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Multi-element analysis of tyre rubber for metal tracers

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A B S T R A C T

The purpose of this study was to identify a characteristic elemental tyre fingerprint that can be utilised in atmospheric source apportionment calculations. Currently zinc is widely used as a single element tracer to quantify tyre wear, however several authors have highlighted issues with this approach. To overcome this, tyre rubber tread was digested and has been analysed for 25 elements by ICP-MS to generate a multielement profile. Additionally, to estimate the percentage of the tyre made up of inert fillers, thermogravimetric analysis was performed on a subset. Comparisons were made between passenger car and heavy goods vehicle tyre composition, and a subset of tyres had both tread and sidewall sampled for further comparison. 19 of the 25 elements were detected in the analysis. The mean mass fraction of zinc detected was 11.17 g/kg, consistent with previous estimates of 1% of the tyre mass. Aluminium, iron, and magnesium were found to be the next most abundant elements. Only one source profile for tyre wear exists in both the US and EU air pollution species profile databases, highlighting the need for more recent data with better coverage of tyre makes and models. This study provides data on new tyres which are currently operating on-road in Europe and is therefore relevant for ongoing atmospheric studies assessing the levels of tyre wear particles in urban areas.

1. Introduction

Tyre rubber has a chemically complex makeup designed to maximise its performance and reliability. It is comprised primarily of rubbers including natural rubber (NR), polyisoprene rubber, polybutadiene rubber (PB), and styrene-butadiene rubber (SBR). Other ingredients include vulcanisation agents and accelerators, fillers, and antioxidants (Sommer et al., 2018; Williams and Besler, 1995). Understanding the chemical and elemental composition of tyre rubber is a challenge, as the composition varies due to the specific make, model and purpose of the tyre and the highly proprietary nature of tyre formulations (Hicks et al., 2021).

Car tyres typically contain around 75% SBR, 10%-25% PB and 0–15% NR, as summarised in Table 1. In contrast, heavy goods vehicle (HGV) tyres typically contain 10% SBR, 10% PB and around 80% NR (Camatini et al., 2001). The difference in composition is due to the different required service conditions (higher load, longer service life, different lateral forces) that truck tyres must endure (Barbin, 2018; Lepine et al., 2022). Sulphur, selenium, and tellurium are used as vulcanisation agents and represent approximately 1–2% of the mass of both HGV and car tyres (Harrison et al., 2012; Hicks et al., 2021). These compounds are added to elastomers in 3–4 parts per hundred parts of rubber (Camatini et al., 2001; Grigoratos and Martini, 2014). Pb, Mg, Zn, some sulphur compounds, and calcium oxides are added as vulcanisation accelerators. Several metals are used as catalysts to convert butadiene into polybutadiene rubber, and commonly include Nd, Co, Ni, Ti, and Li (International Institute of Synthetic Rubber Products Inc, 2012; Rackaitis and Graves, 2017). Other trace metals may be detected in tyre rubber as contaminants of crude oil derived synthetic rubbers (Grigoratos and Martini, 2014; Kocher et al., 2010; Kreider et al., 2010).

Abbreviations: ICP-MS, Inductively coupled plasma mass spectrometry; NR, Natural rubber; SBR, Styrene-butadiene rubber; PB, Polybutadiene rubber; HGV, Heavy goods vehicle; PAH, Polycyclic aromatic hydrocarbon; TGA, Thermogravimetric analysis; sPLS-DA, Sparse partial least squares-discriminant analysis; NTP, National Toxicology Program; PM, Particulate Matter.

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Table 1
Generic tyre compound examples, in parts per hundred rubber (phr).

	Car Tread (phr)	Heavy duty Sidewall (phr)
Natural Rubber		60
SBR	75	
Polybutadiene	25	40
Carbon black	75	60
Zinc oxide	3.0	3.0
Process oil	40	5.0
Sulphur	2.0	3.0

adapted from Barbin, 2018

Tyre rubber, either stored as end-of-life tyres or recycled into rubber products has been linked to metal and polycyclic aromatic hydrocarbons (PAH) runoff into the environment, so an understanding of the metal content of tyres is vitally important to monitor and quantify environmental contributions from tyre wear emissions (Adachi and Tainosho, 2004; Legret and Pagotto, 1999; Mantecca et al., 2009; Rogge et al., 1993; Sadiq et al., 1989; Sieber et al., 2020).

Approximately 1.3 million tonnes of tyre wear are released into the environment in Europe each year (Wagner et al., 2018). Previous work has identified several potential tracer elements that have been proposed to distinguish and quantify tyre rubber particles in complex environmental particulate matter (PM) samples. Elements identified previously include As, Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mo, Na, Ni, Pb, S, Sb, Se, Si, Te, Ti, and V, with Zn being the most frequently used (Grigoratos and Martini, 2014; Klöckner et al., 2019; Kocher et al., 2010). However, no consensus has been reached on which of these metals are the most suitable or reliable tracers as there are sources of all these elements in the environment (Fussell et al., 2022; Grigoratos and Martini, 2014; Klöckner et al., 2019). Without a tracer specific to tyres, there is a fundamental gap in knowledge required by source apportionment, health, and environmental sectors. Authors such as Klöckner et al., (2019) suggest that using a single element marker for tyre wear may only be suitable if a method for removing the environmental matrix components can be developed. Hicks et al. (2021) used zinc as a single element tracer with a scaling factor of 50 to quantify tyre rubber, and with this scaling factor found atmospheric tyre wear concentrations in London to be approximately 1 $\mu g/m^3$. Tyre wear emissions are projected to increase steadily over the next ten years. According to UK data submitted to the United Nations Convention on Long-range Transboundary Air Pollution, non-exhaust emissions (combined brake, tyre and resuspended road wear) are expected to rise to nine kilotonnes by 2030, while exhaust emissions continue to decrease (Convention on Long-range Transboundary Air Pollution, n.d.). To address this, we present a comprehensive analysis of tyre rubber to identify tyre wear tracers to fill the knowledge gap. Elemental tracers have been selected, despite organic alternatives being available (Goßmann et al., 2021), as it allows for the use of x-ray fluorescence detectors, that are already used in the air quality monitoring network (Hicks et al., 2021). Scanning electron microscopy with energy dispersive X-ray spectroscopy methods have been developed and validated with machine learning to identify tyre wear particles based on elemental composition, however, these too are not able to integrate with already existing metal infrastructure (Järlskog et al., 2022a, 2022b).

2. Materials and methods

2.1. Tyre rubber samples

Samples of tyre tread and sidewall were collected from car and HGVs. Tyre tread samples were collected as tyre vent spews, which are the small hair-like protrusions found on the tyre surface as air escapes the mould during tyre moulding. Vent spews were removed from the tyre tread of new, undriven tyres using a clean ceramic blade and stored prior to analysis. Tyre sidewall samples were also vent spews, but taken from the side of the tyre surface.

Samples from 60 car tyres were provided by Emissions Analytics (High Wycombe, United Kingdom). 22 tyres had both their tread and sidewall sampled for comparison. A further 3 tyres had samples of the tread taken using a ceramic knife in-house to give a total of 63 car tread samples, and 22 car sidewall samples.

12 HGV tyres were sampled at the University of Witswatersrand as part of a Centre for Sustainable Road Freight collaboration. Nine HGV samples were tyre vent spews, with the remainder being shavings taken off of the tyre tread surface. An additional HGV tyre was sampled in house. All samples were cut to the correct mass for digestion using a ceramic knife, if required. A full list of tyres sampled is available as Table A1, and a representative image of the samples as Figure B1.

2.2. Digestion method

Tyre samples of 5–50 mg were cut into small (~1 mm) sized pieces and digested to liberate the elements for analysis as soluble nitrates from the rubber using a MARS 6 Microwave Digestion System (CEM, Buckingham, UK) with iWave temperature control and MARSXpress vessels. 9 ml of concentrated (70%) nitric acid suitable for trace element analysis (225711, 99.9999% impurity free, Sigma-Aldrich, Gillingham, UK) and 1 ml of 30% hydrogen peroxide suitable for trace element analysis (95321, Sigma-Aldrich, Gillingham, UK) were used as digestion mixture, following a method recommended by the manufacturer. In brief, samples were digested at 220 °C for 20 min. After digestion, samples were made up to 50 ml in a volumetric flask using inductively coupled plasma mass spectrometry (ICP-MS) grade water and diluted for analysis as appropriate. A full digestion method is available as Appendix B.1.

2.3. ICP-MS analysis

Analyses were conducted using an inductively coupled plasma mass spectrometer (Perkin Elmer Nexion 350D quadrupole-based ICP-MS). Calibration standards for the 25 elements of interest were decided based on literature review and prepared as external calibration solutions using a commercially available standard (109487, Merck Millipore, Gillingham, United Kingdom), two single element high purity standards (50334 and 18021, Sigma-Aldrich, Gillingham, United Kingdom) and a custom high purity standard (Agilent Technologies, Cheadle, United Kingdom). The ICP-MS internal standards were ^{103}Rh, ^{115}In and ^{185}Re, and an independently prepared quality control standard (SPS-SW2, LGC Standards, United Kingdom) was analysed 3–6 times throughout the run to ensure calibration precision. Raw intensities were internal standard corrected and blank subtracted.

2.4. Uncertainty analysis

An uncertainty analysis for the ICP-MS measurement, including the digestion method, was performed by the National Physical Laboratory. Measurement equations were derived for the method (Appendix C), and from these an uncertainty budget was developed. The uncertainty budget and associated uncertainty for each step of the analysis is available in Appendix D. The measurement uncertainty was calculated using an approach adapted from Brown et al., (2010) and derived in accordance with the Guide to the expression of uncertainty in measurement (Joint Committee for Guides in Metrology, 2008). The result of the uncertainty calculation, which uses example data taken from a typical tyre analysis, is a relative expanded uncertainty for the method of 12.6%. The expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor, $k = 2$, providing a coverage probability of approximately 95%.

2.5. Thermogravimetric analysis

The concentration of rubber polymers, carbon black and inert material was estimated in car tyre rubber tread using thermogravimetric analysis (TGA). Five tyres were selected at random, three from the Performance/High End manufactueres, and two from the "mid-range" manufacturers. The TGA method was adapted from ASTM Standard Test Method D6370 − 99. In brief, 5 mg of tyre vent spew was cut into 1 mm lengths for analysis. Samples were heated from room temperature to 600 °C in a nitrogen atmosphere at 10 °C per minute to break down the organic components (rubber polymers, oils, plasticizers, and antioxidants). The atmosphere was then switched to air where the mass lost is due to carbon black. Any remaining mass (ash) is due to tyre fillers. If the tyre sample contains $CaCO_3$ or $Al(OH)_3(3H_2O)$, these will be lost during the heating cycle (ASTM International, 2019).

2.6. Statistical analysis

GraphPad Prism 9.4.0 was used to summarise and graph the data, including calculating means and standard deviations and perform statistical analyses. A Sparse Partial Least Squares Discriminant Analysis (sPLS-DA) was performed in RStudio (Version 2022.07.0 + 548) using MixOmics package (version 6.20.0) (Rohart et al., 2017). The sPLS-DA was tuned to optimise number of components, number of variables and prediction distance. Correlation analysis was also performed in RStudio, using Psych package to generate a correlation matrix.

3. Results

3.1. Metallic composition of tyre rubber

Results of car tread rubber analysis are summarised in Fig. 3-1, and Table E2. The combined results for car and HGV tyres are shown in Table E1. B, Cr, Mo, P, Tl, and W were all not detected above the limit of detection, calculated from 3*σ where σ is the standard deviation of the blanks. As expected, Zn is the most abundant element, followed by Al, Fe, Mg, Ti, Cu, and Ba. Table E2 compares the results of car and HGV tyre analysis with five key previous studies. Overall, the mean values are comparable to what has been reported in the literature (Kocher et al., 2010; Kreider et al., 2010), with a few exceptions (Kennedy and Gadd, 2003; National Toxicology Program, 2019). Al, Fe and Mg levels were all detected at much higher concentrations compared to Kennedy and Gadd's work in 2003, but where lower than results obtained by the National Toxicology Programme in 2019 (Kennedy and Gadd, 2003; National Toxicology Program, 2019). Al and Co concentrations agree well with the literature, except for the experiment conducted as part of the National Toxicology Program's Research Report (National Toxicology Program, 2019). This may be explained by the much larger sample size in this present study and by different digestion methods (although no details are provided by the NTP for comparison). Concentrations differ from the Kennedy and Gadd (2003) report commissioned for the New Zealand Ministry of Transport, for almost every element shared between the two experiments. Kennedy and Gadd (2003) and Kocher et al., (2010) use a dry ashing method to prepare their tyre samples for dissolution in acid, rather than using a microwave assisted method as other studies have done (Klöckner et al., 2019; Kreider et al., 2010; Kennedy and Gadd, 2003).

There were differences in abundance of elements in rubber tread between HGV and car tyres. Mn, Fe, Co, Rb, Sb, and Ba were all significantly ($p < 0.05$) increased in HGV tyres compared to car tyres, as shown in Fig. 3-2. Differences between truck and car tyres are relevant due to the different compositions the tyres have to cope with required service conditions (Barbin, 2018). Literature on specific manufacturing differences and in particular elemental composition of car compared to HGV tyres is scarce, however it is well understood that HGV tyres must be designed to withstand the higher loads and lateral forces that these tyres experience, and to maximise service life compared to cars (Lepine et al., 2022). In Kennedy and Gadd's (2003) study of tyre elemental composition two "truck" tyres were included, one from a light truck, the other from an HGV. While the authors conducted no statistical analysis of the differences between the two tyre types their data shows that Al,

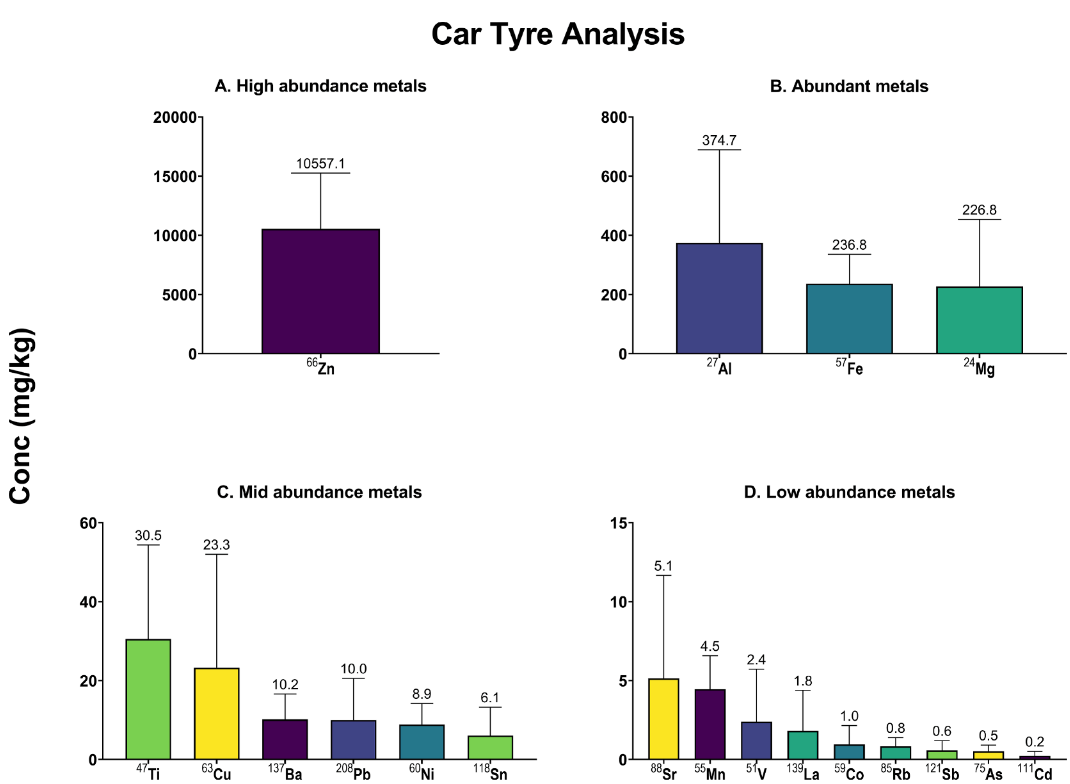

Fig. 3-1. Summary of car tyre tread rubber analysis results, $N = 63$. The elements analysed are shown at the X-axis, and the mean concentration with standard deviation on the Y-axis (mg/kg of dry sample).

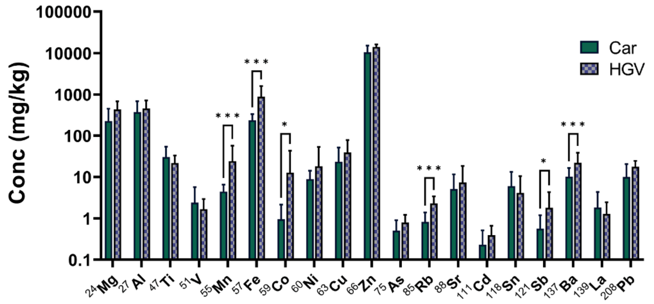

Fig. 3-2. Car (green, solid, $N = 63$) and HGV (grey, patterned, $N = 13$) tread rubber metal composition analysis. The elements analysed are shown at the X-axis and the mean concentration is on the Y-axis with standard deviation bars (mg/kg of dry sample). Significant differences between car and HGV composition were tested for using an unpaired *t*-test, with individual variance computed for each comparison using Holm-Šídák's multiple comparisons test (* $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Mn, Fe, Zn, and Pb were all enriched in truck/HGV tyres, but contrary to our results, they saw that Ba levels were reduced. Having data for both HGV and car tyres allows for a different source profile to be developed for each vehicle type. While there is no significant increase in Zn concentration, differences in Mn, Fe, Rb and Ba could be used to distinguish levels of tyre wear attributable to each vehicle.

3.2. Tread surface and Sidewall comparison

22 car tyres had both the tread surface and sidewall sampled to test if there were differences in the formulation between the sites and the results are shown in Fig. 3-3. Significant differences were observed in Mg, V, Ni, Zn, As, Rb, Sb, Ba, La and Pb concentrations. To the best of our knowledge, this is the first time that the elemental composition of tyre tread has been compared to sidewall. Tyre polymer composition is specifically tailored to the requirements for each part of the tyre. Tyre tread is designed to have "maximum resistance to abrasion, tear, cracking, chipping, heat build-up, and aging" according to Georgia and Mayeau (1963); while the sidewall composition is important for traction and handling influencing, along with inflation, radial and lateral stiffness (Ridha and Theves, 1994).

Table 1, adapted from Barbin (2018), summarises generic tyre rubber compositions, comparing additives to tread rubber vs sidewall rubber. A requirement for rubber with a higher tensile strength may explain the higher levels of zinc observed in sidewall rubber in this experiment

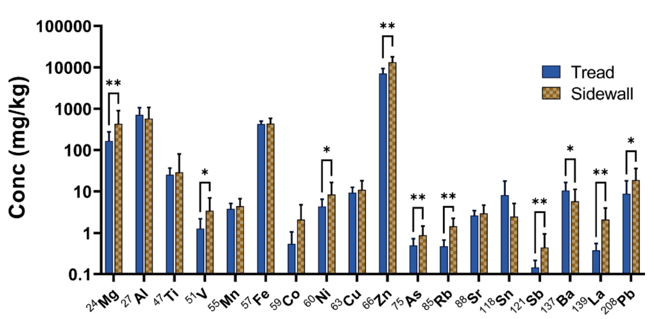

Fig. 3-3. Tread (blue, solid, $N = 22$) vs sidewall (brown, patterned, $N = 22$) metallic composition. The elements analysed are shown at the X-axis and the concentration is on the Y-axis with standard deviation (mg/kg of dry sample). Significant differences between the tread and sidewall composition were tested for using a Ratio paired *t*-test per row, with individual ranks computed for each comparison using Holm-Šídák's multiple comparisons test. (* $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Mostoni et al., 2019). Magnesium is also significantly enriched in sidewall rubber, which too may be explained using magnesium oxide (MgO) as vulcanisation cure activator, acid neutralising agent and crosslinker (Akrochem, n.d.; Roy et al., 2015).

3.3. sPLS-DA

A sparse partial least squares-discriminant analysis (sPLS-DA) was employed to distinguish manufacturers based on their elemental composition by reducing the number of variables, shown as Fig. 3-4. The sPLS-DA was tuned using MixOmics v6.20.0 to include four components, with 5, 6, 10 and 10 variables for each component respectively. The aim of the sPLS-DA analysis is to maximise the covariance between elemental composition and manufacture (Le Cao et al., 2019). A 3D representation of the sPLS-DA is included as Fig. F1, and the variable and contribution plots available as Fig. F2 A-C. The sPLS-DA shows poor separation of the datapoints on the score plot. From this we concluded that there was little variance in elemental composition between manufacturers included in this study. The manufacturers range from high-end, industrial leaders to budget manufacturers. The analysis shown here agrees with the PCA analysis performed by Sjödin et al. (2010) who also saw no grouping with the PCA performed on their data. In conjunction with this dataset, it is concluded that there is no statistical difference in manufacturers, thus making differentiation by manufacturer in ambient environments unsubstantiated due to the range each tyre manufacturer covers across both x-variants.

There was some separation of Manufacturer L, which was driven by Mg concentration based off the variable plot, shown in Fig. F2A. Manufacturer L tyres were found to have significantly ($p < 0.05$) higher magnesium concentrations than three of the manufacturers tested, Manufacturer H, Manufacturer M and Manufacturer Q as shown in Fig. 3-5. The notable exception is Manufacturer N, a budget brand manufactured in China that is not a subsidiary of Manufacturer L, who also had high levels of magnesium. Manufacturers with fewer than one tyre sampled were not included in the sPLS-DA but were included in Fig. 3-5 for illustration.

Magnesium is used both as a filler and as a curing agent for elastomers. The increased concentration of Mg may be the result of manufacturers L and N replacing carbon black or other fillers with magnesium (Akrochem, n.d.; Hebei Meishen Technology Co., Ltd, 2020).

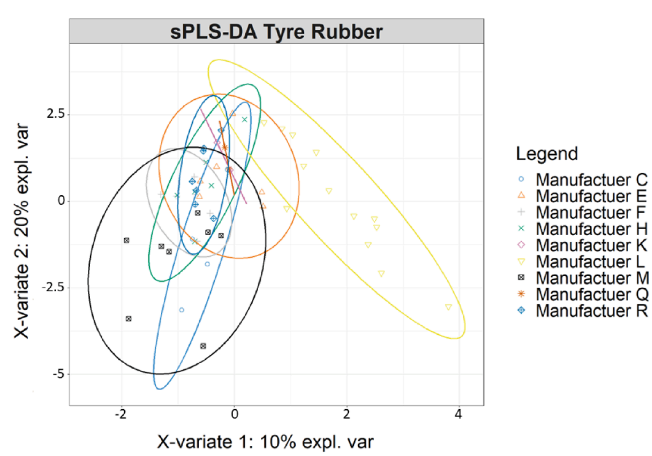

Fig. 3-4. sPLS-DA of tyre rubber samples. Manufacturers are grouped by symbol and circled in their respective colour. X-variate 1 explains 10% of the variance of the data, while 20% is explained by X-variate 2. Only manufacturers with more than one tyre included in the study were included in the sPLS-DA analysis.

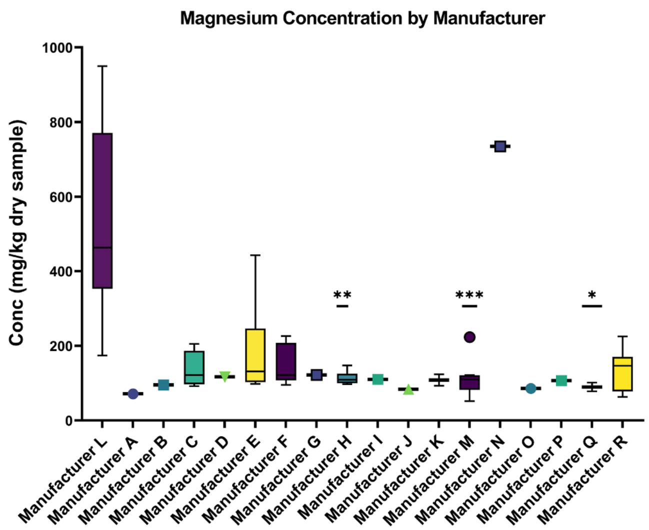

Fig. 3-5. Magnesium concentrations by manufacturer. Significant differences between Manufacturer L and other manufacturers are shown, and were determined via Kruskal-Wallis test with Dunn correction. ($*p \leq 0.05$, $**p \leq 0.01$, $***p \leq 0.001$).

3.4. Correlation analysis

To identify elements that may be suitable as tracers for tyre wear in complex PM samples, a Spearman's correlation analysis was performed for all elements using the results from the car tread rubber analysis. The results are shown as a *S*catter *PL*ot *O*f *M*atrices (SPLOM) diagram as Fig. 3-6. Correlation coefficients for each pair of elements are shown on the top right, with their associated *p*-value. Histograms and density plots are shown along with the element symbol along the diagonal. The bottom left portion of figure displays the bivariate scatter plots, with locally estimated scatterplot smoothing (LOESS) non-linear regression curves. Highly correlated pairs of elements were identified as potential tracer

Table 2
Spearman's Correlations and Mean Ratios.

Elements	Spearman's r	Mean Ratio
Ni:Cu	0.77	0.84
Zn:Sb	0.75	168,409
Fe:Mn	0.74	58.5
Cu:Sb	0.74	98.3
Cu:Sr	0.73	4.94
Zn:Ni	0.73	1375
Ni:Sb	0.73	115
Sb:La	0.69	0.63
Ni:La	0.68	13.5
Zn:Cu	0.64	1172

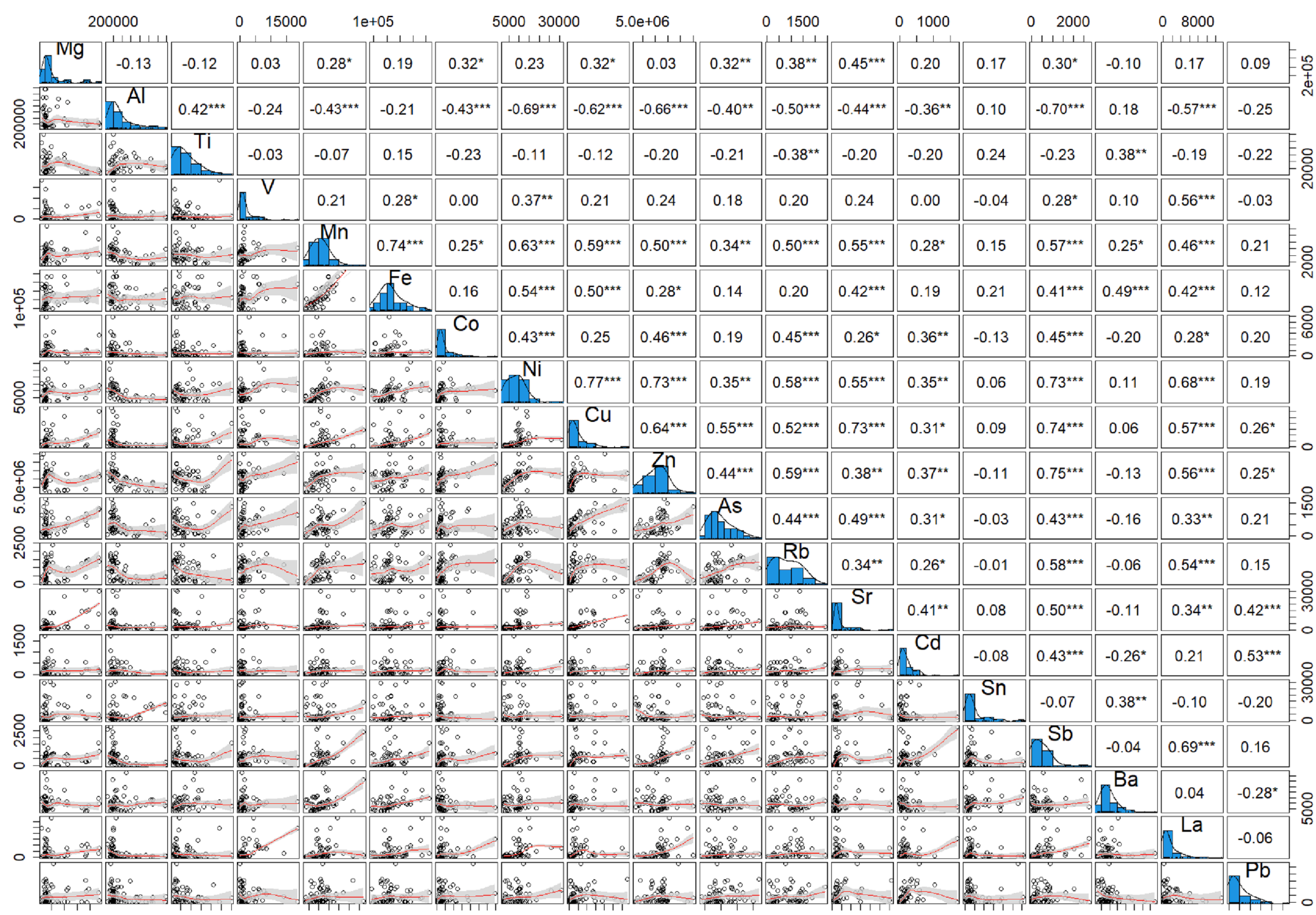

Fig. 3-6. Spearman's Correlation scatter plot matrix of metals found in car tread tyre rubber ($N = 63$ samples). Key: Spearman's correlation values for metals detected in tyre rubber with their associated *p*-value symbol ($*p \leq 0.05$, $**p \leq 0.01$, $***p \leq 0.001$) are shown on the top diagonal, histograms (blue) and kernel density estimation plots for data points are shown along the diagonal, and bivariate scatter plots with LOESS smoothed regression curves (red) are displayed on the bottom diagonal. Concentrations in ppb are displayed along the edge of the plot. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

elements and are summarised as Table 2. The most highly correlated pair was Ni and Cu, with a Spearman's r of 0.77 and mean ratio of 0.84. An ideal tracer would be correlated highly to Zn, as Zn is the most abundant element in tyres. Sb and Ni were the two highest correlations with Zn, with ratios of 168,409 and 1374.6, respectively. A correlation matrix for HGV tyre tread is included as Fig. G1.

Significant negative correlations to Al were also observed. Sb, Ni, and Zn were all inversely correlated with Al with r_s values equal to −0.70, −0.69 and −0.66 respectively. Kennedy and Gadd (2003) reported correlations between metals detected in tyre rubber, however they only reported positive correlations and summarised the correlation *p*-value rather than providing correlation coefficients. Aluminium powder has been shown to decrease vulcanisation time of thick rubber materials and lead to improvements in their longevity, which may explain the strong negative correlation with zinc – by incorporating aluminium you reduce the need for vulcanisation accelerators (Vinod et al., 2001).

Contrary to previous work, there was no strong correlation between zinc and cadmium ($r_s = 0.37$) shown for any of the analysed samples (David and Williams, 1975; Kennedy and Gadd, 2003). David and Williams (1975) stated that the low cadmium levels in their tyres was due to the efficacy of the zinc oxide purification process. In the nearly 50 years since the David and Williams study, Zn, S, and Cd refining has improved and this may contribute to low levels of cadmium being detected, and no strong correlation with zinc (Fthenakis, 2004). The ten highest Spearman's r values and associated mean ratios as summarised in Table 2.

3.5. Comparison of tyre composition and tyre Performance

Comparisons were made between elemental composition and tyre metadata (tyre width, aspect ratio, diameter, load opacity and max speed). The only finding was a non-significant increase in aluminium concentration as wet gripping improves from C to A, as shown in Fig. 3-7. One aluminium concentration was excluded as an outlier, being over two orders of magnitude higher than other samples. A 2001 patent by Sumitomo Rubber Ind Ltd claimed that increasing amounts of aluminium hydroxide added to polymer formulation improved wet grip performance (Kikuchi et al., 2001). A later patent by the same company, however, stated that this increased aluminium hydroxide reduced abrasion resistance, and this resulted in reduced mileage and a shorter tyre lifespan (Miyazaki, 2019). Despite the purported reduction in tyre lifespan, we observed a trend of increased aluminium concentration with improved wet grip rating, but no significant difference was found.

This finding demonstrates how certain chemical species are added to tyres to optimise their performance characteristics. Trends for other elements, in particular those associated with polymer catalysis, may not be as clearly seen due to there being several possible compounds that a manufacturer could include. For example, Nd, Co, Ni, Ti, and Li are all used as catalysts for the polymerisation of butadiene rubber (International Institute of Synthetic Rubber Products Inc, 2012, Rackaitis and Graves, 2017).

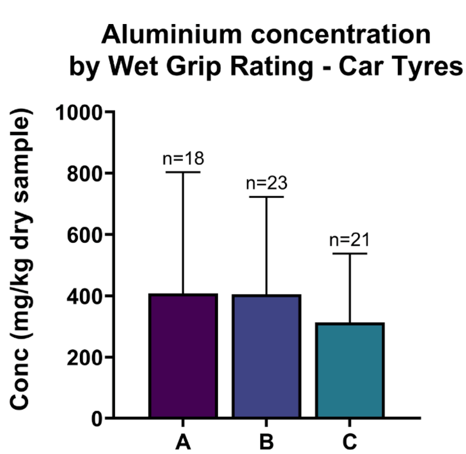

Fig. 3-7. Mean aluminium concentration with standard deviation shown for car tyres compared to wet grip rating found on EU standard tyre label. Number of samples shown above standard deviation. Wet grip ratings are calculated by braking from 80 km/h to 20 km/h in wet conditions according to Regulation (EU), 2020 on the labelling of tyres with respect to fuel efficiency and other parameters. 'A' is the shortest stopping distance in wet conditions, 'E' is the longest. No tyres with wet grip rating 'D' or 'E' were included in the dataset.

3.6. Thermogravimetric analysis

To determine the percentage of inorganic fillers by mass, tread from five tyres were analysed by thermogravimetric analysis (TGA) following a method adapted from the Standard Test Method D6370 − 99. Fig. 3-8 shows the TGA analysis for five manufacturers. The first change in mass represents loss of rubber components and polymers, the second change in mass, under air, is loss of the carbon black filler as described by Standard Test Method D6370 − 99 (ASTM International, 2019). What remains are the inorganic fillers, including silica, titanium dioxide and zinc oxide (Barbin, 2018; Kreider et al., 2010).

Percentage mass remaining ranged from 45.6% − 28.3% with a mean of 35.8%. Manufacturer H (brown) had the highest mass remaining after TGA, and very little mass change associated with carbon black, which suggests that an inert filler such as silica is being used instead of carbon black. Manufacturer O (turquoise) had the highest concentration of carbon black of the five tyres tested, with 11% mass being lost after switching from a nitrogen environment to air. By contrast, Manufacturer L had the lowest mass change when the TGA environment was switched to air. Manufacturer L had a statistically higher magnesium concentration than Manufacturers E, H, O and R, as described earlier in Fig. 3-5. The TGA analysis combined with ICP-MS may suggest that Manufacturer L is using MgO as a filler rather than carbon black. The two tyres with the highest concentrations of carbon black are from "mid-range" cost manufactures (Manufacturer O and R), whereas the "premium" tyre manufacturers had a higher portion of inert filler and lower concentration of carbon black (Manufacturer E, H and L). Silica fillers are more challenging to incorporate into the rubber formulation but have been shown to improve the performance of the tyre. Al-Hartomy et al., (2015) and Bertora et al., (2011) report that wet gripping is improved, and fuel consumption is reduced when silica is used as a reinforcing filler. The tyres from Manufacturers E, H and L were all wet grip class "A" tyres, with short stopping distances, while tyres from Manufacturers O and R were class "B" tyres.

4. Discussion

Table 3 summarises some of the sources and functions of each of the seven most abundant elements detected in this experiment. A current understanding of the composition of tyre rubber is essential if we are to accurately quantify the amount of tyre wear in the atmosphere. Using elemental tracers allows for this measurement using already established infrastructure, despite the challenges highlighted by Fussell et al., (2022), Klöckner et al., (2019) and Grigoratos and Martini, (2014). A multielement tyre fingerprint allows for subtraction of the contributions of the roadside derived particulate matter through positive matrix factorisation (PMF) or through solving a chemical mass balance (CMB) equation similar to work by Font et al., (2022). In the development of a tyre tracer, understanding the differences or similarities in concentrations may be important in selecting the elements to include or exclude from a source profile. While profiles currently exist for several aspects of the tyre industry such as volatile gasses during tyre production, or PM from tyre burning, there is no tyre PM profile included in the US EPA's SPECIATE air pollution profile database (Simon et al., 2010). There is a source profile for tyre wear included in the EU's SPECIEUROPE source profile database (Pernigotti et al., 2016), but this profile is based on the

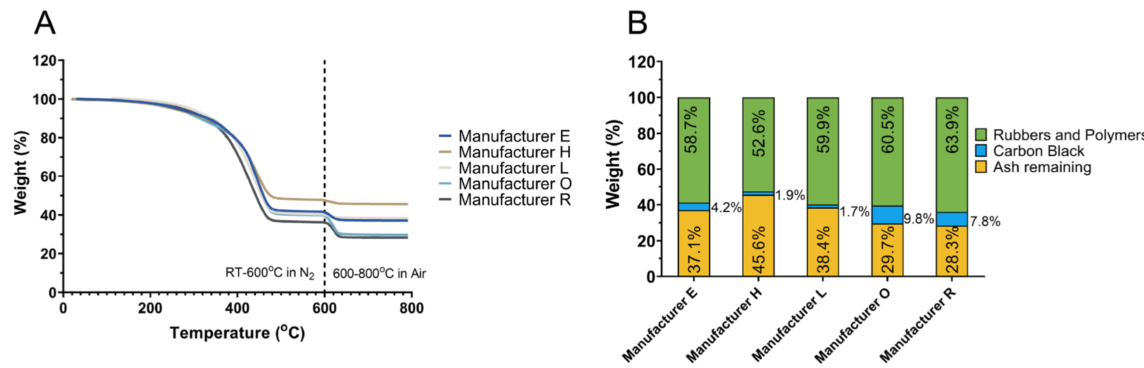

Fig. 3-8. A: TGA thermogram showing temperature vs percentage total weight by manufacturer. B: Bar chart summarising weight associated with tyre components (Rubbers and Polymers, Carbon Black and Ash Remaining). As temperature increases, mass is lost due to liberation of tyre rubber components. Temperature was ramped at 10 °C/min, from room temperature to 600 °C in N_2, then from 600 to 800 °C in air.

Table 3
Possible sources of abundant elements detected in tyre rubber.

Element	Source/Function
Zinc	Vulcanisation activator/accelerator, promoting rubber crosslink formation (Grigoratos and Martini, 2014)
Iron	Component of steel belts in tyre structure (Barbin, 2018)
Aluminium	Aluminium hydroxide may be added to tyres to increase their grip in wet or wintery conditions; however, this has been shown to reduce the life of the tyre through reduced abrasion resistance (Kikuchi et al., 2001; Miyazaki, 2019). Aluminium powder has also been used to reduce the vulcanisation time for thick rubber composites (Vinod et al., 2001).
Magnesium	Magnesium oxide is added to tyres as a vulcanisation accelerator and has been added to rubber since the 1840s. It is more commonly used today as a curing agent and to neutralise acids in polychloroprene and other elastomers, as well as being a filler, and giving the rubber fire, wear, and corrosion resistant properties (Akrochem, n.d.; Hebei Meishen Technology Co., Ltd, 2020).
Copper	Steel cords used in tyre manufacture are coated with a layer of brass to improve adhesion between the rubber and the metal (Barbin, 2018; Paulthangam et al., 2022).
Titanium	Titanium (along with cobalt, nickel, and chromium) are used as catalysts in the conversion of 1,3-butadiene to polybutadiene rubber (Rackaitis and Graves, 2017).
Barium	Barium is added to other rubber products as a filler and for its acid resistant properties (Barbin, 2018; Vijayaram, 2009). Barium products, barite and Blanc Fixe ($BaSO_4$) are advertised as improving "aging resistance and weatherability" of tyres (9X Minerals LLC, 2021; XiMi, N.D.)

WEAREM Wear particles from road traffic report and includes just eight elements. Their data is drawn from a sample of 70% studded and 30% non-studded tyres, and analysed tyre wear particles generated in a simulator (Sjödin et al., 2010). This current data is more appropriate for air quality source profiles, as they are taken from pure rubber samples, allowing for quantification of rubber contribution without being diluted by road or stud wear. When fed into appropriate source apportionment calculations, these data have the potential to enable researchers to quantify tyre wear in complex air pollution samples. Similar ICP-MS analysis has been conducted on a sample of mixed brake dust (Selley et al., 2020), however further work is needed to develop a comprehensive source profile for brake and road surface wear.

Further analysis of light goods vehicle, bus and HGV tyres is required to further explore the possibility of having a unique multielement source profile for these vehicle types. Particularly relevant in cities with restricted car traffic (for example, cities with congestion charges), the ability to attribute the amount of tyre wear to vehicle type would allow for targeted regulation of rubber emissions to reduce total rubber in urban atmospheres. While less relevant for air quality, the elemental composition of the entire tyre is important for environmental monitoring. End of life tyres have many recyclable applications, and previous studies have already demonstrated how metals associated with recycled tyre rubber material can leach into aquatic environments. Zinc levels were significantly enriched in sidewall rubber compared to tread, highlighting the risk posed by zinc leaching from end-of-life tyres (Baensch-Baltruschat et al., 2020; Parker-Jurd et al., 2021; Rhodes et al., 2012; Wik and Dave, 2009).

The relative expanded uncertainty for the method was derived to be 12.6%. This figure was calculated for the entire method including acid digestion. Although no studies have calculated measurement uncertainty specifically for tyre analysis, the value of 12.6% is comparable to other expanded uncertainty estimates made for ICP-MS methods (7.7% to 13.6% for metals in drinking water, (Tanase et al., 2015), and allows for individual results to be reported with the expanded uncertainty of the method.

This study presents the most recent and comprehensive analysis of tyre rubber, to provide a source profile that can be used to identify and quantify tyre rubber emissions. There is not enough variation in elemental composition to be able to reliably distinguish between manufacturers using the elements included in this research, despite TGA analysis showing a range of mass remaining between 28.3% – 45.6%. However, significant differences for certain elements were found for passenger car and HGV, and tread and sidewall comparisons, which may enable tyre wear emissions to be associated with these sources. The next steps for these data are inclusion in a source profile that can be utilised by atmospheric monitoring teams.The composition of tyre wear particles generated from real world or simulated driving conditions should be compared to the pure tyre studies to understand how the composition is diluted from road contributions, and this work is underway (Klöckner et al., 2019; Kreider et al., 2010). Additionally, the *in vitro* toxicity of these particles need to be further assessed, (Fussell et al., 2022) and a detailed understanding of tyre composition may allow for identification of components driving toxicity.

CRediT authorship contribution statement

David P. O'Loughlin: Investigation, Methodology, Formal analysis, Writing – original draft. **Molly J. Haugen:** Methodology, Writing - review & editing. **Jason Day:** Investigation, Methodology, Validation. **Andrew S. Brown:** Investigation, Validation, Writing – review & editing. **Emma C. Braysher:** Validation, Writing – review & editing. **Nick Molden:** Resources. **Anne E. Willis:** Supervision. **Marion MacFarlane:** Supervision, Funding acquisition, Writing - review & editing. **Adam M. Boies:** Supervision, Project administration, Funding acquisition, Writing - review & editing.

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

Tyre metadata & ICP-MS analysis data are available online via Mendeley Data https://doi.org/10.17632/vsf74x9ctz.1. To protect the intellectual property of the manufacturers, it is not possible to link analysis to a specific model of tyre.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2023.108047.

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