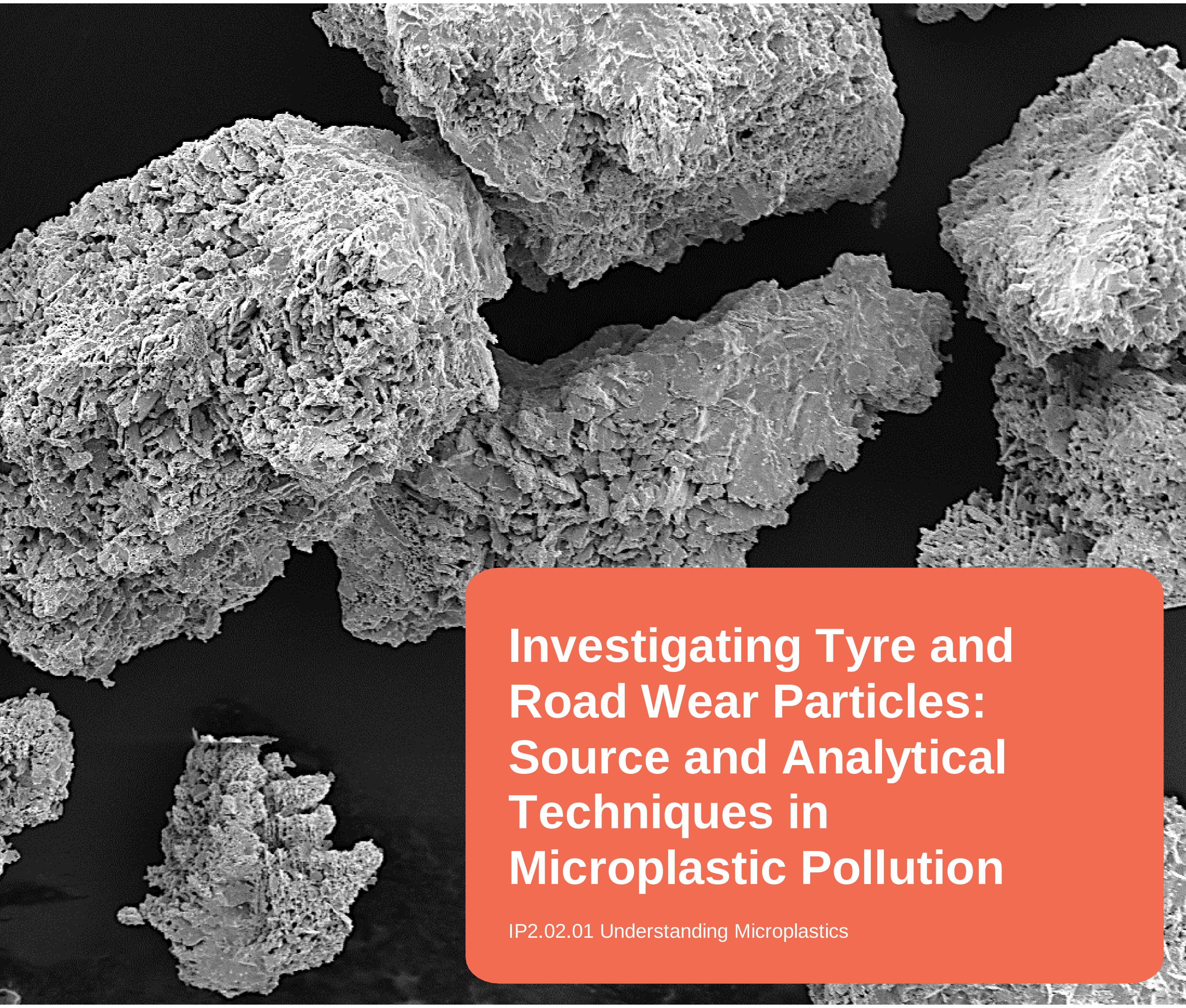
Sustainable Communities and Waste

National Environmental Science Program



Investigating Tyre and Road Wear Particles: Source and Analytical Techniques in Microplastic Pollution

IP2.02.01 Understanding Microplastics

Investigating Tyre and Road Wear Particles: Source and Analytical Techniques in Microplastic Pollution

Revision: 1

Version	Date of issue	Author	Comments
1	30 October 2024	Rumana Hossain	Initial Draft
2	04 November 2024	Rumana Hossain	Report completed
3	13 November 2024	Lucas Way	Formatting
4	19 November 2024	Glenn Walker	Review comments
5	27 November 2024	Rumana Hossain	Revised report
5.1	10 January 2025	Lucas Way	Edit Acknowledgement of Funding
5.2	14 January 2025	Dixit Prasher	Additional acknowledgment removed

Acknowledgement of Country

The Sustainable Communities and Waste Hub acknowledges all Aboriginal and Torres Strait Islander Traditional Custodians of Country and recognises their continuing connection to land, sea, culture, and community. We pay our respects to Elders past, present, and emerging. We support Aboriginal and Torres Strait Islander peoples and their aspirations to maintain, protect and manage their culture, language, land and sea Country and heritage.

Acknowledgement of Funding

The Sustainable Communities and Waste Hub is funded by the Australian Government under the National Environmental Science Program.

SMaRT@UNSW
Sustainable Materials Research & Technology

Metadata Information		
DOI		
Tags		Microplastic; pollution; environment; analytical techniques; tyre dust, Environmental Impact, Sustainability, Research, Microplastic Sources, Environmental Science
Original Author	Name	Rumana Hossein | Anirban Ghose | Lucas Way | Veena Sahajwalla
	Role	Primary Author | Review | Review | Supervision
	Affiliation	Centre for Sustainable Materials Research and Technology, SMaRT Centre UNSW Sydney
Creation Date		5th November 2024
Document type		Report
Document Standard		
Domain-relevant community standard		
Data Usage License		This report is published under a Creative Commons Attribution 4.0 (CC BY 4.0) licence.
Data Access Procedure		Contact Anirban Ghose, a.ghose@unsw.edu.au, for further information
Related Document(s)		
Related Document PID(s)		
Does this document include Indigenous data?		This document does not include any Indigenous Data
Project ID		IP2.02.01 – Understanding Microplastics
Corresponding Grant Milestones		RP2024 Milestone 3, RP2024 Milestone 5

Investigating Tyre and Road Wear Particles: Source and Analytical Techniques in Microplastic Pollution

*Correspondence: Rumana Hossain: r.hossain@unsw.edu.au

Executive Summary

Microplastic pollution is a critical environmental issue of the 21st century. With tyre and road wear particles (TRWP) emerging as a significant contributor. TRWP, generated through the interaction of vehicle tyres and road surfaces, account for approximately 28% of global microplastic contamination. This report examines the various aspect of TRWP, from their generation and release mechanisms to their environmental impacts.

Objective: The primary objective of this report is to explore the sources, characteristics, and environmental pathways of TRWP and to assess the existing analytical techniques for microplastic and TRWP.

Generation and Release Mechanism; TRWP are produced during driving, braking, and acceleration, with their properties influenced by factors such as tyre characteristics, road surface types, and vehicle operation conditions. Emission factors vary be region and vehicle type, affecting the quantification of TRWP emission globally.

Environmental Pathways: TRWP are dispersed through airborne medium, water runoff, and snow removal. A significant portion becomes airborne, while others are

integrated into soil or washed into waterways, contributing to marine and terrestrial pollution.

Sources of Road-borne Microplastics: The primary source includes tyre treads, road markings and bitumen binders. These materials release microplastic through abrasion and degradation, with varying compositions and toxicological impacts.

Toxicological Impacts: The report highlights the presence of toxic chemicals in tyres, such as polycyclic aromatic hydrocarbons, and heavy metals, which pose risk to human health and ecosystems. The leaching of these substances into the environment underscores the need for effective management strategies.

Analytical Techniques: The report details various methods for collecting and analysing TRWP, including road sweeping, air sampling, and road simulators. It discusses about conventionally used material analysis techniques; microscopy, spectroscopy and GC/MS techniques and their efficacy to identify and quantify, TRWP, including the challenges faced from heterogeneous composition and presence of carbon black.

This report underscores the importance of analytical techniques in studying TRWP and provides their role in environmental pollution, emphasizing the need for further research and policy development.

1 Introduction

The issue of microplastic pollution has emerged as one of the most pressing environmental concerns of the 21st century. While public attention has often focused on visible plastic waste in oceans and landfills, a conspicuous but equally significant source of microplastics has been gaining recognition: tyre and road wear particles (TRWP). These microparticles, generated through the continuous interaction between vehicle tyres and road surfaces, represent a substantial contribution to global microplastic contamination. Recent studies by the European Community have highlighted the alarming scale of this problem, estimating that TRWP contribute to approximately 28% of global microplastic contamination [1]. The ubiquity of road transportation in modern society means that this source of microplastic is as widespread as it is persistent, affecting urban, rural, and natural environment alike (figure 1).

The recent focus on microplastic for its issue of environmental pollution and its effects on organisms and living beings have drawn many researchers, and policymaker to identify and counter its issue. The definition of microplastic comprises plastic fragments with size in between 5 mm and 1 μm, generated from several plastic and polymer degradation and wear-tear actions [2]. In 2004, the concept of "microplastics" was publicised as microscopic plastic particles as little as ≈20 μm in diameter. In 2008 NOAA meeting, the experts defined microplastics as plastic particles less than 5 mm in diameter, now a days this has become the most commonly used definition. As the scientific exploration on plastic debris is evolving continuously, a certain nomenclature regarding microplastics has emerged. Nonetheless, the nomenclature remains unclear and inconsistent, especially when it comes to defining the size of the plastic debris [3]. Based on the process of microplastic production and their time of formation in plastic degradation process, microplastics are divided into primary and secondary microplastics. Primary microplastic are manufactured microscopic synthetic particles made for commercial applications such as cosmetics, detergents, paints and pesticides, while secondary microplastics are generated from macro-sized plastic and synthetic materials during their use cycle or after disposal [4, 5]. Likewise, secondary category can be further sub-divided into microplastic being generated during application cycle and after end-of-life disposal [6]. In contrast there has been alternative definition from other researchers, where primary microplastics are those sub 5 mm fragments released into the environment during its manufacturing, use and abrasion, while secondary microplastic are one which further degraded from the release primary microparticles [5, 7].

This review discusses about different kind of microplastic that comes from tyre and road wear particles. The categories of roads like dense asphalt mixture and porous asphalt mixture are found based on the area, which generates particles when vehicle tyres tread on them, containing minerals from road abrasion and tyre and road wear particles (TRWP) [8]. The composition of tyre wear particles (TWP) accounts for half of TRWP [8], with major portion of rubber found in the particle [9]. There has been inconsistency on the classification of rubber as plastic, with a faction of researchers considering it as plastics [10], while International Organization for Standard (ISO) has rubber as separate classification to plastics [11]. Micronised rubber tire particles (i.e. microrubber) have been detected in the environments, mostly originated owing to the abrasion between car tyre and roads. Microrubber share some commonalities with microplastics. The chemical composition of microrubber from tire is a mixture of different polymers, synthetic rubber (a 1:3 blend of styrene: butadiene rubber) being the primary elastomer in passenger car tire and natural rubber in truck and heavy-duty tires. For polymer, repeating monomers form the backbone of the polymer. Microplastics either originated from primary or secondary sources, on the contrary the microrubber mainly originated from secondary sources [12]. Despite of that, it has been identified as major source of microplastic in environment [4, 10, 13, 14] with 5-18% of plastics in the ocean made of TWP and 3 - 7% of particle fractions as PM2.5 in urban air [5]. The major hurdle for analysing TRWP comes from mixed nature of the road particles embedded with rubber particles, which creates ambiguity in identification and quantification of particulate materials, and there has been development towards detection, analysis and quantification, resulting in improved attention [15, 16].

This review is structured to provide a comprehensive analysis of TRWP as a significant source of microplastic pollution. It begins with an exploration of the generation and release mechanisms of TRWP, detailing how tyre-road interactions contribute to microplastic emissions. Following this, the review delves into the factors influencing TRWP generation, such as tyre characteristics, road surface types and vehicle operation conditions. The subsequent section discusses the environmental pathways through which TRWP are dispersed, including airborne transport, water runoff, and snow removal. The review then examines the sources of road-borne microplastics, focusing on tyre-treads, road markings and bitumen binders. Finally, it discusses the existing analytical technological used for TRWP identification and quantification. This structured approach aims to provide a detailed understanding of

TRWP’s role in environmental pollution and the challenges associated with their management and mitigation.

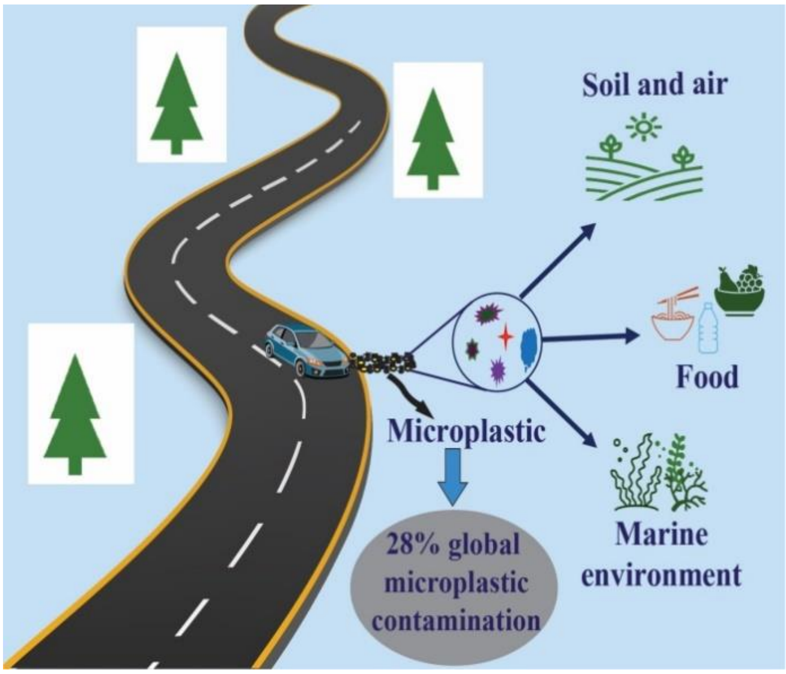


Figure 1. The conceptual schematic of microplastic flow in environment.

2 Generation and Release Mechanism of TRWP

2.1 Generation of TRWP

The generation process of TRWP is fundamentally based on contact between tyre and road surface which occurs during driving, braking and acceleration. The generation process also determines their properties and behaviour in the environment [15]. There are several emission factors which controls the properties of TRWP generated: tyre characteristics (type, chemical composition, and size), type of road surfaces (material, porosity, wetness, and temperature), characteristics of vehicles (braking system and weight), and operation condition of vehicles (speed, braking frequency and duration, and cornering) [10, 17]. Different emission factors reported are tabulated in Table 1 and displayed in figure 2, which were measured by determining the difference in tyre weight, or annual tyre replacement, with respect to mileage [18]. The calculated emission factor is region specific and have multiple variates like region, tyre types, sampling process, and vehicle operation parameters that can affect the values.

Table 1. Emission factors for different vehicle types (mg/Vehicle km).

Vehicle Type	Urban Roads	Rural Roads	Highways	Ref
Light duty vehicle	14	11	9.1	[19]
Heavy duty vehicle	47	27	31	
Bus/Coach	21	17	14	
Passenger Car	132	85	104	[17]
Van	159	102	125	
Motorcycle	60	39	47	
Light Special Vehicle	159	102	125	
Heavy Special Vehicle	850	546	668	

The most common approach of calculating tyre wear particles is by using emission factors and total mileage of the vehicle, or from the total number of tyres and weight loss values of tyres [14, 15]. Countries like Japan, UK, and Italy opt for weight loss approach while Germany, Sweden and Norway use emission factor method (table 2) [20]. India has the lowest emission per capita with USA having highest emission [14]. It is due to fewer number of cars per person in India.

Table 2. Annual TRWP emission for different region.

Country/Region	Total TRWP emission (t/a)	TRWP emission per capita (kg/(cap*a))	Estimation Method	Remarks	Ref
EU	1,327,000	2.6	A	From total vehicle mileage extracted from Germany	[10]
Australia	70,000-80.000	0.9	-	-	[21]
India	292,674	0.2	A	-	[14]
Japan	239/762	1.9	B	Data from [22]	[14]
USA	1,797,480	5.5	A	-	[14]
Brazil	294,011	1.4	A	-	[14]
World Total	5,917,518	0.8	A	Extrapolated from available data	[14]

A = Estimation calculated from emission factors and total vehicle km.

B = Estimation calculated from number of vehicles registered, tyre life expectancy and loss during lifetime.

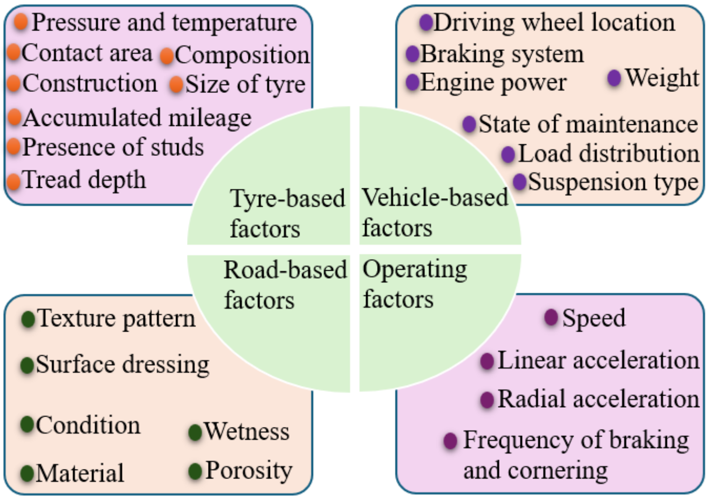


Figure 2. Factors influencing TRWP generation.

2.2 Route to Environment

2.2.1 Airborne Medium

Road dust can swirl up with winds, accelerating vehicles, and continuous vehicle running on the road from the turbulence generated around the contact point of tyre and road; while during wet condition vehicle passing can aid in splash and particulate runoff [6]. Around 0.1 - 10 mass % of the TRWP generated is projected to be airborne, and are fine particles (PM 2.5 to 10) [15], with remaining coarse particulate remains in road surface. The TRWP deposited in adjacent soil generally tends to avoid runoff and are integrated to the soil with the embedded contaminants like heavy metals and minerals [23], with study showing wind accounting for one-third portion of particulate removed by winds [24].

2.2.2 Water Runoff

The coarse fraction of TRWP from road surface are mobilized with 2 mm/day rain and with 5 mm/day rain, major part will wash away to waterways [25], with deposition around small area in adjacent section of the paved road (0.75 - 1.5 m) where road runoff is not available (two-third of deposition) [24]; runoff accounts for 50 - 60% in urban roads, 10% in highways and 20 - 30% in rural roads [26]. The road infrastructure also dictates the amount of run-off [27], with roads with stormwater systems helping in dispersal of the particles [28], and in roads without such system, the TRWP deposits onto adjacent land area from where they are transported into waterways with rain and any human induced water flow [10]. As per OSPAR (Oslo and Paris) Commission, the study from North-East Atlantic Ocean countries, the marine based TRWP was compared to land-based plastic litter [5]. Norway accounts for 3942 tons of tyre wear particles in ocean per annum which is around 32% of plastic dumped in ocean [29], and from Sweden around 8700 tons of TRWP are predicted to reach ocean per year [30].

2.2.2.1 Snow Removal

During wintertime when snow is scraped up from the road and transported elsewhere, it also carries TRWP dispersed in road surface. Typically, roadside snow around per-urban and urban environment has high level of contamination, which during melt off , leads to runoff into water ways [30]. The level of microplastic in sea-salt and rock used in de-icing has been found out to be very low, suggesting major part still intact in snow [31].

2.2.3 Street Cleaning

During street cleaning process, there is possibility of airborne particulate being generated, so, wet cleaning method are generally used. The wet method uses water runoff which can wash away the particulate from road to waterways while the collected sludge which still contains high amount of TRWP are landfilled [6, 28]. Larger microplastic fraction (>100 - 125μm) can be effectively collected during road cleaning [32], thus preventing them from reaching stormwater system, while the smaller fraction can still be suspended in the pavement microstructure [6].

3 Characteristics of TRWP

There has been a clear understanding of the chemical composition and characteristics of the source of TRWP: tyre tread, bitumen binder, and the road marking, but there lacks information regarding the characteristics of TRWP. The interaction of tyres with roads changes the chemical composition of the particulate generated due to the friction, heat, and embedding of road materials [33]. The tyre wear, which is dominantly rubber, gets incorporated with other road elements that come from brake dust, bitumen binder and traffic paints, and labelling [33], changing the chemical composition of TRWP from laboratory-generated particles [34].

The shape, size and density of TRWP influences the dispersion of microplastic in the environment (table 3) [35], and it tends to vary from the sampling points (soil, airborne, road surface, waterways etc.) [20]. Studies have shown that TRWP can range from nanometres to micrometres in size (table 4), with several particle size distribution: ultrafine particles with a size range of 6 to 562 nm, with peak concentration around 30 - 60 nm [36]; bimodal distribution with 90% by mass for less than 1 µm size [37]; single peak mode, with high peak diameters in the range of 10 to 200 nm [38]. Likewise, the mass distribution for the TRWP showed a bimodal distribution with concentration peaks at 0.5 µm and 1.3 - 2.5 µm [39].

Table 3. Physical attributes of tyre wear particle (TWP).

Attributes	Description	Characteristics	Ref

Shape	Ellipsoidal shape with rough surface	Embedded heavy metals and minerals. Elongated shape makes it surface prone in asphalt.	[20, 40]
Size	10 nm to several 100 μm	Depends on speed, temperature, type of road, and tyre tread composition.	[14, 41]
Density	0.94 to 2.5 g/cm^3	Effective density of tyre tread embedded with impurities. Effects the dispersion in soil and floatation in water ways.	[9, 41]

Generally, TRWP exhibit an elongated or ellipsoidal shape, with mineral encrustation derived from road surface materials with elements and minerals like Al, K, Ca, and Mg [42]. This shape originates form complex interaction between tyre tread and road surface with variables like humidity, speed, and pavement types. This creates peculiar surface characteristics of the particles which displays unique organic surface markers like $C_7H_7^+$ ions present in the surface [42]. These TRWP also display resistance to heat-induced deformation due to complex nature of materials with mineral encrustation providing structural stability [42]. It should be stressed that the precise morphology of TRWP significantly varies with tyre composition, pavement types, and specific weather condition [15], which adds the complexity for identification and characterization of TRWP in environmental samples.

Table 4. Number size distribution for TWP.

Method	Country	Measured Size Range	Size Distribution	Ref
Tyre Simulator	China	6 nm - 10 μm	Bimodal (10-13 nm, 23-41 nm)	[39]
Tyre Simulator	Spain	523 nm - 20 μm; 15 - 800 nm; 5 - 160 nm	Bimodal (35 nm, 85 nm)	[43]
Test site	Germany	5.6 - 562.3 nm	Unimodal for low speed: (70 -90 nm) Bimodal for High speed (<10 nm, 30 - 60 nm)	[36]
Road simulation	Denmark	15 - 700 nm	15 - 50 nm (average size distribution)	[44]
Road vacuum cleaning	US	0.3 - 100 μm	Unimodal (50 - 75 nm)	[34]

The chemical composition of TRWP differs from the initial tyre composition and is a function of size of the particles. The coarser particles have higher concentration of Fe, Ca, and Zn with smaller fractions of Ti and Sb [45]; while in finer sizes the concentration of Zn was not found with major composition being Fe, Ca, Ti, and Sb [45]; with airborne particles mainly composed of Si and Al [10, 46]. Likewise, for the sub-micrometre particles sulphur was also found [10]. The vehicle types also effected the composition with Zn composition around 1.1% for passenger

The metallic composition of TRWP mostly consist of zinc, silicon, and sulphur which are found in tyre itself [47], The amount of aluminium and silicon in TRWP is significantly higher than in tyre particles, which can be from asphalt which constitutes these elements [48-50]. Likewise, there are also other elements found in TRWP like magnesium, iron and calcium, which in comparison to tyre particles are in high amount in TRWP. It can be due to presence of their elements in pavements, road surfaces and traffic components like road paintings and markings [34]. There are significant amounts of polyaromatic hydrocarbon (PAH) present in TRWP, which comes from tyres, but studies have shown that the fraction of PAH in tyres are significantly less (<5%) [51, 52]. The concentration of PAH seems to directly correlate with the mileage of the tyre [53], which can be from degradation due to the produced heat between tyres and road [54]. The high amount of PAH found in road particles can be from automobile emission, asphalt, and fuel combustion [47].

4 Sources for Road Borne Microplastic (MP)

The three main source of microplastic from road transport are from tyre treads from the vehicles, road markings, and paints used on the road, and bitumen binder used in the asphalt road [6, 55], which all have different types of polymers in them used as main ingredients or as an additives. The shape and physical properties of the MP generated from these sources varies on the type of abrasion the materials are subjected to and the application of the polymers in the source. The tyre wear particles are generally elongated and has small amount of embedded mineral particles, picked up from the road and surrounding [34]. The road MP are mixed with road dust which contains sand and other particles like more microplastics, toxic elements, and organic and inorganic matter often from the surrounding of the road, with study showing the composition varying from the location of the road, with urban setting consisting more particles from the non-exhaust vehicle emulsion including tyre treads and brake wears [56], from the human activities like vehicular movement and construction work [57], compared to rural settings. The following section will discuss on the physical and chemical characteristics of three major source of road MPs generated from the polymeric composition of tyres, road paints, and bitumen-binders. The discussion is based on the materials that are commercially used in roads and tyres with information provided by the product manufactures and researchers. The toxicological behaviour of the chemicals and materials used in each product has also been discussed to highlight the impact of the chemicals to human beings and the ecosphere around the application area.

4.1 Tyre Tread

Tyre treads are the part of tyres that come in direct contact with road and are subjected to wear and tear, abrading the tyre surface forming micro and macro particles. They are primarily made of natural and synthetic rubber, mixed with fillers to reinforce rubber compounds (commonly used carbon black and silica); softeners (petroleum oil, pine tars, resins, and waxes) used to improve tack of unvulcanised compounds; antidegradants (waxes, antioxidants, and antiozonants) to protect from impact of oxidation, UV, and heat; and curatives (sulphur with accelerators and activators) to transform viscous compounds into elastic material [58]. The composition of additives, and filler materials vary as per the required application and features for tyres such as superior traction in wet condition, heavy duty agricultural use, or long-wearing optimal performance type [59].

A tyre for typical passenger tyre are made of almost 25 components with different types of reinforcement components made of textiles, polymer or metals (steel and brass) and the base material rubber can be made of 12 different types of natural and synthetic rubber and additives [58, 60]. The material composition of tyres has been summarised in table 5. The tyre tread has three parts, tread base, tread cap, and tread wing. Tread base creates bonding between the tyre carcass and the tread, so it is made of high-adhesion property material, while tread cap is the part that comes in contact with the road first, thus are made of abrasion-resistant, high grip rubber material. Tread wings are optional part which is made of adhesive material which connects the tread to the sidewall of the tyres [61].

Table 5. Material composition of tyres in Australia, UK, and USA.

Material		United Kingdom		USA	Australia	
		Passenger Cars	Trucks/Buses	Similar composition	Passenger Cars	Trucks
Rubber	Natural	17%	25%	14-27%	16-35%	29-70%
	Synthetic	31%	15%	14-27%	65-29%	30-13%
Carbon Black		22%	21%	28%	23%	24%
Metal		15%	27%	14-15%	16%	25%
Textile		5%	-		6%	-
	Sulphur	1%	1%	16-17%	1%	1%
Additives	Zinc Oxide	1%	2%	Processing Oil	1%	2%

	Additives	8%	6%		8%	-
References		[62, 63]		[64]	[65]	

4.2 Road Marking and Paints

Road markings are used to warn and guide traffic for the safety, and are made of polymers, pigments, additives and fillers, and additives like glass beads for reflective coating. Based on type of polymers and base materials there are different kind of road marking products found commercially, as mentioned in table 6.

Table 6. Types of road marking products [66-69].

Type	Binding Agents	Feature
Water Based Paints	Thermoplastic acrylic resins.	Less durable and environmentally friendly and can be used in concrete, bitumen, and asphalt.
Solvent Based Paints	Thermoplastic acrylic resin or styrene acrylic mixes used. For solvents: esters or ketones and aromatic solvents permitted in few countries.	Less environmentally friendly but lasts longer and not suitable to be used in bitumen or concrete.

Two-component System/Cold Applied Plastic	Acrylic Systems uses thermosetting resins as binding agents and dibenzoyl peroxide as curing agents. Epoxy systems use epoxy resins as binding agents and with amines as curing agents.	Very durable and easy to apply and less curing time.
Hot Thermoplastic Systems	Pentaerythritol resin ester, C5-hydrocarbon resin, EVA copolymer or styrene block copolymers.	Used in high wear situations.
Road marking tapes	Polyurethane and flexible polymer, with glass beads or crystalline ceramic beads used.	Used in construction sites, road works and temporary usage area.

4.2.1 Water Based Paints

Thermoplastic acrylic resin in water based emulsion is used as binding agent in water based paints [66], and are commonly used road marking paints due to presence of less than 2% of volatile organic compounds and is cheaper and easier to apply [66]. It can be used in all kind of surface like concrete, bitumen, and asphalt and has good reflective bead retention, making it a popular choice for road markings [66]. High pressure piston pumps are used for applying the paint [6].

4.2.2 Solvent Based Paints

The binding agents like thermoplastic acrylic emulsion and styrene acrylic mixes are dissolved in organic solvent like esters and ketones [66]. The presence of chemicals like styrene acrylic mixes and organic solvents makes it durable but less environmentally friendly, limiting its usage in several countries [6]. This paint is not suitable to use in bitumen or asphalt surface as it breaks down the surface [67].

4.2.3 Two-component System/Cold Applied Plastics

Two-component paints are usually acrylic-based or epoxy-based system where the thermosetting component is mixed with curing agent to form a thermoset [70]. Acrylic system uses acrylates like mono and multifunctional esters of methyl resin (MMA resin) [66, 70] ; which are mixed with filler pigment and anti-skid material. The mix is then treated with polymerising agents like dibenzoyl peroxide (BPO) [66]. BPO helps to start the polymerization of acrylate monomers through an irreversible exothermic reaction, accelerating the hardening process in higher temperature [71]. For epoxy systems amines are used as curing agents which is mixed with epoxy resins dissolved with pigments and additives [66].

4.2.4 Hot Thermoplastic System

Thermoplastic polymers (C5 aliphatic hydrocarbon resin or alkyd resins) are used as binding agents for this system, which are mixed with additives, glass beads, pigments and fillers [70]. In addition, polymers like ethylene vinyl acetate copolymer (EVA) are added to make the paints durable in cold region and styrene block copolymers are added to make it more elastic [70]. About half of the paint system is composed of filler material like quartz sand and calcium carbonate, and with around 20% is glass beads [70]. Commonwealth Scientific and Industrial Research

Organization (CSIRO) and its subsidiary, Australian Paint Approval Scheme (APAS) has set guidelines, in accordance with Standards Australia for pavement marking material based on thermoplastic for safety certification [72].

4.2.5 Road Marking Tapes

Road marking tape can be permanent with pressure-sensitive adhesion system or in the form of removable tape for temporary application. Permanent tape includes monocrystalline ceramic beads or glass beads embedded on the surface while for binding agents it uses rubber and polyurethane. Likewise, temporary tapes have self-bonding adhesives on underside with pigmented binding agent with glass beads on the upper surface on the metal foil backing [73].

4.3 Bitumen, Polymer-based Bitumen Binder, and Waste Plastic in Bitumen

Asphalt is a mixture of aggregates and binder agents. Aggregates are made of sand, gravel and crushed rocks, while as binding agent, which constitutes around 4 - 8% of the mixture, bitumen is used. Generally, virgin resins like ethylene vinyl acetate (EVA) and styrene butadiene styrene (SBS) have been used as polymer modified bitumen binder which are extracted from naphtha and produce high performance polymer modified asphalt [74]. The conventional hydrocarbons like EVA and SBS have been gradually replaced by more common thermoplastics such as polyethylene (PE), polypropylene (PP) and Polyethylene terephthalate (PET) [74]. Likewise, the virgin polymer materials have gradually been replaced by waste thermoplastic feedstock to counter the growing issue of waste plastic and use it as a secondary material for construction to support the circular economy chain [75, 76].

4.3.1 Bitumen

Bitumen is extracted form multistage distillation process of crude oil, which can produce over 20 different grades of bitumen from the short residue obtained from the fractionating column [77]. The general chemical composition of bitumen is carbon (82 - 88%), hydrogen (8 - 11%), sulfur (0 - 6%), oxygen (0 - 1.5%) and nitrogen (0 - 1%) [77]. The major chemical constituents of bitumen are asphaltenes and maltenes (resins, aromatics, and saturates) [77]. The features of hydrocarbons in bitumen is explained in Table 7.

Table 7. Hydrocarbons of bitumen [48].

Hydrocarbon Form	Features	Percentage
Asphaltenes	Tar-like materials with hard, solid, and black texture.	5-25%
Polar Aromatics (Resins)	Has adhesive property and semi-solid dark brown in color.	Molecular mass = 500-50,000 gram/mol
Aromatics Oil	Viscous, dark brown liquid.	40-60%
Saturated Hydrocarbons (Paraffins)	Aliphatic hydrocarbons with alkylnaphthalenes and aromatic alkyls.	5-20%

4.3.2 Polymer Modified Bitumen Binder: From virgin and waste polymers

The bitumen portion of the asphalt has been gradually mixed with polymers to improve the mechanical properties of bitumen, thereby making it suitable for heavy-duty traffic and extreme weather condition roads [78, 79]. EVA and SBS are commonly used copolymers in bitumen [74], which enhance the elastomeric properties of the bitumen thus improving cohesiveness, resistance to fatigue and elevated strength [80]. Likewise, rubber crumbs are also used, generally obtained from waste tyres as the polymer modifier [81]. Polymer-modified bitumen decreases the temperature susceptibility, which helps maintaining the mechanical strength of the road during hot weather, while preserving its workability in colder temperatures [82]. These features make polymer-modified bitumen suitable for applications such as strain alleviating membranes (SAM) [83], strain alleviating membrane interlayers (SAMIs) [84], and high-stress seals (HSSs) [85]. To counter the growing stockpile of plastic waste, there has been efforts in using waste plastic to replace the virgin feedstock in polymer-modified bitumen. The use of plastic waste as an alternative to conventional polymer-based bitumen binder seems attractive from an economical and sustainable perspective. This technique has been proven to be a better alternative to incineration and landfilling and also supersedes the use of virgin feedstock in polymer-based binders [86]. There has been development in formulating guidelines to incorporate plastic waste in bitumen, and there has been application in several countries. Austroads, an Australian based company has been developing APT6305 project which outlines guidelines for road industry to identify and handle road-grade plastics, which can be used for polymer modified bitumen [76]. Likewise, Downer has developed ‘reconophalt’, asphalt mix using recycled soft plastic bags and packaging and rubber from end-of-life rubber. ‘Reconophalt’ has been approved by New South Wales Environmental Protection Agency (NSW EPA) and has shown comparable environmental risk to standard asphalts, in terms of BPA leaching and microplastic generations [87]. Similarly, companies like Fulton Hogan have adopted APT6305 guidelines and developed ‘Plastiphalts’, which is asphalt using polymer-modified bitumen, using recycled plastic waste [88]. India has been front runner on incorporating waste plastic in asphalt road, with the early use case since early 2000, when street in Chennai (Jambulingam Street) was built using this concept [89]. Government regulators in India have been very supportive of this technology, with reported 100,000 km of roads being built using polymer-modified bitumen as of 2020 [90]. There are also mandatory regulations set by the Government of India requiring road developers to use waste plastic in any road construction within 50 km periphery of urban areas with population greater than 500,000 [91]. The profuse use of polymers in bitumen has been diverting major portion of plastic waste from incineration and landfill avoiding the environmental impacts through toxic fumes and leaching caused by the process. Different types of polymers used in bitumen has been listed in table 8.

Table 8. Different types of polymers used in bitumen [48-50].

Polymer Group	Polymer Types	Features and Applications
Elastomeric Polymers (Thermoplastic type)	Styrene-butadiene-styrene (SBS), styrene-butadiene rubber (SBR), polybutadiene (PBD), Polychloroprene latex, styrene isoprene (SIS), Styrene ethyl butylene styrene (SEBS)	• Improves elasticity and increases tolerance to temperature change. • Used in HSSs, SAMs and SAMIs

Plastomeric Polymers	Thermoplastics	Ethylene vinyl acetate (EVA), ethylene methacrylate (EMA), atactic polypropylene (APP), polypropylene (PP), ethylene butyl acrylate (EBA), polyethylene (LD and HD)	• Improves stiffness and is used for HSSs
	Thermosets	Epoxy resins, polyurethane resins, acrylic resins, phenolic resins, Ethylene propylene diene monomer (EPDM)	
Rubber or Crumb Rubber (Thermosetting Type)		From shredding of waste rubber tyres, SBR, natural rubber, it can be used as source of elastomer in bitumen	• Same as elastomer

However, the limited study on the long-term impacts of this application is a major concern. Most studies conducted on the application have been confined to controlled environments, with very limited data and studies available from real-time use cases [92-94]. Laboratory-scale studies on the polymer-modified bitumen roads are based on simulation standards like Heavy Vehicle Simulator [95], and Pavement Fatigue

Carousel [96], which are run in an accelerated environment without accounting for factors like microplastic generation due to abrasion from tyres on road [97].

5 Analytical Techniques for TRWP

Most of the analytical studies on TRWP have been limited to lab-generated particles [98-101], while there are few numbers of literature that discusses on quantifying TRWP collected from road dust and stormwater [25, 102-104]. Table 9 presents an outline of recent available methods practised for microplastic analysis. The table provides information such as the volume of sample required, sample preparation methods for individual characterisation method, detection limits of characterisation methods, and particle size. Nonetheless, microplastics are quite complex and different in terms of their physical properties (size, shape, density, type, surface properties, etc). Exploration of such complex samples could look like looking for a needle in a bale of hay. Here, the relevant methods (figure 3) for chemical identification, estimation, and characterization of microplastics has been reviewed. The analysis method can be broadly classified into microscopic methods, micro-spectroscopic methods and gas chromatography-mass spectroscopy (GC-MS). Spectroscopic techniques use infrared radiation (FTIR), laser beam (Raman) and electron beam (SEM) to reveal specific absorption and reflection patterns to analyse the sample which can be used to attain information about shape, size, surface morphology, homogeneity-heterogeneity, and element quality of the samples.

Table 9. Analytical methods used to analyse and quantify microplastic generated from tyre and road wear particles [20, 34].

	Microscopic Methods	Micro-spectroscopic Methods			GC/MS	
	Light Microscopy	SEM-EDX	μ-FTIR	Raman	Pyrolysis GC/MS	TED-GC/MS
Detectable Quantity	-	-	ng to μg	ng to μg	μg	μg
Measurable Particles per Sample	-	-	10^3 to 10^5	10^3 to 10^5	<20 mg	<100 mg
Analysis Duration (including sample preparation)	Hours to days	Hours	Days to weeks	Hours to days	Days to weeks	Hours
Detection Limit	20 to 100 μm	10 μm	20 μm	1 to 10 μm	$<1\mu g^*$	0.5 to 2.5 μg
Sample Preparation	Filtration	Filtration	Special filtration	Filtration	Particle isolation in vial	Material/filtrate in crucible
Type of Polymer	N/A	N/A	Yes (tough)	Yes(tough)	Yes	Yes
Particle Surface Analysis	Yes	yes	N/A	Yes	N/A	N/A

Rate of Degradation	N/A	N/A	N/A	Surface oxidation	Oxidation	N/A
Particle Size, Shape, Morphology and Quantity	Via visual assessment	Yes (quantity)	Yes	Yes	N/A	N/A
Mass Balance	N/A	N/A	N/A	N/A	Yes	Yes
Can be practised for TRWP assessment	Via manual identification (Result uncertain)	Under progress	Under progress	Under progress	Yes (With reference spectrum/library)	Yes (With reference spectrum/library)

*Development

The presence of carbon black in tyres creates some challenges while analysing the samples using microscopy owing to the disruptive fluorescence phenomenon and complete absorption of infrared light when sample is exposed to laser light or electron beam radiation [14, 102]. The sample preparation step for SEM is a time-consuming process and requires careful sample preparation before analysis [105]. SEM can be coupled with EDX (x-ray detector) analysis for elemental mapping. Similarly, GC-MS can be either pyrolysis GCMC (pyr-GC/MS) or Thermal extraction and desorption GC/MS (TED GC/MS).

5.1 Sample Preparation Techniques

Before analysing the microplastic content in TRWPs, it is necessary to prepare the sample and make it suitable for characterisation. Various processes are used to disintegrate organic materials (humic substances, bacteria, and cellulosic compounds) and detach inorganic components (carbonates, silicates, and minerals) from the sample [106, 107]. Sieving is used to remove the larger particles and grit from the collected samples, and then the samples are subjected to oxidation to breakdown and remove the organic compounds [108, 109]. Normally H_2O_2 is used for oxidising the samples, but other chemicals such as alkali/acid, enzymes, ozone, etc. are also used for oxidation purpose [110]. Afterward, the sample is put through density separation.

Different characterisations require different types of sample preparation techniques. However, the particle size and density of the samples play a key role while selecting the suitable analysis methods for the sample and sample preparation methods before analysis. Usually, in density separation, different kinds of salt solution such as NaCl ($\leq$1.2 g/cm^3), $ZnCl_2$ ($\leq$1.7 g/cm^3), sodium polytungstate ($\leq$3.2 g/cm^3), NaI ($\leq$1.9 g/cm^3), $CaCl_2$ ($\leq$1.4 g/cm^3), and KBr ($\leq$1.6 g/cm^3) solution are used [111, 112]. Selection of salt solution depends on the density of the microplastic that is going to be analysed. It has been estimated that the TRWPs collected from environment has density around 1.8 g/cm^3 [25]. Some literature reported that density of tyre particles is around 1.2 g/cm^3, and density of materials collected from the road surface is around 2 g/cm^3. The carbon black used as filler in rubber tyre have density around 1.8 g/cm^3, and the synthetic rubber styrene-butadiene has density of roughly 0.94 - 1.0 g/cm^3. Combining these two densities, the tyre density stands around 1.1 - 1.2 g/cm^3 [113-115]. Based on these statistics it is recommended to use a salt solution with density $\geq$ 1.8 g/cm^3 for tyre and road wear particle separation [30]. However, it reported that it is possible to achieve a satisfactory level of separation if $ZnCl_2$ is used as a salt solution in tyre and road wear particle separation [116]. Usually, the solution or composition used for biological sample separation are not used in tyre and road wear particle separation; however, there might be some ways to improve the level of separation. It is very challenging to separate pure rubber tyre and road wear particle from the field sample because the particles are complexly bonded to each other in the material. For heavy particles (if the samples contain high mineral content) with a density of more than 1.8 g/cm^3, it is recommended to use sodium polytungstate, or NaI salt solution during separation [30].

5.2 Microscopy Methods

Microscopy can be classified into two categories, light, and electron microscopy. A stereo type of microscopy (high-resolution microscopy) can be utilised for identifying the thermoplastic particles (plastic fibres, fragments, chips, film, etc.) and road particles (rubber and bitumen). This optical microscopy method can be combined with the melt test method and then to identify if the particle is thermoplastic or an elastomer [117]. However, visual assessment under an optical microscope can be used in identifying the bitumen and rubber particles.

The microscopy methods used in microplastic analysis require vast sample preparation like density separation, oxidation, sieving, etc. It takes a lot of time to determine the particle number in the microscopy method [118]. If the density separation methods fail to effectively separate the particles during sample preparation, the residual sediment particles or other particles which remain with microplastic hinder the analysis. Besides, if organic materials are added to the samples during sample preparation, the analysis becomes more complicated. Another major drawback of the microscopy method is that the analysis method is solely reliant on visual assessment which makes this method a subjective one and demands long microscopic experience. In the microscopy method, it has been recommended to practice the standard analytical protocol for standardising filtration and sieving, and define the particles based on size, shape, and appearance rather than type of plastic [108, 119]. There is a resolution limit in regular microscopy; usually, they can reach 1 µm. But, if the particle is colourless (tyre wear, bitumen) and smaller than 100 µm, then it becomes quite challenging to characterise the particles [117].

5.3 Micro-spectroscopic Methods

5.3.1 Microscopic Analysis (SEM-EDX)

The SEMs are one of the widely and frequently used instruments for characterising the elemental composition, surface morphology, and conductivity of polymeric materials [120, 121]. There are few limitations to this approach as well, such as if the sample is not conductive enough, no potential difference is created between the sample and SEM detector. This means, non-conductive samples or samples with poor conductivity requires metal coating (e.g., Pt coating) before analysis. The example of detectors used in SEM analysis are secondary electron detector (SEI), and backscattering electron detector (BSE). BSE detector is usually used to distinguish between elements with higher atomic numbers (heavy elements) and lower atomic numbers (light elements). Some x-ray detectors like EDS (Energy Dispersive X-ray analysis) or EDX (Energy Dispersive X-ray spectroscopy) are also used in microplastic analysis. SEM equipped with an EDS/EDX detector can give information about the elemental composition of the test specimen [122]. Sommer et. al. [9], studied some samples having particle sizes bigger than 10 µm collected from different road environment. More than 500 particles and 1500 spectra were surveyed to measure the elemental composition, particle size, shape, and volume of collected specimens from different road environments. It has been revealed that most of the collected specimens (more than 90% by volume) contained particles worn from tyres, asphalt, or brake pads. The findings of the study indicate that tyre wear particles contain microplastic and spread the microplastic in environment. Kreider at. al. [34], conducted a study where they collected the specimens from the road using a special collecting machine connected behind a tyre. Two vacuum cleaners with a power 1200 W each were connected to the machine to create a suction force to collect particles from the road. The tyre and road wear particles they studied were elongated in shape and particle size varied from 0.3 µm to 100 µm. Polukarova et al [123], conducted similar kind of study where they use lower suction force (sample was collected by Wet Dust Sampler). They reported the presence of a few black rubber particles with irregular shape along with elongated shape. Hassellove et al [124] found elongated, curled, and flake-shaped particles in similar kind of study was done by [34] and [123]. Wagner et. al. [105], recommended the SEM-EDX technique to detect trace elements (Zn, S) in tyre wear particles. However, it should be kept in mind that Zn and S may come in the sample from different sources like natural or anthropogenic activities. Particles, with sizes ranging from 10 µm to 80 µm were collected from roadside using a passive sampler for light microscopy and SEM-EDX analysis [9, 125]. The tyre wear particles in the collected samples were revealed as elongated, round, or kidney shaped particles, partially or fully coated with brake or road wear particles. The particles contain elements like carbon and sulphur alongside some minor elements like Zn, Si, Al, Na, Ca, K, Mg, Fe, Cu, Ti, Mo, Mn, Ba, Sn, and W. According to the researchers, the presence of foreign particles indicates that it is not possible to identify the tyre particles via SEM-EDX as a standalone characterisation technique [124].

5.3.2 IR Spectroscopy (FTIR)

Infrared spectroscopy (IR) is a kind of spectroscopic method that assess the absorbed or emitted energy from an IR source having a wavelength of 2 - 20 µm [126]. Atoms in molecules are chemically bonded, different bonds absorb IR of different wavelengths. By analysing the absorbing energy band, it is possible to identify the chemical atomic bonds present in the specimens [126]. Every chemical compound has its individual spectral line based on the atomic bonds present in the compound. An IR spectrum can be utilised for identifying and quantifying various chemical compounds [126, 127]. µ-FTIR is an advanced version of FTIR that measures the molecular structure of organic compounds and polymeric materials [126]. FTIR is a fast analytical technique where solid, liquid, and gaseous samples can be used for characterisation [128]. One major disadvantage of all types of FTIR spectroscopy methods is they need a reference library for identification of the material. Bonds in the chemical compounds are identified based on the IR spectra, then this information is used for identifying different chemical compounds present in the samples [126, 127]. This technique is time-consuming and needs high level of competence. The other limitation in FTIR analysis is depending on the material content, the relative intensity of the peak in the spectrum can vary, which makes the interpretation of the spectrum more challenging. This makes the peak identification of the spectrum difficult, especially when new material is characterised, because of the uncertainty while choosing the reference spectrum for comparison. FTIR spectroscopy can be adopted for quantitative analysis/measurement of specimens provided with proper calibration and reference spectrum/material [129, 130]. FTIR-

ATR (attenuated total reflection) can be used for black particles (tyre and road wear) analysis, which completely absorbs IR light [131]. In this technique, the changes that occur when an internally reflected IR beam encounters the sample are measured. For localising the carbon black at different phases of rubber blends, this technology has been used [132]. This technology has also been used for determining the composition of carbon black containing vulcanised rubber [133]. Cabernard et al [134] compared the µ-FTIR with ATR and µ-Raman for analysing and quantification of microplastics in seawater. The Raman analysis of the specimen indicated a higher concentration of microplastic in the specimen. The study also revealed that, both techniques revealed the presence of rubber particles (10 – 500 µm size) in the seawater specimen. Another study comparing µ-FTIR-ATR to pyrolysis-GC/MS exhibited similar consistent results [135]. However, this study didn't encompass rubber material. TGA and Pyr-IR spectroscopy are also considered as potential analysis methods for analysing the elastomers in rubber tyre without known composition [136]. An alternative approach to µ-FTIR-ATR for characterising the TRWPs is use of diamond compression cell. This technique has exhibited excellent results in analysis. [137]. Simon et. al. [138], developed a technique for measuring the mass of microplastics having sizes 10 µm to 500 µm. The authors concluded that particle number and mass concentration van be used as relevant matrices for microplastic analysis. Identifying the type of polymers based on the assumption of particles' thickness can end up creating difficulties or provide misleading information. Organic and other chemical compounds deposited at the surface of the microplastic particles create difficulties in data interpterion and identification. These studies didn't cover the TRWPs, however they highlighted some of the hurdles which may arise during the field sample analysis which may contain TRWPs.

5.3.3 Raman Spectroscopy

Raman spectroscopy utilizes a laser beam, typically with wavelength from 500 nm to 800 nm to illuminate solid, liquid or gaseous samples using photon scattering phenomena, which is called Raman scattering [139]. During this process, the photon energy can remain unchanged (Rayleigh scattering), increase (Stokes scattering), or decrease (anti-Stokes scattering) [139, 140]. Both Stokes scatterings and anti-Stokes scatterings are considered as Raman scattering and provide valuable information about the sample's molecular structure. One significant advantage of Raman spectroscopy is its ability to characterise small particles as small as 1 µm. However, this technique also presents some challenges, particularly when analysing TRWP. The primary disadvantage is low signal strength, which can make detection and analysis difficult. Additionally, Raman spectroscopy requires intensive sample preparation before analysis. and Raman analysis, individually, is not regarded as a suitable characterisation technique. For TRWPs Raman analysis is not considered a standalone suitable characterisation technique, since the black particles in tyre and road wear can absorb the incident light within the relevant wavelength range, making it impossible to produce a distinct spectrum [10]. There has been research to improve Raman spectroscopy to get the better signal quality by using new detectors, spectrum management tools, automatic particle identification, and to expand the reference library used for identification of the spectrum [141]. Fourier transform Raman spectroscopy (FT-Raman) is a variation of Raman technique with laser wavelength close to IR regio, which can be used for analysing the rubber particles [142]. FT-Raman spectroscopy avoids the fluorescence issues by keeping the laser excitation frequency below the threshold. FT-Raman method utilises one interferometer to produce the interference pattern, which is known as interferogram which is them converted to Raman spectrum. ASPEx-μ-Raman (automated single-particle exploration equipped to μ-Raman) provides quite good results for assessing the microplastics (10 µm – 500 µm) collected from seawater [134]. Another variation of Raman technique is confocal Raman spectroscopy, which incorporates an optical microscope to visualise the sample in high magnification during analysis, allowing for more precise measurements and better spatial resolution [143].

5.4 Gas Chromatography Mass Spectroscopy Method (GC/MS)

5.4.1 Pyrolysis Gas Chromatography with Mass Spectrometry (Pyr-GC/MS)

Pyr-GC/MS usually involves a rapid heating of the samples within a temperature range of 400 ℃ to 900 °C in an inert atmosphere to disintegrate the sample into small molecules. These disintegrated molecules are then separated by gas chromatography and detected using mass spectrometry. The thermal treatment breaks down the long polymeric chains into smaller molecules, which are subsequently detected by gas chromatography [144]. Pyr-GC/MS may require time-consuming specimen preparation before analysis. However, Unice et. al. [145], carried out a study where they directly performed pyr-GC/MS on collected field samples, including soil and sediment, and used quantitative analysis to analyse tyre tread materials in the environmental matrices. In pyr-GC/MS analysis, a pyrogram is created that includes peaks from all the degraded materials, where each peak indicating a single segment. The peaks are marked and quantified using the same technique as traditional gas chromatography [146], where each peaks needs to be measured using appropriate calibration curves. Pyr-GC/MS is often practised in conjunction with the mass spectrometry (MS). In MS, organic compounds released from the GC column are bombarded with electrons under vacuum to break the molecules into positively charged segments [146]. Individual organic compounds degrade in the same manner, resulting in a characteristic spectrum for each molecule. The generated ions are sorted based on their mass and charge, and then a MS spectrum is created. The intensity of the peaks in the MS spectrum indicates the relative signal strength of the ion peaks, and this intensity is not related with number of ions [147]. One key advantage of pyr-GC/MS is the identification of type of polymers and organic additive (alkyl phenol/benzaldehyde/phthalates) through a single analysis [146]. Lower pyrolysing temperature degrades the sample gradually and can produce by product at higher boiling points. Higher pyrolyzing temperature can disintegrate the sample into very small pieces making it challenging to characterise. So, it is crucial to use the optimum pyrolysis condition [147]. The results from pyr-GCMS can vary significantly between laboratories due to several factors: sample preparation, type of pyrolyser, and transformation of pyrolysis gas into gas chromatograph [148]. Among the most used pyrolyser, the Curie-point pyrolyser is particularly useful as it can characterize up to 20 mg of sample at a time. Despite the temperature range between 480 °C and 980 °C, the gas composition remains consistent. This method is fast, provides high accuracy, and aids in the proper quantification of compounds. The high pyrolysis temperature ensures that no unpyrolsed residue remains, making it ideal for field samples without intensive preparation [149]. In a study by Unice et al [25, 145], TRWP collected from Japan, the US, and France were analysed using pyr-GC/MS. The concentration of these particles in the collected samples varied from 25 µg per gram to 11,600 µg per gram. The analysis was conducted using a 20 mg sample at 670 °C in a Curie-point pyrolyser. Pyrolysis markers such as styrene, isoprene, dipentene, butadiene, and vinyl cyclohexene were detected and quantified using deuterium compounds incorporated in the samples as internal reference. The concentration of rubber products and the concentration of TRWP within the sediments were measured based on the relationship of rubber in tyre and road wear particles [34]. Similarly, in a study done by Fischer & Scholz-Böttcher, they used pyr-GC/MS to analyse eight different types of plastic and found that the findings correlate with FTIR and Raman analysis [150]. Likewise, in another study by Käppler [151], it was found that pyr-GC/MS can be a reliable complimentary analysis to µ-FTIR, where data on mass concentration and particle number can be measured respectively.

5.4.2 Thermal extraction and desorption gas chromatography attached with mass spectroscopy (TED-GC/MS)

In this method the sample is heated in a separate chamber to decompose into gas. The gases are concentrated in a sorbent and fed to gas chromatography system for analysis. The GC system is used to distinguish the decomposed materials and mass spectrometry is used to identify the materials just like in pyr-GC/MS. The main difference with pyr-GC/MS is TED-GC/MS uses TGA instead of pyrolysis, and the generated gas is concentrated in a sorbent and then the whole content fed into GC system. In TED-GC/MS, 100 mg of sample can be analysed at a time without any sample preparation [152]. For analysing the microplastics there has been several processes being developed. In one method, 20 mg of samples is placed in an aluminium crucible and TGA is performed at 600 ℃ [153]. The decomposed product from the thermal extraction is concentrated in a sorbent cartridge attached with instrument’s gas outlet. After that the sorbent cartridge is assessed via thermal desorption through automatic injections and cryo-focusing. Now there has been some development to make the system fully automated using TED-GC/MS [154]. Similarly, TED-GC/MS can facilitate minimal sample preparation analysis route for several microplastic and TRWP [155]. Usually, 0.2 mg to 0.4 mg of samples are used for analysis. In case of field samples, 10 mg to 50mg of dry samples are used. The analysis revealed that different markers of rubber tyre such as, antioxidants, vulcanisation agents, decomposed products can be identified [154]. It is also possible to analyse the real field samples which contain thermoplastic and different rubber materials [154]. One disadvantages of this method is, this technique does not give the number of particles and particle size or shape. However, this method can be used as a complement approach to FTIR and Raman techniques.

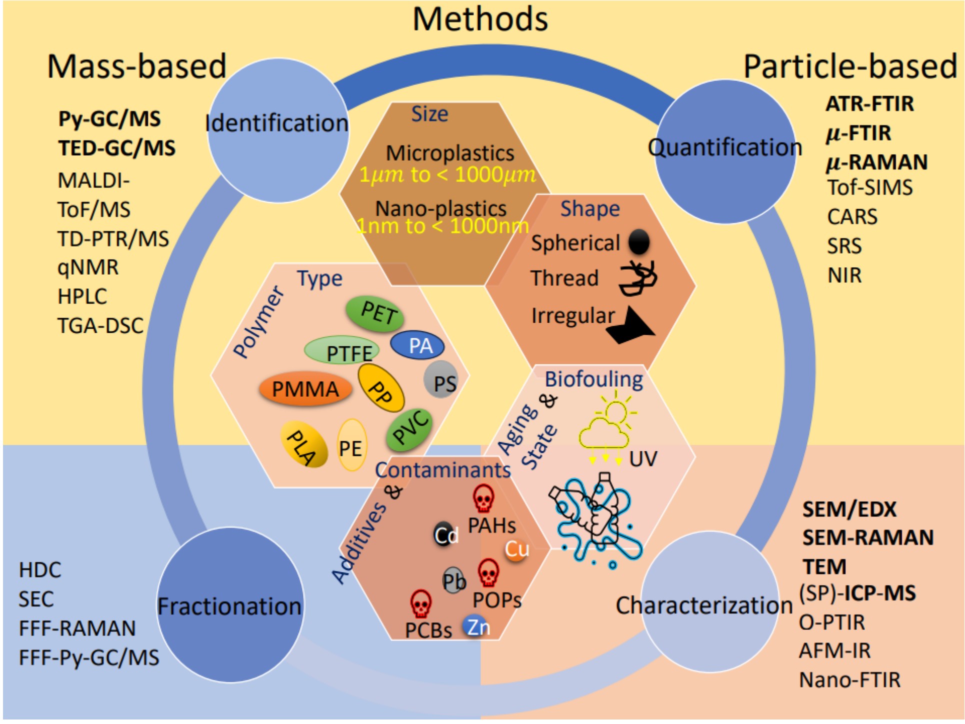


Figure 3. The methods for the chemical identification, estimation, and characterization of microplastics.

6 Conclusion and Discussion

The issue of microplastic pollution, particularly from tyre and road wear particles (TRWP), has emerged as a significant environmental concern. TRWP, generated through the interaction between vehicle tyres and road surfaces, contribute to global microplastic contamination. The pervasive source of pollution affects various environments, from urban to rural and natural settings, and poses challenges for both analysis and mitigation. Several factors influence their generation, including tyre characteristics, road surface types, vehicle characteristics, and operational conditions. Emission factors vary by region and are influenced by local conditions, vehicle types and driving habits. Countries like Japan, the UK, and Italy use different methodologies to estimate TRWP emissions, reflecting the complexity and variability of the issue.

TRWP consist of a mix of rubber particles and road materials, making their analysis challenging. They vary in size, shape, and composition, with common elements including zinc, sulphur, silicon, and calcium. The particles are often elongated or irregularly shaped and can range from nanometres to several hundred micrometres in size. The mixed nature of TRWP complicates their identification and quantification, necessitating advanced analytical techniques such as SEM-EDX, FTIR, and Raman spectroscopy implemented as complimentary techniques to one another. TRWP contribute to both airborne and waterborne microplastic pollution. A portion of TRWP becomes airborne, contributing to urban air pollution, while the remainder is deposited on road surfaces and adjacent soils. Water runoff from roads can transport TRWP into waterways, with significant contributions from urban roads and areas lacking stormwater management systems. Seasonal factors, such as snow removal, also influence TRWP distribution. The main source of road-borne microplastic include tyre treads, road markings, and bitumen binders. Each source contributes diverse types of polymers and compounds influenced by abrasion and environmental conditions. The composition of TRWP varies depending on the location, with urban areas showing higher concentrations of non-exhaust vehicle emissions.

Despite advances in understanding TRWP, several challenges remain:

- The mixed composition of TRWP complicates their analysis, and there is a lack of standardized methods for quantifying and characterizing these particles.
- The variability of regional emission factors and estimation methods further complicates global assessments.
- The long-term environmental and health impacts of TRWP remain under-researched, particularly concerning their chemical leachates and interactions with living organisms.
- The presence of carbon black in tyres can create analytical challenges doe to fluorescence and absorption of infrared light.

To mitigate the shortcomings towards TRWP research and challenges, study needs to focus on following measures:

- Developing standardized methodologies for TRWP analysis and quantification by creating protocols for sample collection, preparation, and analysis to ensure reproducibility and comparability; and developing reference materials and libraries for identifying TRWP in various environmental matrices.
- Utilizing advanced spectroscopy techniques like FTIR-ATR and Raman to overcome challenges of carbon black, and other interfering substances, and combining multiple analytical techniques to provide comprehensive information about TRWP composition and properties.

- Conducting longitudinal studies to assess the long-term environmental and health impacts of TRWP, particularly concerning their chemical components and potential toxicity by establishing monitoring programs to track TRWP concentration and distribution; and evaluating the toxicity of TRWP on various organisms and ecosystems.
- Investigating mitigation strategies such as use of alternative materials in tyres and road surfaces, to reduce TRWP generation, and improving design of road infrastructure with better stormwater management system to reduce TRWP runoff in waterways.
- Encouraging collaborative efforts between researchers, policymakers, and industry stakeholders to address this multifaceted issue through policy development, implementation, and public awareness.

While considerable progress has been made in understanding the generation, characteristics, and environmental impact of TRWP, continuous research and innovation are crucial to mitigate their contribution to global microplastic pollution. Addressing the challenges associated with TRWP requires a comprehensive approach that combines scientific research, technological advancements, and policy interventions. By focusing on standardized methodologies, advanced analytical techniques, longitudinal studies, mitigation strategies, and collaborative efforts, we cand develop effective solutions to reduce the environmental footprint of TRWP and protect our ecosystems.

REFERENCES

1. Europeo, P. *Microplásticos: Causas, efectos y soluciones*. 2018 30/07/2024]; Available from: https://www.europarl.europa.eu/news/es/headlines/society/20181116STO19217/microplasticos-causas-efectos-y-soluciones.
2. Verschoor, A.J., *Towards a definition of microplastics : Considerations for the specification of physico-chemical properties*, in *Naar een definitie voor microplastics*. 2015, Rijksinstituut voor Volksgezondheid en Milieu RIVM.
3. Hartmann, N.B., et al., *Are We Speaking the Same Language? Recommendations for a Definition and Categorization Framework for Plastic Debris.* Environmental Science & Technology, 2019. **53**(3): p. 1039-1047.
4. Essel, R., et al., *Sources of microplastics relevant to marine protection in Germany.* Texte, 2015. **64**(2015): p. 1219-1226.
5. Hale, R.C., et al., *A Global Perspective on Microplastics.* Journal of Geophysical Research: Oceans, 2020. **125**(1): p. e2018JC014719.
6. Vogelsang, C., et al., *Microplastics in road dust–characteristics, pathways and measures.* NIVA-rapport, 2019.
7. Boucher, J. and D. Friot, *Primary microplastics in the oceans: a global evaluation of sources*. Vol. 10. 2017: IUCN Gland, Switzerland.
8. Järlskog, I., et al., *Differentiating and Quantifying Carbonaceous (Tire, Bitumen, and Road Marking Wear) and Non-carbonaceous (Metals, Minerals, and Glass Beads) Non-exhaust Particles in Road Dust Samples from a Traffic Environment.* Water, Air, & Soil Pollution, 2022. **233**(9): p. 375.
9. Sommer, F., et al., *Tire Abrasion as a Major Source of Microplastics in the Environment.* Aerosol and Air Quality Research, 2018. **18**(8): p. 2014-2028.
10. Wagner, S., et al., *Tire wear particles in the aquatic environment - A review on generation, analysis, occurrence, fate and effects.* Water Research, 2018. **139**: p. 83-100.
11. Bustillo Revuelta, M., *Plastics*, in *Construction Materials: Geology, Production and Applications*, M. Bustillo Revuelta, Editor. 2021, Springer International Publishing: Cham. p. 477-502.
12. Halle, L.L., et al., *Ecotoxicology of micronized tire rubber: Past, present and future considerations.* Science of The Total Environment, 2020. **706**: p. 135694.
13. Leads, R.R. and J.E. Weinstein, *Occurrence of tire wear particles and other microplastics within the tributaries of the Charleston Harbor Estuary, South Carolina, USA.* Marine Pollution Bulletin, 2019. **145**: p. 569-582.
14. Kole, P.J., et al. *Wear and Tear of Tyres: A Stealthy Source of Microplastics in the Environment*. International Journal of Environmental Research and Public Health, 2017. **14**, DOI: 10.3390/ijerph14101265.
15. Baensch-Baltruschat, B., et al., *Tyre and road wear particles (TRWP) - A review of generation, properties, emissions, human health risk, ecotoxicity, and fate in the environment.* Science of The Total Environment, 2020. **733**: p. 137823.
16. Järlskog, I., et al., *Traffic-related microplastic particles, metals, and organic pollutants in an urban area under reconstruction.* Science of The Total Environment, 2021. **774**: p. 145503.

17. Luhana, L., et al., *Measurement of non-exhaust particulate matter.* Characterisation of exhaust particulate emissions from road vehicles (PARTICULATES). Deliverable, 2004. **8**.
18. Rauterberg-Wulff, A., *Beitrag des Reifen- und Bremsenabriebs zur Rußemission an Straßen*. 1998: VDI-Verlag.
19. NAEI, *Fleet Weighted Road Transport Emission Factor 2021*, in *Emission Factors for Transport*, N.A.E. Inventory, Editor. 2023 (2021): Online.
20. Miera-Domínguez, H., et al., *What is known and unknown concerning microplastics from tyre wear?* Road Materials and Pavement Design, 2024. **25**(8): p. 1658-1679.
21. O'Farrell, K., *Tyre flows and recycling analysis* 2019.
22. Masakazu Yamashita and S. Yamanaka, *Dust Resulting from Tire Wear and the Risk of Health Hazards.* Journal of Environmental Protection, 2013. **4**(6): p. 509-515.
23. Werkenthin, M., B. Kluge, and G. Wessolek, *Assessment of metal retention in newly constructed highway embankments.* Environmental Science and Pollution Research, 2016. **23**(23): p. 23619-23629.
24. Blok, J., *Environmental exposure of road borders to zinc.* Science of the Total Environment, 2005. **348**(1-3): p. 173-190.
25. Unice, K.M., et al., *Characterizing export of land-based microplastics to the estuary - Part I: Application of integrated geospatial microplastic transport models to assess tire and road wear particles in the Seine watershed.* Science of the Total Environment, 2019. **646**: p. 1639-1649.
26. Kaufmann, P., *Strassenabwasser Filterschacht*, in *Critical Issue in Transportation for 2024 and Beyond*. 2007, Transportation Research Board: Online. p. 455.
27. Sieber, R., D. Kawecki, and B. Nowack, *Dynamic probabilistic material flow analysis of rubber release from tires into the environment.* ENVIRONMENTAL POLLUTION, 2020. **258**.
28. Andersson-Sköld, Y., et al., *Microplastics from tyre and road wear : a literature review*, in *VTI rapport*. 2020, Statens väg- och transportforskningsinstitut. p. 142.
29. Järlskog, I., et al., *Occurrence of tire and bitumen wear microplastics on urban streets and in sweepsand and washwater.* Science of The Total Environment, 2020. **729**: p. 138950.
30. Amato, F., et al., *A review on the effectiveness of street sweeping, washing and dust suppressants as urban PM control methods.* SCIENCE OF THE TOTAL ENVIRONMENT, 2010. **408**(16): p. 3070-3084.
31. Rødland, E.S., et al., *A novel method for the quantification of tire and polymer-modified bitumen particles in environmental samples by pyrolysis gas chromatography mass spectroscopy.* Journal of Hazardous Materials, 2022. **423**: p. 127092.
32. Tian, Z., et al., *A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon.* Science, 2021. **371**(6525): p. 185-189.
33. Legret, M., et al., *Leaching of heavy metals and polycyclic aromatic hydrocarbons from reclaimed asphalt pavement.* Water Research, 2005. **39**(15): p. 3675-3685.
34. Kreider, M.L., et al., *Physical and chemical characterization of tire-related particles: Comparison of particles generated using different methodologies.* Science of The Total Environment, 2010. **408**(3): p. 652-659.
35. Klöckner, P., et al., *Characterization of tire and road wear particles from road runoff indicates highly dynamic particle properties.* Water Research, 2020. **185**: p. 116262.
36. Mathissen, M., et al., *Investigation on the potential generation of ultrafine particles from the tire–road interface.* Atmospheric Environment, 2011. **45**(34): p. 6172-6179.

37. Fauser, P., et al., *TIRE-TREAD AND BITUMEN PARTICLE CONCENTRATIONS IN AEROSOL AND SOIL SAMPLES.* Petroleum Science and Technology, 2002. **20**(1-2): p. 127-141.
38. Kwak, J.-h., et al., *Characterization of non-exhaust coarse and fine particles from on-road driving and laboratory measurements.* Science of The Total Environment, 2013. **458-460**: p. 273-282.
39. Zhong, C., et al. *Characteristics of Vehicle Tire and Road Wear Particles' Size Distribution and Influencing Factors Examined via Laboratory Test*. Atmosphere, 2024. **15**, DOI: 10.3390/atmos15040423.
40. Waldschläger, K. and H. Schüttrumpf, *Infiltration Behavior of Microplastic Particles with Different Densities, Sizes, and Shapes—From Glass Spheres to Natural Sediments.* Environmental Science & Technology, 2020. **54**(15): p. 9366-9373.
41. Parker-Jurd, F.N.F., et al., *Quantifying the release of tyre wear particles to the marine environment via multiple pathways.* Marine Pollution Bulletin, 2021. **172**: p. 112897.
42. Kovochich, M., et al., *Characterization of Individual Tire and Road Wear Particles in Environmental Road Dust, Tunnel Dust, and Sediment.* Environmental Science & Technology Letters, 2021. **8**(12): p. 1057-1064.
43. Dall'Osto, M., et al., *Characteristics of tyre dust in polluted air: Studies by single particle mass spectrometry (ATOFMS).* Atmospheric Environment, 2014. **94**: p. 224-230.
44. Dahl, A., et al., *Traffic-generated emissions of ultrafine particles from pavement–tire interface.* Atmospheric Environment, 2006. **40**(7): p. 1314-1323.
45. Syversen, T., et al., *Oceanic plastic pollution caused by Danish seine fishing in Norway.* Marine Pollution Bulletin, 2022. **179**: p. 113711.
46. Gustafsson, M., et al., *Properties and toxicological effects of particles from the interaction between tyres, road pavement and winter traction material.* Science of the Total Environment, 2008. **393**(2-3): p. 226-240.
47. Kwak, J.H., et al., *Characterization of non-exhaust coarse and fine particles from on-road driving and laboratory measurements.* Science of the Total Environment, 2013. **458-460**: p. 273-282.
48. Porto, M., et al., *The Structure of Bitumen: Conceptual Models and Experimental Evidences.* Materials (Basel), 2022. **15**(3).
49. Rebecchi, J., *Guide to pavement technology Part 4f: Bituminous binders.* 2008.
50. Bahia, H.U., et al., *Characterization of modified asphalt binders in superpave mix design*. 2001, Washington DC: National Academy Press.
51. Kriech, A.J., et al., *Assessing cancer hazards of bitumen emissions – a case study for complex petroleum substances.* Critical Reviews in Toxicology, 2018. **48**(2): p. 121-142.
52. Zakaria, M.P., et al., *Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: A widespread input of petrogenic PAHs.* Environmental Science and Technology, 2002. **36**(9): p. 1907-1918.
53. Sharma, M., *Polycyclic aromatic hydrocarbons, elemental and organic carbon emissions from tire-wear.* Science of the Total Environment, 2010. **408**(20): p. 4563-4568.
54. Kwon, E.E. and M.J. Castaldi, *Mechanistic Understanding of Polycyclic Aromatic Hydrocarbons (PAHs) from the Thermal Degradation of Tires under Various Oxygen Concentration Atmospheres.* Environmental Science & Technology, 2012. **46**(23): p. 12921-12926.
55. Roychand, R. and B.K. Pramanik, *Identification of micro-plastics in Australian road dust.* Journal of Environmental Chemical Engineering, 2020. **8**(1): p. 103647.

56. Theodoros, G. and M. Giorgio. *Non-exhaust traffic related emissions – Brake and tyre wear PM*. 2014.
57. Abbasi, S., et al., *Investigation of microrubbers, microplastics and heavy metals in street dust: a study in Bushehr city, Iran.* Environmental Earth Sciences, 2017. **76**(23).
58. Gent, A.N. and J.D. Walter, *Pneumatic tire*. 2006. 854.
59. Delvet, J.P., *Manufacturer's viewpoint - the Michelin high-performance radial tyre.* 1984. **66:12**.
60. Landi, D., S. Vitali, and M. Germani, *Environmental analysis of different end of life scenarios of tires textile fibers.* Procedia CIRP, 2016. **48**.
61. Niknam, F. *The Science Behind Tread Compounds of Passenger Tires*. [Online Magazine] 2021 [cited 2023 7-7-2023]; Available from: https://www.tirereview.com/science-tread-compounds-passenger-tires/.
62. Lo Presti, D., *Recycled Tyre Rubber Modified Bitumens for road asphalt mixtures: A literature review.* Construction and Building Materials, 2013. **49**: p. 863-881.
63. Rahman, M., *Characterisation of dry process crumb rubber modified asphalt mixtures*. 2004, University of Nottingham.
64. Ghabchi, R., et al. *Technical Challenges of Utilizing Ground Tire Rubber in Asphalt Pavements in the United States*. Materials, 2021. **14**, DOI: 10.3390/ma14164482.
65. Genever, M., et al., *National market development strategy for used tyres 2017–2022 final strategy*. 2017, Sustainability Victoria: Online.
66. Babić, D., T.E. Burghardt, and D. Babić, *Application and characteristics of waterborne road marking paint.* International Journal for Traffic and Transport Engineering, 2015. **5**(2): p. 150-169.
67. Rehman, S.A.U. and A. Duggal, *Suitability of Different Materials Used for Road Marking: A Review.* International Research Journal of Engineering and Technology (IRJET), 2015. **2**(02): p. 622-625.
68. Hadizadeh, E., et al., *Optimizing practical properties of MMA-based cold plastic road marking paints using mixture experimental design.* Progress in Organic Coatings, 2020. **147**: p. 105784.
69. Mirabedini, S.M., F. Zareanshahraki, and V. Mannari, *Enhancing thermoplastic road-marking paints performance using sustainable rosin ester.* Progress in Organic Coatings, 2020. **139**: p. 105454.
70. Harun, M.H., S. Rosdi, and M. Rosmani, *High performance thermoplastic and cold applied plastic road markings: how long do they last?* IOP Conference Series: Materials Science and Engineering, 2019. **512**(1): p. 012002.
71. Hamid Reza Seyyed, H., et al., *The Acrylic Bone Cement in Arthroplasty*, in *Arthroplasty*, K. Plamen, Editor. 2013, IntechOpen: Rijeka. p. Ch. 5.
72. Standard, A., *Paints and related materials - Pavement marking materials Thermoplastic pavement marking materials - For use with surface applied glass beads*. 2005, Standrads Australia: Online. p. 45.
73. Dubey, G.C., *Road markings: A technical review of products and their evolution.* Surface Coatings International, 1999. **82**(11): p. 536-543.
74. Kalantar, Z.N., M.R. Karim, and A. Mahrez, *A review of using waste and virgin polymer in pavement.* Construction and Building Materials, 2012. **33**: p. 55-62.
75. Movilla-Quesada, D., et al., *Use of plastic scrap in asphalt mixtures added by dry method as a partial substitute for bitumen.* Waste Management, 2019. **87**: p. 751-760.
76. Giustozzi, F. and Y. Boom, *Use of road-grade recycled plastics for sustainable asphalt pavements: overview of the recycled plastic industry and recycled plastic types*. 2021, Austroads Ltd: Sydney. p. 42.

77. Hunter, R.N., et al., *The shell bitumen handbook*. Vol. 514. 2015: Ice Publishing London, UK:.
78. Zhu, J., B. Birgisson, and N. Kringos, *Polymer modification of bitumen: Advances and challenges.* European Polymer Journal, 2014. **54**: p. 18-38.
79. McNally, T., *Polymer modified bitumen: Properties and characterisation*. 2011, Oxford, Cambridge, Philadelphia, New Delhi: Woodhead Puiblishing Limited.
80. Sengoz, B. and G. Isikyakar, *Evaluation of the properties and microstructure of SBS and EVA polymer modified bitumen.* Construction and Building Materials, 2008. **22**(9): p. 1897-1905.
81. JAIN, P., A. JAIN, and C. KAMARAJ. *Pavement preservation utilising cost effective crumb rubber modified bitumen seals: a pilot study*. in *ARRB Conference, 23rd, 2008, Adelaide, South Australia, Australia*. 2008.
82. Airey, G.D., T.M. Singleton, and A.C. Collop, *Properties of Polymer Modified Bitumen after Rubber-Bitumen Interaction.* Journal of Materials in Civil Engineering, 2002. **14**(4): p. 344-354.
83. Burman, B. and J.L. Potter, *Strain alleviating membranes-a summary of work in south Australia*. HIGHWAY ENGINEERING IN AUSTRALIA. Vol. 18. 1987.
84. Statton, J. *Impact of Callington ALF findings on rehabilitation practice*. in *Pavement Rehabilitation Workshop, 1990, Darwin, Australia*. 1990.
85. Arnold, G. and B. Pidwerbesky. *Polymer-Modified Bitumens in Chip Seals for High Stress Conditions*. in *COMBINED 18TH ARRB TRANSPORT RESEARCH CONFERENCE AND TRANSIT NEW ZEALAND LAND TRANSPORT SYMPOSIUM, 2-6 SEPTEMBER 1996, CHRISTCHURCH, NEW ZEALAND PART 2*. 1996.
86. Hoxha, E., R.A. Bohne, and A. Passer. *Gap between simplified and detailed calculation of the environmental impacts of road mixtures*. in *Journal of Physics: Conference Series*. 2021. IOP Publishing.
87. Ltd, D.E.W.P.t., *Reconophalt:Environmental Product Declaration in accordance with ISO 14025 and EN 15805*, in *Asphalt containing high-recycled content to AS2150*, E. Environment, Editor. 2020, EPD Australasia Limited: South Australia, Australia.
88. Hogan, F. *Sustainable Products and Processes*. 2022 [cited 2022 03/08/2022]; Available from: https://www.fultonhogan.com/wp-content/uploads/2020/09/Sustainable-Product-PortfolioSept2020.pdf.
89. Yuliana, C.D.D., et al. *Analysis of new asphalt alternatives with polymers: A review*. in *2021 XVII International Engineering Congress (CONIIN)*. 2021. IEEE.
90. Heriawan, A., *Upcycling Plastic Waste for Rural Road Construction in India: An Alternative Solution to Technical Challenges.* ADB South Asia Working Paper Series, 2020. **69**(March 2020): p. 28.
91. *Guidelines for the use of Waste Plastic in Hot Bituminous Mixes (Dry process) in Wearing Courses*, in *Use of Plastic Waste in Road Construction*, P.I. Bureau, Editor. 2019, Government of India: Online.
92. Hassani, A., H. Ganjidoust, and A.A. Maghanaki, *Use of plastic waste (poly-ethylene terephthalate) in asphalt concrete mixture as aggregate replacement.* Waste Management & Research, 2005. **23**(4): p. 322-327.
93. Dalhat, M. and H. Al-Abdul Wahhab, *Performance of recycled plastic waste modified asphalt binder in Saudi Arabia.* International Journal of Pavement Engineering, 2017. **18**(4): p. 349-357.
94. Heydari, S., et al., *The use of plastic waste in asphalt: A critical review on asphalt mix design and Marshall properties.* Construction and Building Materials, 2021. **309**: p. 125185.

95. Du Plessis, L., et al., *Accelerated pavement testing efforts using the Heavy Vehicle Simulator.* International Journal of Pavement Research and Technology, 2018. **11**(4): p. 327-338.
96. Simonin, J.-M., et al. *Progress in monitoring the debonding within pavement structures during accelerated pavement testing on the fatigue carousel*. in *8th RILEM International Conference on Mechanisms of Cracking and Debonding in Pavements*. 2016. Springer.
97. Enfrin, M. and F. Giustozzi, *Recent advances in the construction of sustainable asphalt roads with recycled plastic.* Polymer International. **n/a**(n/a).
98. Allan, I.J., et al., *PAH Accessibility in Particulate Matter from Road-Impacted Environments.* Environmental Science & Technology, 2016. **50**(15): p. 7964-7972.
99. Li, P., et al., *Analysis of physico-chemical properties for crumb rubber in process of asphalt modification.* Construction and Building Materials, 2017. **138**: p. 418-426.
100. Lloyd Lewis, N., et al., *Characterization of Environmental Pollutants in Sediment Collected during Street Sweeping Operations to Evaluate its Potential for Reuse.* Journal of Environmental Engineering, 2019. **145**(2): p. 04018141.
101. Sarkar, M., R. Hossain, and V. Sahajwalla, *Unravelling the properties of microzonal carbon from waste hard rubber by selective thermal transformation via conventional heating and microwave irradiation.* Carbon, 2023. **213**: p. 118274.
102. Eisentraut, P., et al., *Two Birds with One Stone—Fast and Simultaneous Analysis of Microplastics: Microparticles Derived from Thermoplastics and Tire Wear.* Environmental Science & Technology Letters, 2018. **5**(10): p. 608-613.
103. Zhang, J., et al., *Urban pipeline rainwater runoff is an important pathway for land-based microplastics transport to inland surface water: A case study in Beijing.* Science of The Total Environment, 2023. **861**: p. 160619.
104. Campanale, C., et al., *Microplastics and their possible sources: The example of Ofanto river in southeast Italy.* Environmental Pollution, 2020. **258**: p. 113284.
105. Wang, Z.-M., et al., *SEM/EDS and optical microscopy analyses of microplastics in ocean trawl and fish guts.* Science of The Total Environment, 2017. **603-604**: p. 616-626.
106. La Nasa, J., et al., *A review on challenges and developments of analytical pyrolysis and other thermoanalytical techniques for the quali-quantitative determination of microplastics.* Journal of Analytical and Applied Pyrolysis, 2020. **149**: p. 104841.
107. Schymanski, D., et al., *Analysis of microplastics in drinking water and other clean water samples with micro-Raman and micro-infrared spectroscopy: minimum requirements and best practice guidelines.* Analytical and Bioanalytical Chemistry, 2021. **413**(24): p. 5969-5994.
108. Bläsing, M. and W. Amelung, *Plastics in soil: Analytical methods and possible sources.* Science of The Total Environment, 2018. **612**: p. 422-435.
109. Huppertsberg, S. and T.P. Knepper, *Instrumental analysis of microplastics—benefits and challenges.* Analytical and Bioanalytical Chemistry, 2018. **410**(25): p. 6343-6352.
110. Nahak, B.K., et al., *Advancements in net-zero pertinency of lignocellulosic biomass for climate neutral energy production.* Renewable and Sustainable Energy Reviews, 2022. **161**: p. 112393.
111. Liu, M., et al., *Analytical Methods for Microplastics in Environments: Current Advances and Challenges*, in *Microplastics in Terrestrial Environments: Emerging Contaminants and Major Challenges*, D. He and Y. Luo, Editors. 2020, Springer International Publishing: Cham. p. 3-24.

112. Hidalgo-Ruz, V., et al., *Microplastics in the Marine Environment: A Review of the Methods Used for Identification and Quantification.* Environmental Science & Technology, 2012. **46**(6): p. 3060-3075.
113. De Ruijter, V.N., A. Milou, and V. Costa, *Assessment of microplastics distribution and stratification in the shallow marine sediments of Samos island, Eastern Mediterranean sea, Greece.* Mediterranean Marine Science, 2019. **20**(4): p. 736-744.
114. Sagar, M., et al., *A potential utilization of end-of-life tyres as recycled carbon black in EPDM rubber.* Waste Management, 2018. **74**: p. 110-122.
115. Ling, T.-C., H.M. Nor, and M.R. Hainin, *Properties of Crumb Rubber Concrete Paving Blocks with SBR Latex.* Road Materials and Pavement Design, 2009. **10**(1): p. 213-222.
116. Thomas, J., et al., *Method Development for Separation and Analysis of Tire and Road Wear Particles from Roadside Soil Samples.* Environmental Science & Technology, 2022. **56**(17): p. 11910-11921.
117. Rødland, E.S., et al., *Analytical challenges and possibilities for the quantification of tire-road wear particles.* TrAC Trends in Analytical Chemistry, 2023. **165**: p. 117121.
118. Shruti, V.C., et al., *Analyzing microplastics with Nile Red: Emerging trends, challenges, and prospects.* Journal of Hazardous Materials, 2022. **423**: p. 127171.
119. Zarfl, C., *Promising techniques and open challenges for microplastic identification and quantification in environmental matrices.* Analytical and Bioanalytical Chemistry, 2019. **411**(17): p. 3743-3756.
120. Inkson, B.J., *2 - Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for materials characterization*, in *Materials Characterization Using Nondestructive Evaluation (NDE) Methods*, G. Hübschen, et al., Editors. 2016, Woodhead Publishing. p. 17-43.
121. Gniadek, M. and A. Dąbrowska, *The marine nano- and microplastics characterisation by SEM-EDX: The potential of the method in comparison with various physical and chemical approaches.* Marine Pollution Bulletin, 2019. **148**: p. 210-216.
122. Davies, T.E., et al., *Experimental methods in chemical engineering: Scanning electron microscopy and X-ray ultra-microscopy—SEM and XuM.* The Canadian Journal of Chemical Engineering, 2022. **100**(11): p. 3145-3159.
123. Polukarova, M., et al., *Organic pollutants, nano- and microparticles in street sweeping road dust and washwater.* Environment International, 2020. **135**: p. 105337.
124. Hassellöv, M., et al., *Progress towards monitoring of microlitter in Scandinavian marine environments: State of knowledge and challenges.* 2018.
125. Tian, Z., et al., *6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard.* Environmental Science & Technology Letters, 2022. **9**(2): p. 140-146.
126. Berthomieu, C. and R. Hienerwadel, *Fourier transform infrared (FTIR) spectroscopy.* Photosynthesis Research, 2009. **101**(2): p. 157-170.
127. Lavine, B., et al., *Criteria for comparing infrared spectra – A review of the forensic and analytical chemistry literature.* Forensic Chemistry, 2020. **18**: p. 100224.
128. Tkachenko, Y. and P. Niedzielski *FTIR as a Method for Qualitative Assessment of Solid Samples in Geochemical Research: A Review*. Molecules, 2022. **27**, DOI: 10.3390/molecules27248846.
129. Claudia Maria, S., *Application of FTIR Spectroscopy in Environmental Studies*, in *Advanced Aspects of Spectroscopy*, F. Muhammad Akhyar, Editor. 2012, IntechOpen: Rijeka. p. Ch. 2.
130. Mackie, D.M., et al., *Simple, fast, and accurate methodology for quantitative analysis using Fourier transform infrared spectroscopy, with bio-hybrid fuel cell examples.* Methods X, 2016. **3**: p. 128-138.

131. Rosso, B., et al., *Identification and quantification of tire wear particles by employing different cross-validation techniques: FTIR-ATR Micro-FTIR, Pyr-GC/MS, and SEM.* Environmental Pollution, 2023. **326**: p. 121511.
132. Sarma, A.D., et al., *Determination of phase specific localization of carbon black in ternary rubber blends: A macroscopic approach by fourier transform infrared spectroscopy (FTIR).* Polymer, 2018. **150**: p. 64-71.
133. Manohar, N., et al., *A unique application of the second order derivative of FTIR–ATR spectra for compositional analyses of natural rubber and polychloroprene rubber and their blends.* Polymer Testing, 2017. **62**: p. 447-453.
134. Cabernard, L., et al., *Comparison of Raman and Fourier Transform Infrared Spectroscopy for the Quantification of Microplastics in the Aquatic Environment.* Environmental Science & Technology, 2018. **52**(22): p. 13279-13288.
135. Käppler, A., et al., *Comparison of μ-ATR-FTIR spectroscopy and py-GCMS as identification tools for microplastic particles and fibers isolated from river sediments.* Analytical and Bioanalytical Chemistry, 2018. **410**.
136. Fernández-Berridi, M.J., et al., *Pyrolysis-FTIR and TGA techniques as tools in the characterization of blends of natural rubber and SBR.* Thermochimica Acta, 2006. **444**(1): p. 65-70.
137. Karlsson, R. and U. Isacsson, *Application of FTIR-ATR to Characterization of Bitumen Rejuvenator Diffusion.* Journal of Materials in Civil Engineering, 2003. **15**: p. 157-165.
138. Simon, M., N. van Alst, and J. Vollertsen, *Quantification of microplastic mass and removal rates at wastewater treatment plants applying Focal Plane Array (FPA)-based Fourier Transform Infrared (FT-IR) imaging.* Water Research, 2018. **142**: p. 1-9.
139. Gardiner, D.J., *Introduction to Raman Scattering*, in *Practical Raman Spectroscopy*, D.J. Gardiner and P.R. Graves, Editors. 1989, Springer Berlin Heidelberg: Berlin, Heidelberg. p. 1-12.
140. Weber, W.H. and R. Merlin, *Raman Scattering in Materials Science*. 2013: Springer Berlin Heidelberg.
141. Araujo, C.F., et al., *Identification of microplastics using Raman spectroscopy: Latest developments and future prospects.* Water Research, 2018. **142**: p. 426-440.
142. Jackson, K.D.O., et al., *Fourier transform raman spectroscopy of elastomers: An overview.* Spectrochimica Acta Part A: Molecular Spectroscopy, 1990. **46**(2): p. 217-226.
143. Li, F., et al., *Detection of microplastics via a confocal-microscope spatial-heterodyne Raman spectrometer with echelle gratings.* Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2024. **313**: p. 124099.
144. de Carvalho, A.R., et al., *Determination of Polystyrene Microplastic in Soil by Pyrolysis – Gas Chromatography – Mass Spectrometry (pyr-GC-MS).* Analytical Letters, 2024. **57**(10): p. 1576-1594.
145. Unice, K.M., M.L. Kreider, and J.M. Panko *Use of a Deuterated Internal Standard with Pyrolysis-GC/MS Dimeric Marker Analysis to Quantify Tire Tread Particles in the Environment*. International Journal of Environmental Research and Public Health, 2012. **9**, 4033-4055 DOI: 10.3390/ijerph9114033.
146. Fries, E., et al., *Identification of polymer types and additives in marine microplastic particles using pyrolysis-GC/MS and scanning electron microscopy.* Environmental Science: Processes & Impacts, 2013. **15**(10): p. 1949-1956.
147. Li, Q., et al., *Influence of particle characteristics, heating temperature and time on the pyrolysis product distributions of polystyrene micro- and nano-plastics.* Journal of Chromatography A, 2022. **1682**: p. 463503.

148. Silva, A.B., et al., *Microplastics in the environment: Challenges in analytical chemistry - A review.* Analytica Chimica Acta, 2018. **1017**: p. 1-19.
149. Funck, M., et al., *Identification of microplastics in wastewater after cascade filtration using Pyrolysis-GC–MS.* MethodsX, 2020. **7**: p. 100778.
150. Fischer, M. and B.M. Scholz-Böttcher, *Microplastics analysis in environmental samples – recent pyrolysis-gas chromatography-mass spectrometry method improvements to increase the reliability of mass-related data.* Analytical Methods, 2019. **11**(18): p. 2489-2497.
151. Käppler, A., et al., *Analysis of environmental microplastics by vibrational microspectroscopy: FTIR, Raman or both?* Analytical and Bioanalytical Chemistry, 2016. **408**(29): p. 8377-8391.
152. Kittner, M., et al., *Decomposability versus detectability: First validation of TED-GC/MS for microplastic detection in different environmental matrices.* Applied Research, 2024. **3**(2): p. e202200089.
153. Elert, A.M., et al., *Comparison of different methods for MP detection: What can we learn from them, and why asking the right question before measurements matters?* Environmental Pollution, 2017. **231**: p. 1256-1264.
154. Duemichen, E., et al., *Automated thermal extraction-desorption gas chromatography mass spectrometry: A multifunctional tool for comprehensive characterization of polymers and their degradation products.* Journal of Chromatography A, 2019. **1592**: p. 133-142.
155. Braun, U., et al., *Accelerated Determination of Microplastics in Environmental Samples Using Thermal Extraction Desorption-Gas Chromatography/Mass Spectrometry (TED-GC/MS)*. 2020.