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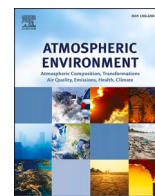
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Review article

Measurement of tyre dust particles in the atmosphere using chemical tracers

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HIGHLIGHTS

- Tyre wear particles are a major contributor to particulate matter in urban air.
- There are few measured concentration data in the literature.
- The specificity and stability of organic and inorganic tracers is evaluated.
- No current method meets the requirements for fully quantitative measurements.

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ABSTRACT

Control of airborne particulate matter is a high priority due to its adverse effects upon human health. Road traffic contributes to both coarse and fine particle concentrations, both through exhaust and non-exhaust emissions of particles. Tyre dust is recognised as making an important contribution to non-exhaust emissions from road traffic, which in many countries now exceed exhaust emissions. The analysis of tyre dust in the atmosphere is challenging, and most methods depend upon use of chemical tracers, which are both inorganic and organic. None is wholly specific and fully quantitative, and this article reviews those which have been used and highlights some of their strengths and weaknesses.

1. Introduction

According to the Global Burden of Disease project (Cohen et al., 2017), exposure to fine particles (PM_{2.5}) is a major cause of illness and death worldwide. In recognition of these effects, the World Health Organization has recently reduced its guideline for PM_{2.5} to 5 µg/m³ annual mean (WHO, 2021). Coarse particles (PM_{2.5-10}) also exert a toxic effect, and the WHO recommends a guideline also for PM₁₀, which includes both coarse and fine particles. Policy measures are being developed across the world to reduce population exposures.

Vehicle emissions contribute appreciably to airborne concentrations of particulate matter (PM), as evidenced by the elevation of roadside concentrations above the urban background (Harrison et al., 2021a). As vehicle exhaust emissions of particulate matter have reduced in

developed countries due to the implementation of highly effective control technologies, so non-exhaust emissions have become a more prominent component of traffic-generated air pollution (Amato et al., 2014; Harrison et al., 2021b). In the United Kingdom and the European Union, non-exhaust emissions now exceed exhaust emissions from the road vehicle fleet. The increasing market penetration of battery-electric vehicles will have little benefit for total non-exhaust emissions (Beddows and Harrison, 2021), but may increase the tyre wear component due to greater average vehicle weight (AQEG, 2019). Non-exhaust emissions arise from the abrasion of tyres, brakes and the road surface, and the resuspension of street dust.

A number of review articles have given a detailed overview of non-exhaust emissions (Thorpe and Harrison, 2008; Harrison et al., 2021b; Piscitello et al., 2021), and a review has dealt explicitly with brake wear

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particles (Rahimi et al., 2021). Far less attention has been paid to tyre wear emissions, and although this source has been reviewed (Zhang et al., 2020a; Baensch-Baltruschat et al., 2020; Wagner et al., 2018), measurement methods were not considered in detail. There have been rather few reliable measurements of total non-exhaust emissions, and even fewer which have quantified tyre wear particles. Currently, although there are recommended methods for quantifying tyre rubber, there are no generally accepted or adequately standardised procedures for the analysis of tyre rubber in the atmosphere. Since evidence suggests that tyre wear particles contribute significantly to total non-exhaust emissions, and can make a significant contribution to airborne particulate matter, reliable measurements are a high priority, although as demonstrated below there remain considerable challenges. Such measurements are needed at roadside where they can be used to estimate emission factors, but also more widely in order to evaluate their contribution to public exposure to particulate matter. The objectives of this article are to review critically the methods available for quantitative analysis of tyre wear particles in the atmosphere, and to consider how reliable measurements might be made.

1.1. Characteristics of tyre wear particles

During use, vehicle tyres lose a great deal of mass due to attrition by contact with the road surface. The majority of particles are large (Kreider et al., 2010), and remain on the road surface until washed off by rainfall or road surface cleaning. Tyre treads are composed predominantly of organic matter (Kennedy et al., 2002) with 40–60% of mass comprising a blend of rubbers. Kreider et al. (2010) report a bulk composition of 46% polymer, 19% plasticiser and oils, 19% carbon blacks and 16% minerals. The rubber polymer may comprise different relative amounts of synthetic styrene-butadiene rubber (SBR), butadiene rubber (BR) and natural rubber (NR). At high temperatures, as may occur with wheel spin or hard cornering, ultrafine particles (<100 nm) can be generated in large numbers, but contribute little to mass, by virtue of their small size. They are reported to have a composition dominated by carbon, silica and sulphur (Park et al., 2018). There are many additives which include naphthenic and aromatic extender oils that are added to tyres to improve stress resistance, as well as pigments, vulcanising agents and accelerators such as zinc, to speed up vulcanisation (Boulter, 2005). The noise regulations introduced in recent years may have influenced the tread pattern and formulation of tyre rubber. The impact upon generation of tyre dust and differences between summer and winter tyres do not appear to have been studied systematically.

Grigoratos et al. (2018) compared the wear properties of a number of tyre brands and tread patterns, finding that the tyre tread mass loss rating showed no significant relationship to PM₁₀, PM_{2.5} or particle number emissions. Woo et al. (2022) found that in general, tyres with a higher tread wear grade generated a lower particle load than those of softer compound, but there was one major exception amongst the tyres which they studied.

1.1.1. Association of tyre wear and road surface wear particles

Single particle analysis methods have been applied to elucidate the composition and morphology of tyre dust particles. By use of electron microscopy, Kreider et al. (2010) and Panko et al. (2013) have demonstrated that tyre dust particles collected from on-road studies contain an internal mixture of tyre rubber with other constituents derived from road surface wear or other particles from the road surface. They propose the term “Tyre Road Wear Particles (TRWP)” to describe the aggregated material. Individual particles sampled from the atmosphere by an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) also showed an association of crustal elements with particles derived from tyre dust (Dall’Osto et al., 2014), consistent with an association of road pavement or road dust particles with the tyre rubber.

In recognition of the association of road wear with tyre wear particles, Panko et al. (2018) draw a clear distinction between tyre wear

particles and tyre tread particles. In this, the former have a composition reflecting the presence of road wear material, while the latter are comprised solely of material deriving from the tyre tread. Panko et al. (2018) show major compositional differences between tyre wear and tyre tread particles. Tyre wear particles are enriched in several elements including most markedly Al, Ca, Fe, Mg, Si, and Ti, which are all crustal elements likely to be present in both road pavement materials and soil-derived road dust. Elements present at higher concentrations in tread particles are S and Zn, due to their incorporation during manufacture of the tyre, with lesser concentrations present in road wear materials. Polycyclic aromatic hydrocarbon (PAH) congeners showed a mixed picture, with some compounds enriched in the tyre wear particles and presumably deriving from the asphalt of the road surface, while others are depleted relative to the tread particles.

This compositional difference between the tyre tread itself and the tyre wear particles raises important issues for the quantification of tyre wear in the atmosphere using chemical tracers. Those chemical tracers which are specific to the rubber quantify the tyre rubber alone if calibrated using the composition of tyre tread. The use of crustal element tracers of road dust resuspension and road wear will account also for the road wear material in the combined TRWP particles. Only methods which examine individual particles, or receptor modelling methods are able to quantify TRWP as a distinct entity, as chemical tracer methods quantify only the tyre wear rubber component.

1.2. Methods applied to analysis of airborne tyre dust

Methods based upon electron microscopy, as mentioned above, have been instrumental in revealing the nature of TRWP. Although electron microscopy/X-ray analysis methods have also been applied to “super-coarse” airborne particles (Sommer et al., 2018), they are unlikely to be practicable for routine analysis of tyre dust in the atmosphere. While the careful application of multivariate receptor modelling methods such as Positive Matrix Factorization can differentiate a tyre/road wear contribution to particulate matter mass, this requires a large measurement dataset, as the estimation of the tyre wear contribution requires analysis of a multiple air samples. The ideal would be to have a tracer element or compound meeting the requirements listed by Wagner et al. (2018): the tracer should

- be present in all tyre materials in comparable portion, largely independent from manufacturer or manufacturing process,
- not leach easily from tyre particles into the surrounding environment,
- not be easily transformed while the tyre particles reside in the environment (air, water, soil),
- be sufficiently specific for tyres, namely not present in relevant concentration in other traffic-related particulate matter, such as brake dust, roadway particles or surface runoff,
- have a concentration in tyre material significantly higher than in the particles forming the sample matrix (soil, sediment, road dust, suspended matter, aerosol),
- be analytically accessible by methods of high precision, accuracy, and sensitivity at reasonable analytical effort.

It is questionable whether any tyre wear tracer used to date meets these criteria, and Wagner et al. (2018) conclude that no suitable quantitative techniques exist for quantitative analysis of tyre rubber. Relevant studies and methods applied to atmospheric samples are summarised in Table 1, and are discussed below.

1.2.1. Pyrolysis – gas chromatography

Pyrolysis of natural and synthetic rubbers releases lower molecular weight hydrocarbons as pyrolysis products, and this is used in an analytical procedure. Early work by Cardina (1973) used styrene and dipentene as tracers, while Cardina (1974) measured styrene, dipentene

Table 1

Analytical methods or target tracer used in published studies of tyre dust in the atmosphere.

Authors	Method principle
Cardina (1973; 1974)	Pyrolysis/GC
Cadle and Williams (1979)	Extraction/IR; Pyrolysis-GC
Lee et al. (1989)	Pyrolysis/GC-FID
Sakamoto et al. (1999)	Pyrolysis/GC-FPD
Schauer et al. (2002)	Alkanes/CMB model
Panko et al. (2013, 2019)	Pyrolysis/GC-MS
Toyosawa et al. (1977)	Pyrolysis/GC
Kim et al. (1990)	Pyrolysis/GC-FPD
Kumata et al. (2011)	Hydrogenated resin acids
Fausser et al. (1999, 2002)	Organic zinc
Harrison et al. (2012)	Inorganic zinc/particle size
Kwak et al. (2013)	Inorganic zinc/particle size
Fomba et al. (2018)	Inorganic zinc
Hicks et al. (2021)	Inorganic zinc

and vinylcyclohexene. Lee et al. (1989) used isoprene and styrene respectively as tracers for NR and SBR. Unice et al. (2012) recommend the analysis of vinylcyclohexene and dipentene with deuterated internal standards of similar polymeric structure to the rubber. Tonegawa and Sasaki (2021) used styrene as the analyte. According to Rauert et al. (2021), the following have been used as marker compounds: 4-vinyl cyclohexene (from pyrolysis of styrene-butadiene rubber and butadiene rubber), SB hybrid dimer (C₁₂H₁₄; benzene, 3-cyclohexen-1-yl) and SBB (styrene-butadiene-butadiene) hybrid trimer (C₁₆H₁₂), both markers of styrene-butadiene rubber, and dipentene, a marker for natural rubber. Both GC-flame ionisation detector and GC-mass spectrometry techniques are used for separation and quantification, and deuterated standards to assist in quantification.

The pyrolysis technique has been adopted in an ISO protocol for determination of tyre tread particles in the atmosphere (ISO, 2017). The ISO method is predicated upon there being few likely interferences which also release these compounds upon pyrolysis, and depends upon assumptions of tyre tread composition which may not be correct. It assumes that the total rubber content is 50% of the mass of the tread and that passenger car tyres contain 44% SBR + BR and truck tyres contain 45% NR. The calculation of the total mass of tyre rubber is dependent upon these assumptions, which Rauert et al. (2021) demonstrate may be incorrect. Rauert et al. (2021) used the marker compound, 4-vinylcyclohexene recommended by the ISO protocol to quantify the synthetic rubber content of 32 tyres sourced from two continents. The mass of synthetic rubber was found to vary from <0.05% to 28% without a systematic dependence upon the brand or model of tyre. They estimate that this may lead to an under-estimation of at least 5-fold in the airborne concentrations of tyre road wear particles by using the mean concentration of synthetic rubber estimated. They also highlight the risk of interferences from other polymers with the same building blocks, including some used in road surface asphalt (Rauert et al., 2021). In the light of these issues, Rodland et al. (2022) developed a method which analysed a number of pyrolysis products and recommended use of locally sourced traffic data to provide the necessary data upon tyre rubber composition.

Other pyrolysis methods have depended upon pyrolytic release of benzothiazole as a tracer of tyre rubber (Kim et al., 1990), with analysis by GC with flame photometric detection. This compound is semi-volatile and is unlikely to be well conserved in tyre rubber, due to loss to the atmosphere (see also Section 1.2.5).

1.2.2. Polycyclic aromatic hydrocarbons

The naphthenic and aromatic extender oils that are added to tyres contain PAHs, and tyre tread can contain 17–357 mg kg⁻¹ of PAHs (Valle et al., 2007). In a study of a range of tyre types, Sadiqtsis et al. (2012) found a factor of 22.6 between the highest and lowest total concentrations of PAH. Five dominant PAHs (benzo[ghi]perylene,

coronene, indeno[1,2,3-cd]pyrene, benzo[e]pyrene, and benzo[a]pyrene) made up around 92.3% of the total extractable content, and had similar ratios between different types of tyre. Kreider et al. (2010) reported only low concentrations of PAHs in tyre wear particulate matter and questioned the suitability of PAHs as markers for tyre debris, especially as PAHs are not easily extracted from tyre wear particulate matter. This view was also expressed by Larnesjo (1999) who considered PAH concentrations to be too variable to be used as a marker for tyre emissions. PAHs arise also from vehicle exhaust and other combustion emissions, and Kumata et al. (2011) found that tyre wear particles accounted for only a very small proportion of pyrene and benzo[a]pyrene in roadside and rooftop air. From January 2010, the European Union has restricted the permissible PAH content of tyres in Europe by statute (Directive 2005/69/EC) (EU 2005), with a specific requirement that benzo[a]pyrene (BaP) does not exceed 1 mg kg⁻¹, and that the sum of benzo[a]pyrene (BaP), benzo[e]pyrene (BeP), benzo[a]anthracene, chrysene (CHR), benzo[b]fluoranthrene (BbFA), benzo[j]fluoranthene (BjFA), benzo[k]fluoranthene (BkFA) and dibenzo[a,h]anthracene (DBaHA) does not exceed 10 mg kg⁻¹. Analysis of PAH alone is very unlikely to give a useful estimate of tyre dust concentrations due to the multiple sources in the roadside atmosphere.

1.2.3. Inorganic zinc

Pant and Harrison (2013) report that zinc may comprise up to 1% by weight (10,000 ppm) of tyre tread material making it the dominant metallic element in tyre tread, with the zinc content being largely independent of tyre type (Weckwerth, 2001). Jeong (2022) reports analyses of seven tyres for Zn with a range of 9500 to 13,300 mg kg⁻¹ (ppm), with less variability than in most other elements analysed. Zinc is also present in brake linings, but emissions of the element from brakes were estimated to be around one quarter the mass of zinc emissions from tyres in Stockholm (Hjortenkrans et al., 2007). Klockner et al. (2019) analysed 21 tyre samples and reported a mean zinc concentration of 8.7 ± 2.0 mg g⁻¹ (8700 ± 2000 ppm), and recommended Zn as the best elemental marker for tyre wear. Kreider et al. (2010) report a Zn concentration of 9000 ppm in tyre tread (and 3000 ppm in tyre wear particles). Gehrig et al. (2010) estimated PM₁₀ emissions from tyre wear in a simulator using Zn as a tracer. Dong et al. (2017) measured the isotopic composition of zinc in PM₁₀ in London, concluding a significant contribution arose from tyre wear.

For tracers such as zinc, which have many other sources of emissions to atmosphere, precautions adopted by some workers are to measure a size distribution (Harrison et al., 2012; Fomba et al., 2018), and to subtract urban background concentrations from those at roadside (Harrison et al., 2012; Fomba et al., 2018; Hicks et al., 2021). The size distribution measurement allows the subtraction of a fine particle component which most probably arises from high temperature sources such as metallurgical industries or the combustion of zinc-containing oil additives such as the zinc dialkyldithiophosphates. The subtraction of the urban background allows quantification of a traffic-related component free of zinc emitted from other urban and advected emissions. An implication, however is that the method is susceptible to interferences from other sources when deployed at urban and rural background locations, and is therefore likely to prove unsuitable.

1.2.4. Organic zinc

A fraction of the zinc added to rubber tyres is complexed by organic accelerants, and can be extracted into an organic solvent. Other than the zinc dialkyldithiophosphates used as oil additives in vehicles, tyre rubber should be the only source of organic-extractable zinc. A method applicable to analysis of tyre rubber in the atmosphere was developed by Fausser et al. (1999, 2002), which involved extraction into dichloromethane, mineralisation of the zinc and atomic absorption analysis, who reported measurements from Copenhagen. It does not appear that other researchers have adopted this method. The constancy of the relationship between extractable zinc and rubber mass across tyre types and across

time would need to be checked if this method were to be employed further. The particle size-dependence of extraction efficiency also needs to be tested.

1.2.5. Organic tracers

Benzothiazole derivatives are used as vulcanising agents in rubber production and are observed widely in the environment (Liao et al., 2018). These have been used extensively in analysis of rubber particles in aquatic samples, and in a few studies of road dust and Standard Reference Material (Reddy and Quinn, 1997), but not in airborne particles. Zhang et al. (2018) found benzothiazole and 2-hydroxybenzothiazole in debris from 17 major brands of tyres from 8 countries to be the dominant species within this group in both tyres and road dust samples. N-cyclohexyl-2-benzothiazolamine (NCBA) and 2-(4-morpholinyl) benzothiazole (24MoBT) were used as markers for tyre tread wear by Allen et al. (2006) and Kumata et al. (2002). Some of this group of compounds are appreciably volatile, and may be subject to photo-oxidation (Liao et al., 2018), reducing their value as atmospheric particle tracers. According to Zhang et al. (2018), based upon analysis of 17 tyre samples, the mass fraction of the sum of the seven analysed benzothiazoles can vary by almost five-fold, hence creating considerable uncertainty in estimating mass concentrations of tyre rubber. This group of compounds may also be present in bitumen used in road surfacing.

Hydrogenated resin acids have been proposed as markers of tyre rubber by Kumata et al. (2011) as synthetic compounds claimed to be specific to rubber. Four dihydroresin acids, that is, 8-isopimaren-18-oic acid (I), 8-pimaren-18-oic acid (II), 13 β (H)-abieten-18-oic acid (III), and 13 α (H)-abiet-8-en-18-oic acid (IV) were analysed in samples of road dust and suspended particulate matter. Kumata et al. (2011) critically evaluate their suitability as tyre-wear markers, revealing potential for evaporation, water leaching and photo-oxidation. They state that the concentrations of resin acids in tyres and environmental samples are higher than those of benzothiazoles by up to two orders of magnitude, but the differential in concentrations is not so large when comparing with the data presented by Zhang et al. (2018). Further work is needed to establish the specificity of these compounds as tracers, and to evaluate their relative concentrations in different brands and types of tyres.

1.2.6. Receptor modelling methods

Rather than using a single tracer element or compound, several recent studies have used multi-element analysis to characterise airborne particles, followed by a receptor modelling procedure for source apportionment. Although not strictly a use of tracers, the multivariate statistical receptor models depend upon chemical profiles, most often of elemental composition, to identify source-related factors, and in the Chemical Mass Balance Model, such chemical profiles are used as model inputs. Both method types use a chemical mass conservation approach.

Specific receptor modelling studies which have been applied and have shown success in identifying a tyre/road wear component include Zhang et al. (2020b) (Chemical Mass Balance), Vlasov et al. (2021) (Principal Component Analysis) and Matthaios et al. (2022) (Positive Matrix Factorization). Many such studies have, however, failed to differentiate tyre wear from other non-exhaust components, presumably due to a strong temporal correlation of non-exhaust sources at a given sampling site.

2. Discussion

In the introduction, two main criteria were described for the ideal tracer; specificity to the source, and constancy of composition. Most of the tracers used to date for tyre rubber match one or other criterion, but none matches both. The methods and some of their weaknesses are listed in Table 2. The ISO pyrolysis method for rubber analysis is likely to have a high degree of specificity, unless it were to be shown that another component of airborne particles such as road surface asphalt could also pyrolyse to form the same volatile hydrocarbons. Since some road

Table 2

Tracers, methods of analysis and weaknesses of tyre dust analysis procedures applied to the atmosphere.

Tracer/substance analysed	Method of analysis	Weaknesses
Natural and synthetic rubber/volatile pyrolysis products	Pyrolysis/GC	<ul style="list-style-type: none"> • Lack of definite specificity • Dependence upon rubber formulation
Hydrogenated resin acids	Solvent extraction GC-MS	<ul style="list-style-type: none"> • Variable abundance in tyres • Potential for evaporation, water leaching and photo-oxidation
Benzothiazole derivatives	Solvent extraction GC-MS	<ul style="list-style-type: none"> • Variable abundance in tyres • Potential for evaporation, water leaching and photo-oxidation • Low concentrations • Lack of definite specificity
Organic zinc	Solvent extraction Acid digestion Atomic absorption or ICPMS	<ul style="list-style-type: none"> • Variable abundance in tyres • Variable extraction efficiency • Lack of specificity
Inorganic zinc	Acid digestion Atomic absorption or ICPMS	<ul style="list-style-type: none"> • Low specificity • Need to subtract background

surface materials contain tyre rubber crumbs, this is quite likely, but will potentially affect all methods using a tracer for the rubber. However, Rauert et al. (2021) show that the assumptions inherent in the method concerning consistent tyre rubber composition may not be borne out in practice, and could potentially lead to large errors. This may not however be an insurmountable problem. There is an analogy in brake wear particle tracers. Hulskotte et al. (2014) have shown that brake pads of different brands and from different vehicles have a highly variable composition. Hence no single pad can be taken as representative of the entire vehicle fleet. However, in electing to use Ba as a brake wear tracer, Gietl et al. (2010) took the view that collecting an air sample over hours or days would average across the entire vehicle fleet at that location, and hence an average value of the Ba mass to the brake wear particle mass could be estimated, and was used subsequently by Harrison et al. (2012) to estimate brake wear particle mass on the same road. This is clearly an approximation, and may fail in a location where the vehicle fleet composition differs appreciably from that used to establish the “fleet average” value. Indeed, Rodland et al. (2022) recommend using locally specific traffic data to inform the interpretation of pyrolysis product information. There is clearly a need to investigate more widely the range of tyre rubber composition and the associated release of pyrolysis products, and to consider whether a fleet average, widely representative of trafficked locations can be identified. Similar considerations apply to the hydrogenated resin acids recommended by Kumata et al. (2011), and benzothiazole derivatives used in several studies. Their specificity to tyre rubber needs to be established, as well as their range of concentrations across different brands and styles of tyre. Without this, their use as a quantitative tracer will be very limited. One interesting possibility suggested by Rodland et al. (2022) is use of a Monte Carlo approach using different tracer abundances to generate a range of possible concentrations, which could be expressed as a Probability Density Function.

The main alternative to the pyrolysis method is based upon the use of Zn as a tracer. In this case, there are a number of studies which show a very consistent picture of Zn comprising a rather constant percentage of tyre tread mass. On the negative side, there are many other sources of Zn in the atmosphere, and estimations of tyre rubber based solely upon a measurement of airborne Zn are likely to be a significant over-estimate due to other source contributions. The only way to correct for this is to measure at both roadside and nearby urban background, and to estimate

the highway contribution by difference. Measurements of the particle size distributions of the Zn can provide useful confirmatory evidence (Harrison et al., 2012). There still remains an unresolved problem of the presence of Zn in brake pads, and how to correct for this. Ba concentrations could provide the basis for such a correction, if a fleet average Zn/Ba ratio for brake wear particles were known, but there are problems in obtaining this as it would require atmospheric measurements of brake wear in the absence of tyre wear.

Organic Zn has not been widely tested as a tracer, and raises questions of both specificity and constancy of composition, neither of which has been addressed adequately. Organic compounds of Zn are used as lubricating oil additives, and their presence in the atmosphere has not been investigated. It seems likely that they will in part be emitted uncombusted, particularly during cold engine conditions, and will also leak onto the road surface, from which they can be resuspended in road dust. This potential interference needs to be investigated, as well as the extraction efficiency and constancy of concentration across different brands and types of tyre.

There are also other important considerations. The organic tracers, benzothiazoles and hydrogenated resin acids, are semi-volatile, meaning that they partition actively between the particulate and vapour phases. If a significant proportion exists as vapour, this should also be sampled and analysed as it will need to be accounted for when the tracer mass is used to estimate an emitted concentration of tyre dust. If it is appreciably reactive in the atmosphere, it may be reduced in concentration by chemical loss, hence introducing error. This point was investigated by Kumata et al. (2002) in respect of the hydrogenated resin acids. A further issue is that of analytical detection limits. These will depend upon sample size (such as air volume sampled), tracer loading and specific instrumentation, but may prove limiting in some applications. For a tyre tread concentration in air of $1 \mu\text{g}/\text{m}^3$, if the Zn content is 1%, the airborne concentration of Zn will be only $10 \text{ ng}/\text{m}^3$. This is demanding of good laboratory practice, clean reagents and a sensitive analytical endpoint, but is well within the range typically measured in the atmosphere. However, organic Zn accounts for only about 16% of Zn in tyre tread (Fauser et al., 1999), so substantially larger air samples would be required. Some of the organic tracers are present at only part per million concentrations in the tyre tread (e.g. the sum of 7 benzothiazoles average $99 \mu\text{g}/\text{g}$ in Zhang et al., 2018), and hence exist in air at sub- ng/m^3 concentrations, requiring either large air samples or very sensitive instrumentation. Much the same considerations apply to the pyrolysis methods due to typically small sample sizes, and hence mass of material. Rodland et al. (2022) estimate limits of quantification of around 1–5 μg of styrene butadiene rubber and styrene butadiene styrene (a component of polymer modified bitumen used in road surfacing), which should allow analysis in a few tens of cubic metres of air, which can be collected in a few hours. Much larger sampling volumes/times are likely to be needed when organic tracers are used.

3. Recommendations

It is challenging to make research recommendations, as so much needs to be done. A key requirement is to establish the compositional diversity of tyres with respect to the various tracers. This work needs to take into account factors such as the differing rubber formulations in summer and winter tyres used in some parts of the world. Where possible, fleet average composition needs to be established to provide a sound basis for quantification, although this may have limited geographic relevance. Ideally this should include supplementary data such as Zn/Ba ratios in brake pads so that corrections for this as a source of Zn can be made. Sources other than tyre rubber of the potential tracers need to be studied in order to understand any challenges to specificity. Typical analytical detection limits are needed in order to specify the size of air samples needed for reliable quantification and are not always well specified in the literature. For the organic tracers, there are also pertinent questions concerning partitioning to vapour, and

chemical breakdown which need to be addressed.

There are also important questions regarding calibration. It is difficult to generate tyre tread particles of appropriate sizes in the laboratory. Many studies have used substantial chunks of tyre, which ignores the possibility that some properties such as extraction efficiencies or pyrolysis products may show a particle size dependence. There is a need for standard materials representative of the atmosphere to allow confident calibration, as well as traceability to ensure comparability between laboratories. Milling of cryogenically hardened tyre tread samples has been used, as have abrasion methods to generate fine particle standards. These need to be checked against one another, and any particle size-dependencies of actual or apparent composition identified.

Only when such questions have been addressed in detail will it be possible to quantify tyre dust in the atmosphere with confidence.

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

No data was used for the research described in the article.

References

- Allen, J.O., Alexandrova, O., Kaloush, K.E., 2006. Tire Wear Emissions for Asphalt Rubber and Portland Cement Concrete Pavement Surfaces. Arizona Department of Transportation. Contract KR-04-0720-TRN, Final Report. <https://azdot.gov/sites/default/files/2019/05/tire-wear-emissions-for-asphalt-rubber-portland-cement-concrete-April2006.pdf>.
- Amato, F., Cassee, F.R., Denier van der Gon, H.A.C., Gehrig, R., Gustafsson, M., Hafner, W., Harrison, R.M., Jozwicka, M., Kelly, F.J., Moreno, T., Prevot, A.S.H., Schaap, M., Sunyer, J., Querol, X., 2014. Urban air quality: the challenge of traffic non-exhaust emissions. *J. Hazard Mater.* 275, 31–36.
- AQEG, 2019. Non-Exhaust Emissions from Road Traffic. Air Quality Expert Group, Defra, London. https://uk-air.defra.gov.uk/assets/documents/reports/cat09/1907101151_20190709_Non_Exhaust_Emissions_typeset_Final.pdf.
- Baensch-Baltruschat, B., Kocher, B., Stock, F., Reifferscheid, G., 2020. Tyre and road wear particles (TRWP) - a review of generation, properties, emissions, human health risk, ecotoxicity, and fate in the environment. *Sci. Total Environ.* 733, 137823.
- Beddows, D.C.S., Harrison, R.M., 2021. PM_{10} and $\text{PM}_{2.5}$ emission factors for non-exhaust particles from road vehicles: dependence upon vehicle mass and implications for battery electric vehicles. *Atmos. Environ.* 244, 117886.
- Boulter, P.G., 2005. A Review of Emission Factors and Models for Road Vehicle Non-exhaust Particulate Matter. TRL Report PPR065. <https://trl.co.uk/sites/default/files/PPR065.pdf>.
- Cadle, S.H., Williams, R.L., 1979. Gas and particle emissions from automobile tires in laboratory and field studies. *Rubber Chem. Technol.* 52, 146e158.
- Cardina, J.A., 1974. Particle size determination of tire tread rubber in atmospheric dusts. *Rubber Chem. Technol.* 47, 271e283.
- Cardina, J.A., 1973. The determination of rubber in atmospheric dusts. *Rubber Chem. Technol.* 46, 232–241.
- Cohen, A.J., Brauer, M., Burnett, R., Anderson, H.R., Frostad, J., Estep, K., Balakrishnan, K., Brunekreef, B., Dandona, L., Dandon, A. R., Feigin, V., Freedman, G., Hubbell, B., Jobling, A., Kan, H., Knibbs, L., Liu, Y., Martin, R., Morawska, L., Pope III, C.A., Shin, H., Straif, K., Shaddick, G., Thomas, M., van Dingenen, R., van Donkelaar, A., Vos, T., Murray, C.J.L., Forouzanfar, M.H., 2017. Estimates and 25-year trends of the global burden of disease attributable to ambient air pollution: an analysis of data from the Global Burden of Diseases Study 2015. *Lancet* 389, 1907–1918.
- Dall'Osto, M., Beddows, D.C.S., Gietl, J.K., Olatunbosun, O.A., Yang, X., Harrison, R.M., 2014. Characteristics of tyre dust in polluted air: studies by single particle mass spectrometry (ATOFMS). *Atmos. Environ.* 94, 224–230.
- Dong, S., Ochoa Gonzalez, R., Harrison, R.M., Green, D., North, R., Fowler, G., Weiss, D., 2017. Isotopic signatures suggest important contributions from recycled gasoline, road dust and non-exhaust traffic sources for copper, zinc and lead in PM_{10} in London, United Kingdom. *Atmos. Environ.* 165, 88–98.
- Fauser, P., Tjell, J.C., Mosbaek, H., Pilegaard, K., 2002. Tire-tread and bitumen particle concentrations in aerosol and soil samples. *Petrol. Sci. Technol.* 20, 127–141.
- Fauser, P., Tjell, J.C., Mosbaek, H., Pilegaard, K., 1999. Quantification of tire-tread particles using extractable organic zinc as tracer. *Rubber Chem. Technol.* 72, 969–977.
- Fomba, K.W., van Pinxteren, D., Müller, K., Spindler, G., Herrmann, H., 2018. Assessment of trace metal levels in size-resolved particulate matter in the area of Leipzig. *Atmos. Environ.* 176, 60–70.

- Gehrig, R., Zeyer, K., Bukowiecki, N., Lienemann, P., Poulikakos, L.D., Furger, M., Buchmann, B., 2010. Mobile load simulators: a tool to distinguish between the emissions due to abrasion and resuspension of PM₁₀ from road surfaces. *Atmos. Environ.* 44, 4937–4943.
- Gietl, J.K., Lawrence, R., Thorpe, A.J., Harrison, R.M., 2010. Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road. *Atmos. Environ.* 44, 141–146.
- Grigoratos, T., Gustafsson, M., Eriksson, O., Martini, G., 2018. Experimental investigation of tread wear and particle emission from tyres with different treadwear marking. *Atmos. Environ.* 182, 200–212.
- Harrison, R.M., Vu, T.V., Jafar, H., Shi, Z., 2021a. More mileage in reducing urban air pollution from road traffic. *Environ. Int.* 149, 106329.
- Harrison, R.M., Allan, J., Carruthers, D., Heal, M.R., Lewis, A.C., Marner, B., Murrells, T., Williams, A., 2021b. Non-exhaust vehicle emissions of particulate matter and VOC from road traffic: a Review. *Atmos. Environ.* 262, 118592.
- Harrison, R.M., Jones, A., Gietl, J., Yin, J., Green, D., 2012. Estimation of the contribution of brake dust, tire wear and resuspension to non-exhaust traffic particles derived from atmospheric measurements. *Environ. Sci. Technol.* 46, 6523–6529.
- Hicks, W., Beevers, S., Tremper, A.H., Stewart, G., Priestman, M., Kelly, F.J., Lanoisellé, M., Lowry, D., Green, D.C., 2021. Quantification of non-exhaust particulate matter traffic emissions and the impact of COVID-19 Lockdown at London Marylebone Road. *Atmosphere* 12, 190.
- Hjortenkrans, D.T., Bergback, B.G., Haggerud, A., 2007. Metal Emissions from brake linings and tires: case studies of Stockholm, Sweden 1995/1998 and 2005. *Environ. Sci. Technol.* 41, 5224–5230.
- Hulskotte, J.H.J., Roskam, G.D., Denier van der Gon, H.A.C., 2014. Elemental composition of current automotive braking materials and derived air emission factors. *Atmos. Environ.* 99, 436–445.
- ISO, 2017. **Ambient Air - Determination of the Mass Concentration of Tire and Road Wear Particles (TRWP) - Pyrolysis- GC-MS Method.** Technical Report ISO/TS 20593: 2017(E). <https://www.iso.org/standard/68470.html>.
- Jeong, H., 2022. Toxic metal concentrations and Cu-Zn-Pb isotopic compositions in tires. *J. Anal. Sci. Technol.* 13, 2.
- Kennedy, P., Gadd, J., Moncrieff, I., 2002. Emission Factors for Contaminants Released by Motor Vehicles in New Zealand. Ministry of Transport, New Zealand.
- Kim, M.G., Yagawa, K., Inoue, H., Lee, Y.K., Shirai, T., 1990. Measurement of tire tread in urban air by pyrolysis-gas chromatography with flame photometric detection. *Atmos. Environ.* 24, 1417–1422.
- Klockner, P., Teemtsma, T., Eisentraut, P., Braun, U., Rujl, A.S., Wagner, S., 2019. Tire and road wear particles in road environment – quantification and assessment of particle dynamics by Zn determination after density separation. *Chemosphere* 222, 714–721.
- Kreider, M.L., Panko, J.M., McAtee, B.L., Sweet, L., Finley, B.L., 2010. Physical and chemical characterization of tire-related particles: comparison of particles generated using different methodologies. *Sci. Total Environ.* 408, 652–659.
- Kumata, H., Mori, M., Takahashi, S., Takamiya, S., Tsuzuki, M., Uchida, T., Fujiwara, K., 2011. Evaluation of hydrogenated resin acids as molecular markers for tire-wear debris in urban environments. *Environ. Sci. Technol.* 45, 9990–9997.
- Kumata, H., Yamada, J., Masuda, K., Takada, H., Sato, Y., Sakurai, T., Fujiwara, K., 2002. Benzothiazolamines as tire-derived molecular markers: sorptive behaviour in street runoff and application to source apportioning. *Environ. Sci. Technol.* 36, 702–708.
- Kwak, J.H., Kim, H., Lee, J., Lee, S., 2013. Characterization of non-exhaust coarse and fine particles from on-road driving and laboratory measurements. *Sci. Total Environ.* 458–460, 273–282.
- Larnesjo, P., 1999. Applications of Source Receptor Models Using Air Pollution Data in Stockholm. Undergraduate thesis performed at the Department of Analytical Chemistry in co-operation with the Institute of Applied Environmental Research, Air Pollution Laboratory, Stockholm University. https://www.slb.nu/slb/rapporter/pdf8/uni1999_Ex4.pdf.
- Lee, Y.-K., Kim, M.G., Whang, K.-J., 1989. Simultaneous determination of natural and styrene-butadiene rubber tire tread particles in atmospheric dusts by pyrolysis-gas chromatography. *J. Anal. Appl. Pyrolysis* 16, 49–55.
- Liao, C., Kim, U.-J., Kannan, K., 2018. A review of environmental occurrence, fate, exposure, and toxicity of benzothiazoles. *Environ. Sci. Technol.* 52, 5007–5026.
- Matthaios, V.N., Lawrence, J., Martins, M.A.G., Ferguson, S.T., Wolfson, J.M., Harrison, R.M., Koutrakis, P., 2022. Quantifying factors affecting contributions of roadway exhaust and non-exhaust emissions to ambient coarse and fine particles. *Sci. Total Environ.* 835, 155368.
- Panko, J., Kreider, M., Unice, K., 2018. In: Amato, F. (Ed.), Chapter 7 - Review of Tire Wear Emissions: A Review of Tire Emission Measurement Studies: Identification of Gaps and Future Needs. Non-exhaust Emissions. Academic Press, ISBN 9780128117705, pp. 147–160.
- Panko, J.M., Hitchcock, K.M., Fuller, G.W., Green, D., 2019. Evaluation of tire wear contribution to PM_{2.5} in urban environments. *Atmosphere* 10, 99.
- Panko, J.M., Chu, J., Kreider, M.L., Unice, K.M., 2013. Measurement of airborne concentrations of tire and road wearparticles in urban and rural areas of France, Japan, and the United States. *Atmos. Environ.* 72, 192–199.
- Pant, P., Harrison, R.M., 2013. Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: a review. *Atmos. Environ.* 77, 78–97.
- Park, I., Kim, H., Lee, S., 2018. Characteristics of tire wear particles generated in a laboratory simulation of tire/road contact conditions. *J. Aerosol Sci.* 124, 30–40.
- Piscitello, A., Bianco, C., Casasso, A., Sethi, R., 2021. Non-exhaust traffic emissions: sources, characterization, and mitigation measures. *Sci. Total Environ.* 766, 144440.
- Rahimi, M., Bortoluzzi, D., Wahlström, J., 2021. Input parameters for airborne brake wear emission simulations: a comprehensive review. *Atmosphere* 12, 871.
- Rauert, C., Rodland, E.S., Okoffo, E.D., Reid, M.J., Meland, S., Thomas, K.V., 2021. Challenges with quantifying tire road wear particles: recognizing the need for further refinement of the ISO technical specification. *Environ. Sci. Technol. Lett.* 8, 231–236.
- Reddy, C., Quinn, J.G., 1997. Environmental chemistry of benzothiazoles derived from rubber. *Environ. Sci. Technol.* 31, 2847–2853.
- Rodland, E.S., Samanipour, S., Rauert, C., Okoffo, E.D., Reid, M.J., Heier, L.S., Lind, O.C., Thomas, K.V., Meland, S., 2022. A novel method for the quantification of tire and polymer-modified bitumen particles in environmental samples by pyrolysis gas chromatography mass spectroscopy. *J. Hazard Mater.* 423, 127092.
- Sadiktsis, I., Bergvall, C., Johansson, C., Westerholm, R., 2012. Automobile tires - a potential source of highly carcinogenic dibenzopyrenes to the environment. *Environ. Sci. Technol.* 46, 3326–3334.
- Sakamoto, K., Hirota, Y., Nezu, T., Okuyama, M., 1999. Contribution of rubber dust generated from tire-dust by travelling of heavy-duty and passenger vehicles on the road to atmospheric particulate matter. *J. Aerosol Res.* 14, 242e247.
- Schauer, J.J., Fraser, M.P., Cass, G.R., Simoneit, B.R.T., 2002. Source reconciliation of atmospheric gas-phase and particle-phase pollutants during a severe photochemical smog episode. *Environ. Sci. Technol.* 36, 3806–3814.
- Sommer, F., Dietze, V., Baum, A., Sauer, J., Gilge, S., Maschowski, C., Gieré, R., 2018. Tire abrasion as a major source of microplastics in the environment. *Aerosol Air Qual. Res.* 18, 2014–2028.
- Thorpe, A., Harrison, R.M., 2008. Sources and properties of non-exhaust particulate matter from road traffic: a Review. *Sci. Total Environ.* 400, 270–282.
- Tonegawa, Y., Sasaki, S., 2021. Development of tire-wear particle emission measurements for passenger vehicles. *Environ. Sci. Technol.* 7, 56–62.
- Toyosawa, S., Umezawa, Y., Ikoma, Y., Kameyama, Y., 1977. Analysis of tire tread rubber in airborne particulate matter by pyrolysis-gas chromatography. *Anal. Chem. Japan (Bunseki Kagaku)* 26.
- Unice, K.M., Kreider, M.L., Panko, J.M., 2012. Use of a deuterated internal standard with pyrolysis-GC/MS dimeric marker analysis to quantify tire tread particles in the environment. *Int. J. Environ. Res. Publ. Health* 9, 4033–4055.
- Valle, S., Panero, M.A., Shor, L., 2007. **Pollution Prevention and Management Strategies for Polycyclic Aromatic Hydrocarbons in the New York/New Jersey Harbour.** New York Academy of Sciences, New York. https://austintexas.gov/sites/default/files/files/Watershed/coaltar/nyas_pah_harbor_study_final.pdf.
- Vlasov, D., Kosheleva, N., Kasimov, N., 2021. Spatial distribution and sources of potentially toxic elements in road dust and its PM₁₀ fraction of Moscow megacity. *Sci. Total Environ.* 761, 143267.
- Wagner, S., Huffer, T., Klockner, P., Wehrhahn, M., Hofmann, T., Reemtsma, T., 2018. Tire wear particles in the aquatic environment - a review on generation, analysis, occurrence, fate and effects. *Water Res.* 139, 83–100.
- Weckwerth, G., 2001. Verification of traffic emitted aerosol components in the ambient air of Cologne (Germany). *Atmos. Environ.* 35, 5525–5536.
- WHO, 2021. **Global Air Quality Guidelines. Particulate Matter (PM_{2.5} and PM₁₀), Ozone, Nitrogen Dioxide, Sulfur Dioxide and Carbon Monoxide.** World Health Organization.
- Woo, S.-H., Jang, H., Mun, S.-H., Lim, Y., Lee, S., 2022. Effect of treadwear grade on the generation of tire PM emissions in laboratory and real-world driving conditions. *Sci. Total Environ.* 838, 156548.
- Zhang, X., Chen, P., Liu, F., 2020a. Review of tires wear particles emission research status. *IOP Conf. Ser. Earth Environ. Sci.* 555, 012062.
- Zhang, J., Peng, J., Song, C., Ma, C., Men, Z., Wu, J., Wu, L., Wang, T., Zhang, X., Tao, S., Gao, S., Hopke, P.K., Mao, H., 2020b. Vehicular non-exhaust particulate emissions in Chinese megacities: source profiles, real-world emission factors, and inventories. *Environ. Pollut.* 266, 115268.
- Zhang, J., Zhang, X., Wu, L., Wang, T., Zhao, J., Zhang, Y., Men, Z., Mao, H., 2018. Occurrence of benzothiazole and its derivatives in tire wear, road dust, and roadside soil. *Chemosphere* 201, 310–317.