



Analytical challenges and possibilities for the quantification of tire-road wear particles



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ABSTRACT

As one of the largest sources of microplastic particle emissions, tire-road wear particle mixtures (TRWPs) pose a potentially high threat to various environmental compartments. Their heterogenous properties, from varying particle size, density, shape, texture, elemental and chemical composition, cause challenging analytical workflows. Current analytical methods for TRWP can be summarized in two main groups: single-particle-based and bulk-based methods. Both groups include a large variation of methods, with different demands for sampling and sample pre-treatment, and different possible outputs. This review provides an overview of the current analytical methods used for TRWP studies and in particularly quantifications, with focus on methods that have been peer-reviewed and tested for environmental samples. The review presents current possibilities and limitations with the different analytical approaches, as well as highlighting gaps in the current TRWP knowledge and information needed to move this research field forward.

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1. Introduction

Plastic pollution has become a global issue [1] and is threatening the environment due to its high estimated emissions [2], low degradability [3], heterogeneous chemical content and its potential to impact organisms [4]. Plastic particles in the environment originate from various sources, including both synthetic polymers e.g., polyethylene terephthalate (PET) used in water bottles and synthetic copolymers such as styrene butadiene rubber (SBR) used in tires [5]. Microplastic particles (MPs) are defined as plastic particles in size range of 11000 μm [5], although the different types of polymers and copolymers have vastly different characteristics such as density, chemical additives, solubility, colour, structure, bio-reactivity, among other features [5].

Tire-road wear particle mixtures (TRWPs) are globally recognized as one of the largest sources of MPs to the environment [6–9]. TRWPs are heterogeneous aggregates that result from the

friction between the tire and the road surface. Therefore, they consist of a mixture of tire tread, and other particles derived from road surface brake wear, and natural sources. Emission estimates vary between 0.6 and 5.5 kg/capita per year [8,10–13], resulting in global emissions of approximately 6 000 000 tonnes/year [8]. Whilst TRWPs are an important contribution to total environmental MP burdens, this review only focusses on TRWPs and not MPs in general. The main reason to exclude other MPs is that the analytical techniques used to identify and quantify TRWPs are significantly different from the analytical techniques commonly used for other MPs due to the differences in polymer types as well as the complexity of TRWPs in terms of chemical composition, colour, mixtures with other road components, and thus, lower polymer content compared to most MP particles.

As already described by previous authors TRWPs are not uniform, but rather a heterogenous group of particles [8,13–16] with particle sizes ranging from <50 μm and up to 350 μm [17,18], various characteristics in terms of texture and morphology [17,19,20], density ranging from 1.2 to 2.1 g/cm³ [18,21–23] and a vast array of different chemical components [17,24]. The variations

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in TRWP properties are both due to the large number of tire manufacturers and available tire types as well as to different road surfaces (both compositionally and texturally) and driving conditions [25]. The observed heterogeneity of TRWPs creates challenges for analytical methods, as they need to accurately identify and quantify the whole range of TRWPs. These challenges have yielded a high number of different analytical approaches, from methods focusing on identifying single TRWPs in different matrices [19,20,26–31] to bulk-based measurements identifying and quantifying the presence of TRWPs based on various markers [32–45].

Current literature also includes various methods for both sampling [15,20,28,46–51] and sample preparation, such as removal of organic material [46,51] or separation of TRWPs from other particles [36,46,51] for different environmental matrices. There is, however, limited information on the impact on TRWP identification and quantification from these different pre-treatment techniques.

We initially set out with the aim of this review to incorporate a decision tree, in which the reader would be able to select their environmental matrix and research question (for example mass concentration of TRWPs in soil) and choose the most suitable and effective analytical method available for their specific needs. This proved not to be possible with the current existing knowledge and data on TRWPs, especially due to the lack of comparative studies using different analytical techniques for analysis of the same environmental sample. This review therefore focusses on giving an overview of the current analytical techniques available for identification and quantification of TRWPs in environmental samples stemming from the different environmental compartments reported (Fig. 1). The advantages and limitations of each analytical approach identified up to date are further described in the following chapters, as either bulk-based or single-particle analysis. Based on the reviewed literature, we introduce an overview table (Table 3) to support the selection of the most suitable analytical method for the detection and quantification of TRWPs based on the current available data and the data output from each analysis method.

2. Discussion

2.1. Bulk-based analysis

Bulk-based methods can provide the mass concentrations of tire tread, and thereafter, of TRWPs in a range of different sample matrices, based on various markers present in tires. However, they do not provide characterization information at a particle level such as size, colour, morphology, or degree of heterogeneity of particle properties. The main bulk-methods currently used for quantification of TRWPs can be divided into three classes; methods using markers for elemental composition, organic composition, and thermal decomposition. It is important to note that these methods are related to the composition of the tire tread, and not the complete composition of the TRWP. The TRWP content can thereafter be quantified by calculations based on the assumed composition of TRWPs (e.g., degree of mixing with other road-related particles, such as minerals and metals).

2.1.1. Elemental composition

Tire material consists of a variety of elements with carbon as the most abundant; approximately 23.3% corresponds to elemental carbon and 54.4% to organic carbon [52]. Organic carbon is the backbone of the rubber polymer and part of the numerous organic additives. Other elements such as silicon (in form of silicon dioxide, SiO₂), zinc (Zn), copper (Cu), lead (Pb), tin (Sn), antimony (Sb), nickel (Ni), cadmium (Cd), and sulphur (S) are used in tire components or required for the production process [13]. Metal concentrations are reported in the mg/kg to g/kg range with declining concentrations starting from Zn > Cu = Pb > Sn > Sb > Ni > Cr > As <> Cd [53,54]. Since tire particles were shown not to occur in a pure form in the environment but mostly as heterogeneous aggregates together with abrasion particles from the pavement and brakes, elements like silicon (Si), aluminium (Al), calcium (Ca), titanium (Ti), S, potassium (K), Cu, iron (Fe), Sb, Sn, barium (Ba), Pb, magnesium (Mg), tellurium (Te), selenium (Se),

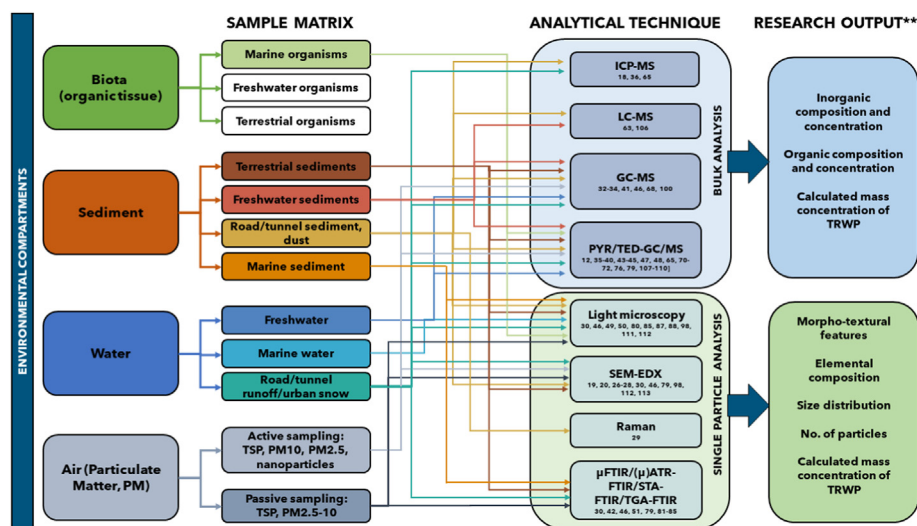


Fig. 1. Summary of current analytical methods for identification and quantification TRWPs in environmental samples by various analytical methods (references in brackets): ICP-MS[†] [18,36,65][†], LC-MS[†] [63,106][†], GC/MS [32–34,41,46,68,100][†], Pyr/TED-GC-MS[†] [12,35–40,43–45,47,48,65,70–72,76,79,107–110][†], light microscopy[†] [30,46,49,50,80,85,87,88,98,111,112][†], SEM-EDX [19,20,26–28,30,46,79,98,112,113], Raman [29] and μFTIR/(μ)ATR-FTIR/STA-FTIR/TGA-FTIR[†] [30,42,46,51,79,81–85][†]. All references are peer-reviewed publications, except for those marked with asterisk (*) and more information on each study can be found in Appendix tables AP1, AP2 and AP3. The research output** is further described in Table 3.

and Cd were also detected in TRWPs [55]. Zinc is added in tires as ZnO and Zn stearate as both are required for the vulcanization process resulting in mass concentrations up to 1%. Sulphur is used for the polymerization process in similar concentrations [54]. Amorphous SiO₂ is used as a filler [17].

Metals like Zn, Cu and Cd as well as S have been suggested as a potential chemical marker for TRWP in particulate environmental samples [13,56]. However, metals do not fulfil all criteria for suitable marker elements (Table 1) and some limitations arise in their application. The metal content in tire particles depends on the type of tire [57] and, as demonstrated, also on the particle size [13]. In the PM_{2.5}–10 fraction, the concentrations of Fe, Ca, and Zn were found to be high compared to concentrations of Ti and Sb. In the fine fraction of particles (PM_{2.5}), the concentrations of Fe, Ca, Ti, Ba, and Sb dominated, but Zn was not found [58]. Metal analysis may also only be useful in case of a low(er) background concentration. For Zn this is mostly not the case as it is often contained in other particle types/sources ubiquitous in urban environments (e.g., brake wear [59]; zinc surfaces like guardrails [20]) or it can leach into the surrounding environment [60]. Therefore, the particulate matrix needs to be separated from the tire material before further analysis. Separation can be achieved by chemical digestion of the matrix [54] or by density separation [18]. The major challenge of the latter is that the separation is usually incomplete. The residual background concentration of the marker limits its applicability to near-road environments where relatively high tire particle concentrations are expected. The elemental content can be determined using inductively coupled plasma mass spectrometry (ICP-MS) instrumentation providing high sensitivity in the µg/L range. However, sufficient method validation has not been carried out, but has been limited to a results comparison between the ICP-MS method and a thermal extraction desorption (TED)-GC-MS method as well as a recovery test with recoveries of 95 ± 17% by spiking a TWP mixture to a sediment sample [36]. Recent analytical approaches make use of characteristic multi-isotope techniques to trace tire particles in the environment [53].

2.1.2. Organic composition

In rubber and tire manufacturing, many organic compounds are intentionally added to support production and improve tire performance, or unintentionally formed through production processes [13]. Some of these have previously been linked to road pollution, such as PAHs and aliphatic hydrocarbons, with sources being for example tires, brakes, the road surface and oil spills. Thus, these compounds are not specific for tires and cannot be used as markers

Table 1

Potential marker substances with their marker properties C1 to C5; C1 present in all tire materials; C2 stable and no leaching from tire particles; C3 specific for tires; C4 concentration of tire marker well above background concentration; C5 simple and robust analysis; a '+' indicates that the marker complies with the marker property and a '-' that it does not.

Inorganic and organic marker substance	C1	C2	C3	C4	C5
Zn	+	-	-	+	+
BT	+	-	-	-	+
24MoBT	-	-	-	-	+
NCBA	+	-	-	-	+
2-MBT	+	-	-	-	+
2-MTBT	+	-	-	-	+
2-OHBT	+	-	-	-	+
2-ABT	+	-	-	-	+
6-PPD-Q	+	+	+	+	+
N-Formyl-6PPD	+	+	+	+	+
QDI-OH	+	+	+	+	+
Oleamide	+	+	-	+	+
DPG	+	-	+	+	+

for tire wear quantification. However, there are several other organic compounds related to tires that have been suggested as markers for tire wear particles (Table 1). These include benzothiazoles which are impurities or decomposition products originated from sulphur cure accelerators of benzothiazole sulphonamides [34,61], diphenylguanidine (DPG) [62], oleamide [41], hydrogenated resin acids [32] and N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine-quinone (6-PPD-Q) [63]. The benzothiazole derivative 2-(4-morpholinyl) benzothiazole (24MoBT), a minor component in the vulcanization accelerator N-oxy-diethylenebenzothiazolylsulfenamide (OBS), was one of the first organic markers applied for TRWP quantification (Appendix Table AP1) [33]. Nowadays, however, its application as a marker is limited as a change from OBS to N-Cyclohexyl-2-benzothiazole sulfenamide (CBS) as predominant vulcanization accelerator for tire rubber was observed. Thus, the CBS contained N-cyclohexyl-2-benzothiazoleamine (NCBA) was identified as a more suitable marker [34,64]. Further proposed and applied markers are the decomposition products benzothiazole (BT), 2-hydroxybenzothiazole (2-OHBT), 2-mercaptobenzothiazole (2-MBT), 2-methylthiobenzothiazole (2-MTBT) and 2-aminobenzothiazole (2-ABT). Yet, the variation in the contents of benzothiazole sulphonamides in tire tread compounds and their leaching tendencies also limit their applicability as marker. DPG was also found to readily leach out of tire wear particles, thus is not utilized as marker for TRWP quantification but to determine tire wear particle presence in surface waters [16]. The approach of hydrogenated resin acids as markers has not been pursued due to the limited stability against photooxidation [32]. Recently [63], proposed three transformation products of the antioxidant 6-PPD as promising tire markers, 6-PPD-Q, N-Formyl-6-PPD and hydroxylated N-1,3-dimethylbutyl-N-phenyl quinone diamine (QDI-OH). Their application for TRWP quantification yielded similar results utilizing Zn (after density separation) as a marker [65], and a systematic study revealed potential marker properties of these 6-PPD transformation products (Table 1). Also, the quantification of tire wear materials based on oleamides is promising and needs further systematic assessment regarding suitability of the compound [41].

The quantification of organic compounds in environmental matrices are often based on mass spectrometry techniques such as liquid chromatography mass spectrometry (LC-MS) and gas chromatography mass spectrometry (GC-MS) after extraction of the target compounds with a suitable extraction agent. The sample preparation, however, is often elaborate (Appendix Table AP1) and method development and validation require reference and test materials. Such materials must represent the diversity of tires in use as well as the effect of aging processes on their composition [66]. Method validation on this method has not been performed yet, besides the assessment of marker selectivity and stability [32,63]. While reproducibility has been shown in a few studies by analysis of subsamples [32,63,64,67] and the method recovery is assessed by internal standards [32] or spiking experiments with the organic compound itself [64,68], only Klöckner et al. [63] performed a standard addition experiment with TWP to environmental samples to show the linear relationship between increasing TWP content and signal intensity of the selected markers. Before chemical markers can be used for reliable and robust determination of TRWPs in the environment, the challenges described must be overcome. Since this has not yet been achieved, quantification of TRWPs is often determined by analysing rubber using thermo-analytical methods.

2.1.3. Thermal decomposition

Thermal gravimetric methods for the bulk-based quantification of TRWPs have primarily been undertaken with pyrolysis (Pyr) or

thermal extraction desorption (TED) methods coupled with gas chromatography mass spectrometry (Pyr-GC/MS or TED-GC/MS). These methods provide an indirect quantification of the total mass of TRWPs in a sample as they monitor thermal decomposition products (for example the BR dimer; Table 2) of polymers within tire tread, such as natural rubber (polyisoprene (NR)) and synthetic rubber (styrene butadiene rubber (SBR) and butadiene rubber (BR)). These decomposition products are separated and detected with GC/MS and quantified against polymer calibration standards to calculate the total mass of natural and/or synthetic rubber in the sample. These concentrations can then be used to calculate the concentration of tire tread and TRWPs in the original sample.

Pyrolysis products of tire tread have been investigated since the 1970s within the context of resource recovery [69], but it has only been since 2012 that mass spectrometry methods have been applied to quantify the mass of tire tread in environmental samples [38]. Two ISO Technical Specifications [70,71] document methods for monitoring TRWPs in soil and air, however, there are still limitations with the proposed methods, as discussed in Ref. [72]. This has resulted in various adaptations to quantify TRWPs using thermal methods (Appendix A, Table A2). A wide range of thermal decomposition products are produced from the SBR + BR copolymer and NR, although only few markers have been used for quantifying tire tread as marker selection is generally a compromise between sensitivity and selectivity (Table 2), where selectivity indicates compounds that are exclusively or not related to tires with few known additional sources or matrix interferences and sensitivity indicates markers that have high enough instrument sensitivity with GC-MS analysis in order to be detected at environmentally relevant concentrations. The majority of TRWP studies have monitored single markers [38,39,70,71], however, recent studies have also suggested the use of combined multiple markers [37]. Generally, method detection limits of both Pyr and TED-GC/MS are in the low $\mu\text{g}/\text{injection}$ to $\text{ng}/\text{injection}$ range [35,70,71], however, this is dependent on the type of pyrolyser unit used, where different sample masses can be injected, and different ranges of linearity are reported between different models [70,71].

As thermal bulk-based methods are indirect analysis methods, there is the potential for the sample matrix to provide significant interferences by forming the same monitored thermal decomposition products [38]. For example, the 1,3-butadiene monomer also occurs in vehicle exhaust emissions, while organic matter is an interference for isoprene [38]. 4-VCH is also a pyrolysis product of acrylonitrile butadiene styrene (ABS) although this source is expected to be negligible as compared to TRWPs in environmental samples [38]. Plant material has been reported as a significant interference of NR dimers and oligomers [35] with no interferences for SBR + BR copolymer reported [39]. also reported significant NR pyrolysis product interferences from orange peel and pine needles, but interferences were removed if the samples were treated with oxidative digestion processes e.g., Fenton's reagent or hydrogen peroxide. Other possible clean-up steps include the use of thermal

desorption (TD) prior to pyrolysis [72], in order to remove certain volatile and semi-volatile matrix interferences.

Furthermore, different types of road surfaces including stone mastic asphalt can be reinforced using polymer-modified bitumen (PMB). This technique is used in several countries, such as Norway, Australia, China, Denmark, Russia, Sweden, and the United Kingdom [73]. Both styrene butadiene styrene (SBS), which forms many of the same pyrolysis products as SBR [37,74], and scrap tires [75] have been used in PMB. Therefore, more investigation into potential matrix interferences and appropriate pyrolysis products to monitor is needed.

Method validation data of thermal methods is limited. While the use of internal standards (d5-PS and d6-PB) and replicate sampling/replicate analyses is common [12,35,45,76] only few studies have assessed method recoveries. Unice et al [38] reported recoveries of 71–88% from artificial soil spiked with cryoground tire particles and Rødland et al. [37] reported mean recoveries of 83–104% from SBR spiked tire and sediment samples. Both studies reported high variability at low concentrations and more validation data is needed for these analysis methods.

2.2. Single particle analysis (microscopy-based)

TRWPs can also be identified and characterized using single particle analyses, where particle properties such as size, morphology, texture, and elemental composition can be detected and are used as diagnostic criteria to recognize TRWPs. Currently, such methods include light microscopy (LM) [30,49,50,77,78] and scanning electron microscopy (SEM), often combined with energy dispersive x-ray spectroscopy (EDX) [19,20,28,30,79]. Different types of spectroscopy techniques, such as Fourier-transform infrared spectroscopy (μ -FTIR, ATR-FTIR, μ -ATR-FTIR, STA-FTIR-PARAFAC [30,42,46,51,79–84]) and Raman spectroscopy [29] have also been suggested for identification of tire tread. Validation on these methods has to our knowledge not been performed yet. Some studies have used a multimethod analytical strategy for the identification of TRWPs [27,30,85], but no cross validation or method recoveries have been presented yet.

2.2.1. Visual and tactile analysis

Light microscopy (LM) is a common method to analyse coarser fractions of MP, normally $>100 \mu\text{m}$ [49,50,86], but has been used to identify TRWP down to $10 \mu\text{m}$ [30,77]. It has the advantage of needing relatively simple requirements, low instrument costs and visualizing the true colours of particles, which is helpful for identification. In addition to the dark and opaque colour, the TRWPs are identified by elongated to round morphologies, irregular contours, and heterogeneous surface textures. Additionally, sometimes the above-mentioned optical characteristics have been combined with tactile properties and melt tests. Here, TWP and TRWP has been identified based on their elasticity and that the particles remain visually unaltered after a melt test, compared to e.g., bitumen that

Table 2

Thermal products from tire rubber and their potential as marker compounds demonstrated as selectivity (M1) and sensitivity (M2). The '+' indicates that the monitored product is either selective or sensitive (as compared to the other products) and '-' indicates it is not.

Rubber	Thermal products	M1	M2
SBR + BR	BR dimer (4-vinylcyclohexene, 4-VCH)	+	+
SBR + BR	SB dimer (3-phenylcyclohexene)	+	-
SBR + BR	SBB trimer	+	-
SBR + BR	Sum of benzene, α -methylstyrene, ethylstyrene and butadiene trimer	+/- ^a	+
NR	Dipentene	-	+

^a Note that the sum of benzene, α -methylstyrene, ethylstyrene and butadiene trimer may be selective in certain matrices that do not have a large matrix interference of benzene [37].

Table 3

Overview of method characteristics and output data delivered by different analytical techniques used for analysis of tire wear particles. Cells depicted with "+" indicates that the suggested output is available, cells depicted with "-" indicates that the output is not possibly obtained. *Light microscopy and FTIR techniques are often applied in combination with additional techniques using visual and tactile parameters to confirm the identity of TRWPs. **estimated based on number of particles, assumed three-dimensional size and density.

Parameters/Method	Light microscopy*	μ -FTIR/(μ)ATR-FTIR*	SEM-EDX	PYR/TED-GCMS	ICP-MS	GC-MS	LC-MS/MS
Method characteristics	Parameter/marker	Shape, dark colour, heterogeneous surface texture	FTIR spectra of isobutylene isoprene rubber	Morpho-textural properties & elemental composition (C, Si, O \pm S, Zn)	SBR; BR; NR	Zn	Oleamide, BT, 2-OHBT, 24MoBT, NCBA, 2-ABT, 6-PPDQ, hydrogenated N-Formyl-6-PPD, QDI-OH
	Requirements of the (processed) sample	Isolated particles; dry sample	Isolated particles; dry sample	Isolated particles; dry sample	Bulk sample; solid sample, dried filter	Particle extract; liquid sample	Particle extract; liquid sample
	Filter/substrate type for analysis	Glass surface	Filter: anodisc, silver, glass fiber, diamond ATR/compression cell	Carbon pad, polycarbonate filter, boron substrate	Crucible; PYR (80 μ L), TED (150 μ L)	Extract vials/ tubes	Extract vials
Output data	Minimum size LOD/LOQ	>10 μ m	>10 μ m	>1 μ m Depends on the number of particles measured (e.g. 0.5 rel. % particle number if 800 particles/sample are measured)	– ng to low μ g/injection	–	– Low mg TWP/g sample range
	Confirmation of TRWP	–/+*	–/+*	+	+	+	+
	Size distribution	+	+	+	–	–	–
	Morphology	+	+	+	–	–	–
	Surface texture	+	+	+	–	–	–
	Elemental composition	–	–	+	–	+	–
	Organic compounds	–	+	–	+	–	+
	Polymers	–	+/-	–	+	–	–
	Particle number	+	+	+	–	–	–
	Mass concentration	+**	+**	+**	+	+	+

melts [49,78,87,88]. Being dependent on the operator's perception of visual and tactile properties, makes the method operator dependent and time-consuming. This could lead to misinterpretation of other dark particles displaying similar morphologies as TRWPs (e.g., opaque minerals like amphibole and pyroxene, wood fragments and other organic material). These possible interferences largely depend on the resolution of the used LM device and the optimization of the analytical properties, both directly influencing the image quality obtained. The later also applies for the SEM/EDX methodology. To identify the actual polymers or elemental composition, it needs to be complemented with additional spectroscopy methods, SEM/EDX, or bulk-based methods (see chapter 2.2). Based on literature, LM is particularly suitable for first screening of samples and for analysis of coarser particles (>50 μ m) [89].

2.2.2. Morpho-chemical analysis (combination of image and spectroscopy)

FTIR and Raman are commonly used techniques for the identification of MP [29,90–93]. Both methods are based upon the interaction of light with the chemical bonds within a material enabling the identification of molecules and providing a structural fingerprint (spectra) by which the chemical structure, phase, polymorphism and crystallinity of Raman, respectively IR active materials can be identified. Both FTIR and Raman techniques provide the operator with particle size, shape, and additionally, polymer type. In a laboratory study, optical tweezers have been used in combination with Raman spectroscopy to trap and analyse ground tire particles even below 1 μ m [29]. In Ref. [30], μ -ATR-FTIR was tested on presumed TRWPs and could be shown to generate

relatively high-quality spectra useful for the confirmation of TRWPs. Likewise [80], used ATR-FTIR on particles >500 μ m already visually identified as tire tread and could confirm spectra strongly resembling that of commercially available crumb tire rubber [51]. identified TRWP with FTIR and used Raman to confirm the origin of the particles by comparing spectra from environmental collected particles with reference spectra of natural rubber. Mattsson et al. [85] photographed environmental collected TRWPs under a light microscope, chemically identified the particles with FTIR and compared the spectra with TRWPs generated in a road simulator as well as with tire tread cut in ultrathin sections with promising results. However, one of the main challenges of these techniques for TRWP identification is the non-specificity of carbon black, which is one of the main components in TRWPs that can be analysed with FTIR and Raman spectroscopy technologies [15]. The presence of mineral encrustment on the surface of environmental TRWPs may further complicate the identification of TRWPs based on spectroscopy. Automated analysis using FTIR and Raman is available [94–96], but so far not applied in scientific publications on the analysis of TRWPs.

SEM/EDX analyses have been applied for TRWP identification and quantification in several recent studies [19,20,26,28,30,31,79,85,97]. This approach provides elemental composition (by EDX) of individual particles besides size, shape, surface texture (e.g., degree of heterogeneity, which in the case of TRWPs refers to mixing), and indirect approximate density based on grey levels obtained from BSE (backscatter electrons) imaging. Each study has used a set of morpho-textural-chemical parameters to identify TRWPs. For acquiring the elemental composition of TRWP some studies rely on SEM/EDX mapping [27] while other studies make

use of a bulk elemental composition for single particles [19,20]. Other main differences between the available studies using SEM/EDX for TRWP identification and quantification are the particle size range (e.g., >10 μm in Ref. [26] vs. > 1 μm in Ref. [20]), the inclusion of the element carbon as an additional diagnostic criterion owing to the use of boron substrates as analytical surface [19,20,28,30], the analysed environmental compartment (e.g., air: [20,26]; road surface, road runoff and roadside gully pot sediments: [19,27,28]), and the degree of automatization of the SEM/EDX analysis and subsequent data treatment (for more details see Appendix A Table A3). One advantage of performing automated vs. manual analysis and data treatment is the significantly larger number of particles that can be analysed per sample (hundreds to thousands), and therefore, the statistical relevance, the efficiency, and the reproducibility of the results. Repeatability tests of five subsamples from the same sample (filter) using automated SEM/EDX were shown in Järskog et al. [28] as well as analysis of blank samples.

As SEM/EDX largely relies on specific morpho-textural parameters of single particles [20], the identification of TRWPs is best when particles are pristine (i.e., relatively fresh after emission). The more characteristic features are masked due to dissolution/corrosion, coatings from precipitations on the surface, etc., the more difficult it is to identify TRWPs, and the more likely that misclassification occurs [19]. This is a drawback of the SEM/EDX method as the EDX is not capable of determining the molecular structure of the carbon bonds. And relying mainly on the elemental composition is subjected to larger errors in the identification and quantification because the combination of elements alone (i.e., without the morpho-texture) is not specific to TRWPs. Therefore, the more intact the morpho-textural features, the more accurate the quantification of TRWPs by SEM/EDX.

2.3. Estimation of total tire-road wear particles

In most environmental studies of TRWPs, there is a need to utilize the obtained data from the analysis performed to assess the levels of TRWPs detected and potentially identify the sources of the TRWPs in the sample.

For single particle analyses, the output of the analysis is delivered as number of TRWP/L or kg [20,30,49,50,78,87,98] or as relative number concentration of TRWP in a given sample [19,20,28,30]. Based on the measured length and width of particles (2D projection) and the assumed depth of the particle (3D morphology), the volume can be extrapolated, and the total mass can be estimated, assuming a plausible particle density [20,30,99]. This means that the results obtained by microscopy-based measurements initially deliver the particle count of TRWP mixtures as they occur in the environment. Based on subsequent image analysis and/or estimations of the input of elements stemming from "foreign" minerals and metals, the amount of tread can be roughly estimated [20].

For bulk-analysis methods, there is a need to convert the monitored marker to the mass of tire tread and subsequently to the mass of TRWP. These calculations are needed for different reasons. The mass of tire tread is useful for assigning the source of these rubber particles to tires and understanding the release of tire tread particles into the environment. The mass of TRWP is, however, more interesting when considering the environmental fate of these particles. The mineral mixture of TRWPs will have a substantial impact on the morphology and density of the tire tread in the environment, thus it's important to include these calculations for estimation studies and transport modelling.

For all bulk-analysis markers, the first step is to establish the expected % contributions of these markers in tire tread. Marker % contributions have been established by analysing pure tire rubber

or tire tread and utilizing the results to back calculate the tire tread concentrations in environmental samples [32–34,36,37,39,41,68,72,100,101]. In these studies, the number of tire tread samples analysed varied between 1 and 31, including both car and truck tires. This potentially introduces a large uncertainty, as studies reported a large variation in % contributions for several markers in different commercial tires [37,72]. These variations suggest that the recipes of commercial tires are complex and the use of standardized marker levels for all tires may increase the uncertainty of environmental concentration estimations. Utilizing tire treads from relevant tires (e.g., locally sourced, season-dependent or other factors) could potentially improve this uncertainty. And the usefulness of prediction models applying relevant tire data has been demonstrated in recent studies [37,47,48,76]. An additional approach is to use standard addition of reference tire rubber in samples for validation [63]. Yet, as for the tire tread calculations, this method also relies on the availability of a representative tire sample. As the tire composition varies depending on the manufacturer, the tire type, and the tire age, it is crucial that the reference tire material represents the diversity of tires and the geographical area related to the environmental samples. However, the knowledge on how tire tread material age in the environment and how this affects their monitored marker products is currently limited [66]. Another issue that must be addressed is the potential leaching of the marker substances from the TRWPs. In order not to underestimate the TRWP mass, the leaching behaviour of each marker must be assessed, and a corresponding individual correction factor must be determined and applied. Such correction factors are not implemented or assessed yet. In one study, the marker concentration in the liquid phase and in the suspended particulate matter was assessed under the assumption that the marker originates solely from the suspended particulate matter [34]. However, it is questionable how valid this assumption is.

An additional calculation is also required to convert tire tread to concentrations of TRWP. For the methods where specific mass components of TRWPs are monitored (such as Zn and SBR), no information on the level of mineral encrustment on the tire particle can be provided, which is a major part of the TRWP from environmental samples. The current limited knowledge on mineral encrustment of TRWPs shows a range between 6 and 53% [17,18,26]. This suggests that the mineral encrustment on TRWPs is not constant, and as demonstrated by Ref. [48], a prediction model to calculate from tire tread concentrations to TRWPs can be set up. As for the tire tread markers, more data on the mineral mixture within TRWPs is needed to lower the uncertainty of these prediction models.

2.4. Deciding on an analytical approach for TRWP quantifications

The first step in any research project should be to define the research questions at hand. In doing so, certain analytical methods will potentially be discarded (e.g. due to unrealistic size range) or identified as potentially reliable. Single-particle methods can be suitable when the aim is to increase knowledge about transport routes, fate, and potential risks of TRWPs, in which the size, morphology and number of particles may be the most important output. When the research focus is based on mass-balance or establishing environmental mass levels within size classes, bulk-sample methods may be more useful. However, a comprehensive analysis of TRWP requires more than one method, and a multi-method strategy to cover different aspects and research questions related to the sample is preferable.

Based on the reviewed literature, we graphically illustrate the vast diversity of methods currently used for identification and quantification of TRWPs in different environmental matrices (Fig. 1). This also illustrates which analytical techniques have been

most used by researchers so far, from which types of environmental matrices TRWP data has been collected and perhaps more concerning, what types of environmental matrices are we still lacking information on. As seen in Fig. 1, PYR-GC/MS and TED-GC/MS are currently the most used analytical techniques in terms of number of environmental studies (21), whereas we found no peer-reviewed studies in which identification and quantification of TRWPs in freshwater organisms or terrestrial organisms have been reported. The current data on marine organisms, marine sediments and freshwater sediments are also limited, whereas there are currently numerous studies on identification and quantification of TRWPs in environments close to the road, such as road runoff, road dust, road-related sediments and airborne samples at urban and traffic sites. This shows that there is a need to expand the research efforts and the use of analytical techniques to investigate the transport of TRWPs further away from the road environment. More details on each study can be found in the Appendix, tables AP1, AP2 and AP3. In addition, we present an analytical overview chart (Table 3), where the requirements and the expected output of the different methods are demonstrated and could be used to evaluate which methods meet the criteria set by the research questions.

In addition to these currently used methods, there are also some potential upcoming methods addressing MPs in broader sense that have so far only been explored for TRWPs to a limited extent, such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) [31], thermogravimetric analysis (TGA) [46] and Laser-Induced Breakdown Spectroscopy (LIBS) [102]. Nile Red fluorescence microscopy has potential for identification of MP in road dust, however, as demonstrated by Myszka et al. [103], no identification of TRWP was possible due to the lack of fluorescence at 488 nm wavelengths. For research projects there is also a potential of increasing the abilities of both FTIR and elemental analysis such as micro-X-ray fluorescence (μ XRF) if they are coupled to synchrotron technology [104,105].

3. Conclusion

The current knowledge on TRWPs demonstrates that these particles are not uniform, but rather heteroaggregates of tire and road-related particles with a wide range of sizes, densities, morphologies, and chemical components. This further complicates the tasks of identifying and quantifying TRWPs in environmental samples. Here, we present an overview of analytical methods for both bulk-analysis and single-particle analysis and describe the possibilities and the type of information that can be obtained from each method. However, it also shows the limitations and uncertainties related to the different methods. As described in both the sections of single-particle analysis and bulk-analysis, there is a general lack of validations presented for the methods used in environmental studies, for example by applying spike and recovery tests for different sample types. Tests such as these are common in the field of environmental chemistry and would also provide valuable information about the performance of the different analytical techniques for TRWPs and their ability to successfully identify and quantify TRWPs across different environmental samples.

The presented overview also demonstrates that any comprehensive analysis of TRWPs would require the use of complementary methods in order to understand all aspects of TRWPs present in a sample. Thus, analysis of TRWPs demands for a combination of methods and flexibility to adapt the suggested methods to the research questions at hand and the type of sample (e.g., matrix). So far, only two peer-reviewed study has performed a cross-validation of TRWP identification and quantification between different analytical techniques in environmental samples [79,85], thus

highlighting the current limitations of comparing between different TRWP studies applying different analytical techniques.

To compare results between studies, it is also important to strive for standardization in terms of sampling, pre-treatment of samples, analytical settings, TRWP mass calculations and data reporting. Especially, standardization of separation techniques such as size fractionation and density separation, and uniform definition of size fractions to be analysed would drastically improve the comparability between studies.

Current methods apply different markers to identify and quantify the mass of tire tread, thus relying on information on the % contribution of these markers in tires. Applying real values from locally used tires may be useful to lower uncertainty and target differentiation of specific tire use. However, it demands for analysis of relevant tires in each study based on a minimum number of tire samples; or the creation of a tire database that can provide data for different types of tires across the globe [37]. This work also needs to include the topic of aging, as the current knowledge on change in markers and particle morpho-texture of TRWPs due to environmental weathering is limited. There is also a need to improve the quality of calculations of TRWPs from tire tread, as the current data on minerals and other particles associated with tire tread is limited, which causes a high uncertainty in reported levels of TRWP. An improved understanding of the components associated with TRWPs in various environmental samples may reduce this uncertainty and increase our knowledge on TRWP transport and fate in the environment. These issues should be addressed to improve the current analytical methods for TRWP quantification.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.trac.2023.117121>.

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