



Development and application of an analytical method for the quantification of tire wear in atmospheric deposition

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Abstract. Tire wear particles (TWP) are a major source of microplastic pollution and a carrier of rubber additives and metal-containing compounds that can be released into the environment and adversely affect ecosystems. Reliable quantification of TWP remains challenging because tire materials are compositionally heterogeneous and environmental samples contain
10 complex organic and inorganic matrices that interfere with their analysis. Here, we present a pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) method for the quantification of TWP in atmospheric deposition samples. The method combines targeted sample pretreatment, including density separation and removal of organic matrix components, with the analysis of six characteristic pyrolysis products of tire rubber, namely butadiene, 4-vinylcyclohexene, isoprene, limonene, styrene, and α -methylstyrene. The sum of the integrated peak areas of these markers is used to quantify TWP mass.
15 Instrumental parameters, including pyrolysis temperature (set to 500 °C) and gas chromatographic separation, were systematically optimized to maximize sensitivity, reproducibility, and chromatographic resolution. Calibration was established using cryo-milled tread materials from 23 used passenger car and truck/bus tires as well as a mixture of cryo-milled tread materials representative of the U.S. tire market. The sum of the six marker signals showed a strong linear relationship with tire tread mass across different tire types ($r^2 = 0.93$). The method achieved a limit of detection of 0.16 μg TWP and a dynamic
20 range extending to approximately 450 μg TWP. A comprehensive uncertainty assessment identified variability in tire composition as the dominant source of uncertainty. The expanded uncertainty for the quantification of TWP in a single atmospheric deposition sample ranged from -58% to $+63\%$.
Application of the method to duplicate atmospheric deposition samples collected at two suburban sites demonstrated its suitability for environmental monitoring. Mean TWP mass deposition rates of $843.9 \mu\text{g m}^{-2} \text{ day}^{-1}$ were measured at a site
25 located near a busy road, compared with $253.4 \mu\text{g m}^{-2} \text{ day}^{-1}$ at a nearby suburban background site. These results demonstrate that the proposed multi-marker Py-GC-MS approach enables quantitative TWP measurements in complex environmental samples while providing an explicit characterization of the associated measurement uncertainty.



1 Introduction

Frictional forces between the tires and the road surface cause abrasion on both the tire tread and the road surface during driving (Kreider et al., 2010). This leads to the generation and release of tire and road wear particles (TRWP), consisting of a mixture of aggregated tire and road wear. The term tire wear particles (TWP) is often used to refer to the proportion of tire wear in TRWP. Tire wear and road wear each account for approximately 50% of the mass of TRWP. Tire wear consists of roughly 40-50% polymer by weight, i.e., natural rubber (NR, polyisoprene) and synthetic rubber, mainly styrene butadiene rubber (SBR) and butadiene rubber (BR) (Baensch-Baltruschat et al., 2020). The content of synthetic rubber in tire wear ranges between 85% of total rubber in passenger cars and 20% of total rubber in tires for trucks and explains why TWP are generally classified as microplastics (Hartmann et al., 2019; Wagner et al., 2018). An estimated amount of 3 to 6 million tons of tire wear particles are released worldwide into the environment annually, making tire wear an important source of microplastics (Kole et al., 2017; Sommer et al., 2018). Besides rubber (natural and synthetic polymers), TWP contains additional compounds, including fillers, softeners, vulcanization agents, and additives. Leaching of these compounds over time releases heavy metals and organic pollutants that are harmful to ecosystems and to human health (Boisseaux et al., 2024; Mayer et al., 2024; Thodhal Yoganandham et al., 2024; Wang et al., 2024). Some of the TRWP gets into the air and is distributed through the atmosphere, even reaching remote areas such as oceans and high mountains, making tire wear a pollutant of global concern (Evangelidou et al., 2020). For an exposure assessment, it is, thus, crucial to develop methods to estimate the amount of TWP generated, transported, and deposited in the environment. However, quantifying TRWP and/or the associated TWP in environmental matrices is analytically challenging because i) the chemical composition of tires varies between different brands and ii) organic and inorganic substances present in environmental matrices interfere with the target analytes (Rauert et al., 2021; Rødland et al., 2023). Current analytical methods for quantifying TRWP can be categorized into two classes: particle-based and mass-based quantification methods (Kovochich et al., 2021; Rødland et al., 2023). Particle-based methods mainly rely on characteristic features of TRWP (e.g., color, morphology, and elemental composition), which are detected using optical or electron microscopy approaches (Foetisch et al., 2024; Rausch et al., 2022; Sommer et al., 2018). Other particle-based micro-spectroscopy approaches commonly used in microplastic particle analysis, such as Fourier-transform infrared (FTIR) and Raman micro-spectroscopy, are less suitable for analyzing TRWP because of their strong absorption of visible and mid-IR light, caused by the presence of carbon black as a filler. Mass-based quantification methods rely on detecting selected markers characteristic of tire wear. Ideal markers are specific to tire wear, are chemically stable over time, and remain within the tire material. Since TWP in the environment is present as a mixture of tires of different compositions, a suitable marker should also be representative of that mixture. Zinc (Zn^{2+}), for example, was used as a marker, but because of its ubiquity in the environment, its suitability as a marker for TWP has been questioned (Klößner et al., 2019). Specific organic compounds (additives such as oxidation retardants, accelerators, vulcanizing agents, and plasticizers) were also used as markers for the quantification of TWP in environmental samples. However, the use of these markers is challenging as they leach from the tires or are chemically transformed over time, as for example documented for N-(1,3-dimethylbutyl)-N'-phenyl-p-



65 phenylenediamine (6-PPD) which transforms to N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine-quinone (6-PPD-Q) (Klößner et al., 2021; Rødland et al., 2023; Tumwet et al., 2025). The rubber materials used in tires, however, are chemically stable over the lifetime of a tire, and therefore the compounds formed during the thermal decomposition of rubber (i.e., NR, SBR, and BR) represent promising markers for TWP (Thomas et al., 2022). Thus, thermoanalytical methods, such as pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) and thermal extraction and desorption gas chromatography mass spectroscopy (TED GC-MS), have been established as leading techniques to quantify TWP in complex (environmental) matrices (Eisentraut et al., 2018; Unice et al., 2012). In Py-GC-MS, TWP are thermally decomposed, and the volatile products of thermal rubber decomposition are chromatographically separated, allowing their identification and quantification using a mass spectrometer (Gueissaz and Massonnet, 2017; Primpke et al., 2020). To limit interferences between the target compounds and pyrolysis products from other organic matter and for signal enhancement or reduction due to the presence of inorganic materials, Py-GC-MS measurements require a sample-specific pre-treatment procedure (Dierkes et al., 2019). Furthermore, chromatography parameters need to be optimized to improve the signal-to-noise ratio and to prevent saturation of the mass detector (Möller et al., 2022; Picó and Barceló, 2020). Various Py-GC-MS methods have been applied to quantify TWP by detecting pyrolysis products from rubber components (Goßmann et al., 2021; Gueissaz and Massonnet, 2017; Rødland et al., 2022; Unice et al., 2012). The main types of rubber used in tires are NR, SBR, and BR, with tires for passenger cars and light-duty vehicles containing more synthetic rubber (SBR and BR) than natural rubber, while NR dominates in tires for heavy-duty vehicles (e.g. trucks and buses) (Unice et al., 2012). However, detailed quantitative information on the proportions of these main types of rubber in the various tire types are currently lacking. Nevertheless, the thermal decomposition of NR, SBR, and BR yields butadiene, isoprene, 4-vinylcyclohexene (VCH), limonene (or dipentene, DP), 4-phenylcyclohexene (PCH), styrene, and α -methylstyrene as the dominant pyrolysis products (Ding et al., 2015; Gueissaz and Massonnet, 2017). Since the proportions of NR, SBR, and BR are specific for the tire type and the tire manufacturer, the amount of the respective pyrolysis products varies greatly for the different tires. Thus, quantifying TWP in environmental samples based on the measurement of a single pyrolytic compound is uncertain and has recently been questioned (Rauert et al., 2021; Rødland et al., 2023). Among the available Py-GC-MS methods for determining TWP in environmental samples, those described in the technical specifications ISO/TS 20593:2017 and ISO/TS 21396:2017 are most widely used (Anon, 2017; ISO/TS 20593:2017(E), 2017). However, both methods come with severe limitations, as they both exclusively rely on VCH and limonene as markers for synthetic rubber (SB+SBR) and natural rubber, respectively, and assume that the amount of synthetic and natural rubber is known and constant in all car and truck tires (Rauert et al., 2021).

In this study, we present a novel Py-GC-MS method that includes the signals of the six most abundant characteristic markers resulting from thermal decomposition of NR, SBR, and BR. The linear relationship between the sum of the integrated signals of the six pyrolysis markers and the mass of tire tread, established for a selection of different tires, allows quantifying the mass of TWP in complex (environmental) samples. We describe a targeted sample processing to minimize possible interferences between the target compounds and the environmental matrix. The Py-GC-MS method was used to quantify TWP in duplicate



atmospheric deposition samples collected from a suburban site close to a busy road and from a suburban site several hundred meters away from roads to demonstrate the potential of this approach.

100 2 Materials and methods

2.1 Chemicals and materials

Cis-polybutadiene (butadiene rubber, BR) was purchased from Sigma-Aldrich (United States of America, USA). Polyisoprene (natural rubber, NR) and styrene-butadiene rubber (SBR-1500) were purchased from Polymer Source, Inc. (Dorval, Canada). Tetrahydrofuran (THF) and acetone were purchased from Merck (Buchs, Switzerland), and dichloromethane (DCM) was
105 purchased from Acros Organics/Thermo Scientific Chemicals (Zurich, Switzerland). All these chemicals were used as received without further purification. The sodium polytungstate (SPT) solution (2.0 g/mL) was prepared by dissolving the required amount of sodium metatungstate monohydrate (Thermo Scientific - Alfa Aesar) in deionized (DI) water and filtering the solution through a 0.45 μm cellulose acetate filter. Stainless steel pyrolysis Eco-cups (PY1-EC80F) were obtained from Frontier Lab (Fukushima, Japan). Cylindrical borosilicate glass containers (internal diameter 9.2 cm, volume of 1.5 L), used
110 for collecting atmospheric deposition, were purchased from a local household goods store. These glass containers were heated at 600°C in a furnace to remove organic contaminants, followed by sonication in DI water (2×30 minutes). Subsequently, the borosilicate glass containers were carefully washed with acetone and ethanol to eliminate residual particles. Finally, the opening was covered with aluminum foil and stored at room temperature until the glass containers were deployed in the field.

2.2 Tire tread materials

115 Cryo-milled tire tread (CMTT) samples, supplied by the U.S. Tire Manufacturers Association (USTMA), were used as received and served as reference material (denoted as US-CMTT). The US-CMTT has been used in previously reported studies addressing tire wear and tire-derived chemicals in the environment. It is a mixture of tire tread from new tires representative of those sold on the U.S. market. The US-CMTT comprises 41% of passenger car tires, 14% light truck tires, and 45% truck/bus tires (USTMA, 2026). In addition, tread from used tires was collected from tire dealers in Zurich. Samples of 18 tires for
120 passenger cars and light-duty vehicles and 5 tires for trucks and buses, including one re-treaded truck tire, were collected (Table S1). These tire tread samples were sliced at a depth of approximately 2-5 mm from the surface using a stainless-steel knife blade, washed thoroughly with ethanol and nanopure DI water, and then dried overnight at 70°C. Afterwards, the isolated tire tread samples were cryo-milled in a Retsch M400 ball mill using 35 mL stainless steel containers and containing a 25 g stainless steel ball. The stainless-steel bucket was cooled in liquid nitrogen for 20 minutes before being used. The mill was
125 operated twice at a frequency of 20 Hz for 60 seconds each. The resulting TWP powders were sieved through a 400 μm steel mesh (Zivipf, Treuchlingen, Germany), dried overnight at 70°C, and stored in an airtight container. The cryo-milled tire tread samples from used passenger cars and light-duty vehicle tires are referred to as cryo-milled car tire tread (CMCTT); those from truck and bus tires are referred to as cryo-milled truck tire tread (CMTTT).



2.3 Sample collection

130 The atmospheric deposition samples were collected in Dübendorf (Switzerland), at a suburban site of the Swiss national air pollution monitoring network NABEL (DUE), and an additional traffic site (DUET) also located in Dübendorf, 200 m from DUE and 20 m from a road (Ueberlandstrasse) with a daily traffic volume of 19'000 vehicles. The DUET site represents a suburban location in the proximity of a busy road. Bulk atmospheric deposition, i.e., the sum of wet and dry deposition, was collected passively using the cylindrical borosilicate glass containers described above and in accordance with a method used in monitoring networks.(VDI, 2012) The sample collectors were installed on poles 1.5 m above the ground; a free and unobstructed air flow to the collectors was ensured. Sampling took place over a period of four weeks, and the volume of the containers was sufficient to collect all precipitation. Images of the sampling sites and of the sample collectors are provided in Figure S1.

2.4 Sample treatment

140 In contrast to the CMTT samples used for method development and calibration, the atmospheric deposition samples were complex mixtures of biogenic particles (insects, fungi, pollens, and plant debris) containing larger organic biomolecules and particles from anthropogenic (e.g., road dust) and natural sources (e.g., mineral dust). Furthermore, limonene may be introduced into the environment through domestic and industrial chemical applications, while aromatic hydrocarbons such as toluene and benzene are typically derived from vehicle exhaust emissions and petrochemical processes. During pyrolysis, these larger biomolecules can generate molecular fragments that overlap with the pyrolysis markers generated from TWP. To limit matrix interferences with target analytes, the following treatment steps were applied:

2.4.1 Filtration and chemical digestion

One hundred milliliters (100 mL) of DI water were added to the glass flasks containing the collected atmospheric deposition samples. The walls of the glass flasks were thoroughly scrubbed with a glass rod and carefully rinsed. Then, the liquid sample was passed through a 400-micron stainless steel mesh to remove plant and insect debris, and the filtrate was collected in a 1000 mL Erlenmeyer flask. The flask was rinsed twice to prevent TWP loss. Moreover, the stainless-steel mesh was thoroughly rinsed with DI water. After adding 100 μ L of 5 M H_2SO_4 to the collected filtrate, the Erlenmeyer flask was placed in a water bath at 90°C until the volume of the liquid was reduced to approximately 50 mL. The liquid containing the TWP was neutralized by adding 2 mL of 0.1 N NaOH and placed again in a water bath at 90°C to reduce the volume to approximately 25 mL. The remaining liquid was transferred into 50 ml polypropylene centrifugation tubes. The walls of the Erlenmeyer flask were carefully rinsed with 25 mL of DI water, which was also added to the centrifugation tubes.



2.4.2 Density separation

The liquids in the centrifugation tubes were centrifuged (5000 rpm, 2 hours, in DI water), and the supernatant (40 mL) containing solids with a density $< 1\text{ g cm}^{-3}$ (e.g., polyethylene and polypropylene) and digested water-soluble organic compounds was discarded. This step was repeated three times, with the discarded supernatant always replaced by DI water. The pellet remaining at the bottom of the centrifugation tube after the three centrifugation steps in DI water was resuspended in an SPT solution (2.0 g mL^{-1} , 50 mL). This suspension was also centrifuged at 5000 rpm for 2 hours. The resulting supernatant ($\sim 40\text{ mL}$), containing particles with a density $< 2\text{ g cm}^{-3}$ and thus including the TRWP, was collected for subsequent filtration. The remaining pellet was resuspended in fresh SPT solution, centrifuged, and the supernatant was combined with the supernatant from the previous density separation step. The combined supernatants were filtered through a $1.6\text{ }\mu\text{m}$ glass microfiber filter (Whatman Grade G/F, binder-free, 13 mm diameter) using an in-house-fabricated glass microfiltration unit.

2.4.3 Solvent cleanup and thermal desorption

To remove sorbed organic compounds and soluble polymers, the glass fibre filters containing the TRWP were sequentially rinsed with 20 mL of THF, 20 mL of DCM, and 20 mL of acetone in the microfiltration unit. The air-dried filters were carefully transferred to pyrolysis cups and dried overnight at 70°C . Afterward, the samples were heated to 100°C for 1 hour to remove any remaining volatile compounds before Py-GC-MS measurement. The efficiency of the applied solvent cleanup was evaluated based on spiking experiments using deuterated polystyrene and deuterated polyisoprene (section S3). The applied density separation and solvent cleanup are therefore expected to eliminate possible interferences from sorbed organics and soluble polymers such as polystyrene in environmental samples.

2.5 Pyrolysis-GC-MS

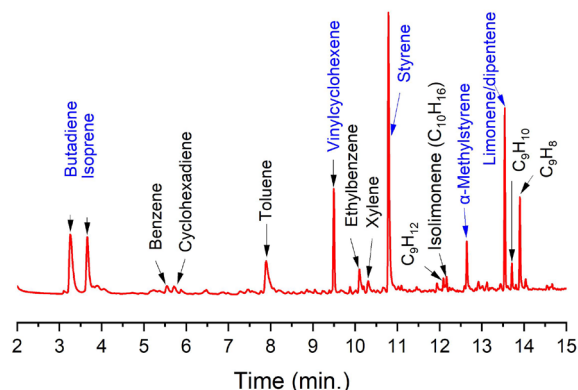
For analysis of CMTT samples, the CMTT material was filled into pyrolysis cups, each sample was weighed using a microbalance. The mouth of the pyrolysis cups was covered with a glass fibre filter to prevent loss of material during sample handling. The collected and pre-treated environmental samples were also transferred to pyrolysis cups and treated in the same way.

A multi-shot pyrolyzer (EGA / Py-3030D) from Frontier Laboratories Ltd. (Koriyama, Fukushima, Japan) was used for pyrolysis. The pyrolysis temperature was set to 500°C to i) prevent the formation of secondary degradation products from limonene (More et al., 2023) and to ii) limit interferences of decomposition products of NR, SBR, and BR with compounds formed from carbon black and other fillers (Hermabessiere et al., 2018). The instrument was operated in single-shot mode. The temperature of the transfer line was maintained at 320°C . A Thermo Scientific™ TRACE™ 1310 gas chromatography (GC) instrument (Thermo Fisher Scientific, USA) equipped with an Agilent DB-5MS ($60\text{ m} \times 0.25\text{ mm i.d.}$, $0.25\text{ }\mu\text{m}$ film thickness, non-polar phenyl arylene polymer GC column) was used in combination with helium as mobile phase, a purge flow of 10 mL/min and an injection temperature set at 300°C . The GC measurement was performed at a split ratio of 400:1. A



Thermo Scientific ISQ 7000 single quadrupole mass spectrometer (MS) with an interface temperature of 300°C was used to record the mass spectra of the eluents. The ion source temperature was also maintained at 300°C. All the mass spectra were acquired using electron ionization (EI) of eluents at an electron energy of 70 eV and an ion dwell time of 15 ms. A synchronous scan and total ion count (TIC) monitoring mode were used with a mass spectrometer scan range of 50–550 m/z to record spectra of all separated fragments in the measurements.

The GC oven temperature ramping was carefully optimized to achieve sufficient separation between the pyrolysis products of tire rubbers and high-molecular-weight molecules (Figures S3 and S4). Each pyrolysis cup was heated twice at 500°C, but no signal of the tire rubber markers was observed the second time. This demonstrated that the components of tire rubber that can be thermally decomposed at this temperature were completely decomposed during the first single-shot measurement (Figure S5).



Pyrolysis Product	Structure	Quantifier ion (m/z)	Qualifier ion (m/z)	Retention time (min)	Tire rubber
Butadiene		54	53, 50	3.26	BR, SBR
Isoprene		68	53, 67	3.98	NR
Vinylcyclohexene (VCH)		54	79, 67	9.57	BR, SBR
Styrene		104	78, 103	10.84	SBR
α-Methylstyrene		118	103, 78	12.75	SBR
Limonene (Dipentene)		68	136, 107	13.57	NR

Figure 1: Typical chromatogram of cryogenically milled tire tread sample (CMCTT-13), illustrating the various pyrolysis products generated at 500 °C (left). The blue labeled markers were commonly found in all CMTT samples used in this study. The table (right) lists the tire-specific pyrolysis markers including retention time, quantifier and qualifier ion fragments.

All the data were processed using Thermo Scientific™ Dionex™ Chromeleon 7.2.10 software using the Cobra MS detection algorithm. The detection window was set to 0.07-0.2 min for the retention time of the specific individual markers. The component-matching algorithm based on retention time and peak height, as implemented in Chromeleon, was applied. The extracted ion chromatograms (EIC) for the tire-specific markers (butadiene, isoprene, VCH, α-methylstyrene, styrene, and limonene) were selecting one quantifier and two qualifier ions at the corresponding retention times (Figure 1). The peak areas of individual markers were calculated using their quantifier marker ions, while two qualifier ions were monitored to confirm the chemical identity of those markers.



3 Results and discussions

For the Py-GC-MS method development, the CMTT samples were individually processed as described in section 2.4 and analyzed by Py-GC-MS. In all chromatograms, we consistently observed six distinct peaks, which represented the formation of the following pyrolysis products (Figure 1, blue labels): butadiene, isoprene, VCH, α -methylstyrene, styrene, and limonene. The quantifier ions of butadiene, isoprene, styrene, and α -methylstyrene corresponded to their molecular ion (M^+). Conversely, VCH and limonene were fragmented into their main building blocks, butadiene and isoprene. Hence, we chose the substructure fragment ions ($m/z = 54$ and $m/z = 68$) as a quantifier for VCH and limonene at their respective elution times of 9.57 min and 13.57 min (Figure 1, right side). The Py-GC-MS analysis of reference polymers (SBR-1500, BR, and NR), which are commonly used in tire manufacturing, enabled assignment of the different pyrolysis products to the respective rubber types (Figure S6). Butadiene and VCH were identified as characteristic pyrolysis products of butadiene rubber (BR) and styrene-butadiene rubber (SBR). Styrene and α -methylstyrene were primarily generated from SBR. It should be noted that α -methylstyrene is also produced during the thermal decomposition of styrene-butadiene-styrene (SBS), a compound found in polymer-modified bitumen, which is also used in road asphalt (Rødland et al., 2022). In Switzerland, however, the amount of SBS used in road construction is negligible (section S8). Limonene and isoprene were pyrolytically formed from NR. These identified markers are consistent with the NIST/EPA/NIH Mass Spectral Library (NIST 08 program) and have been used as markers for the quantification of TWP in road dust (Evans et al., 2025). In addition to the identified pyrolysis products associated with different rubber types, we detected signals from common tire additives, including benzothiazole, 2-mercaptobenzothiazole, 6-PPD, aniline, toluene, and long-chain saturated fatty acids (C_{16} and C_{18}) (Figure S7). These additives, however, were not consistently detected in the CMCTT and CMTTT samples, possibly because these substances can leach over time from the tires (Thodhal Yoganandham et al., 2024). Therefore, these compounds were not suitable for the assessment of TWP in this study. Analysis of the different CMTT samples demonstrated that the relative shares of the 6 characteristic pyrolysis products varied between passenger car and heavy-duty vehicle (trucks and buses) tires and differed within passenger car and truck/bus tire categories (Figure 2). Styrene was often the dominant pyrolysis product in passenger car tires, whereas isoprene and limonene were the dominant pyrolysis products in truck and bus tires. This can be explained by the dominance of synthetic rubber in the rubber mixture of passenger car tires, whereas the proportion of natural rubber is higher in truck tires (Wagner et al., 2018). The US-CMTT samples had isoprene and limonene as the dominant markers, which resulted from the high fraction of truck and bus tires in the mixture (USTMA, 2026). Similar to Figure 2, the differences in the signals of the six pyrolysis markers in the different tire samples can be investigated using principal component analysis (PCA). Principal component analysis of the composition data of the six pyrolysis markers measured in all CMTT samples resulted in two first principal components (PC1 and PC2) that explain 92.2% of the variance in the data. PC1 (84.6% explained variance) has high negative loadings for styrene and high positive loadings for limonene and isoprene. Projection of the measurements of CMTT samples onto the plane spanned by the first two principal components allows a separation of the CMTT samples according to the relative signals of these markers for synthetic and natural rubber



240 and therefore a (partial) separation of CMTT from tires for cars and trucks/buses (Figure S9). PC2 explains 7.6% of the variance with high loadings for butadiene and α -methylstyrene, two markers indicative for synthetic rubber.



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260 **Figure 2. Relative contribution of the selected six markers (individual signal intensity relative to the sum of the intensities of all six peaks) for all cryo-milled tire tread samples. CMCTT-1 to 18 are samples from used tires for passenger cars, and CMCTT- 1 to 5 are samples from used truck/bus tires, and US-CMTT is a mixture of car, truck and bus tires.**

3.1 Method calibration

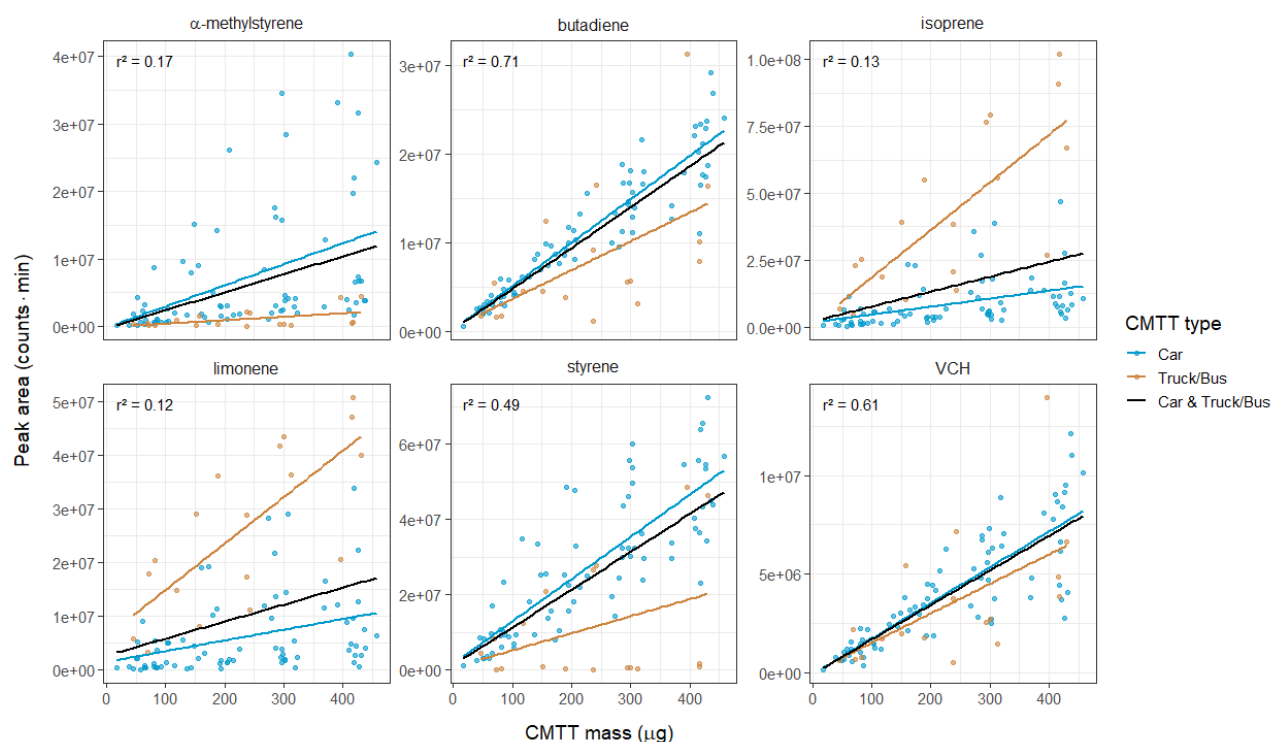
265 The relationship between the integrated signals of the selected quantifier ions related to the characteristic pyrolysis products and the mass of the tire tread material was determined. For that purpose, different amounts (15 μg to 430 μg) of various CMTT samples were investigated using Py-GC-MS. The maximum quantification amount of CMTT at the 400:1 split ratio was approximately 450 μg . Above this upper limit, detector saturation and peak tailing in the chromatograms were observed.

270 The integrated peak areas of the quantifier ions from the six tire-specific pyrolysis products were linearly correlated to the mass of the individual CMTT samples (Figure S10). However, the slope of the linear regression between the integrated peak areas of the quantifier ions from the six characteristic pyrolysis products and the mass of CMTT varied greatly between individual tires presumably due to the different mix of rubber compounds in the different tire tread samples. This can best be seen when merging the data from all individual CMTT samples (Figure 3).



The correlations between the integrated signals of the quantifier ions of the characteristic pyrolysis products and CMTT mass, as expressed by the coefficients of determination (r^2), ranges from 0.12 for limonene to 0.71 for butadiene (Table S2). For most markers, the dependence of the peak area on CMTT mass is different for passenger car tires than for tires for trucks and buses, reflecting the different compositions of the tires as mentioned before. Butadiene ($r^2=0.86$) and VCH ($r^2=0.70$) showed the highest coefficients of determination when CMTT from passenger car tires were considered separately. For the CMTT samples from truck/bus tires, the highest coefficients of determination were found for isoprene ($r^2=0.57$) and limonene ($r^2=0.56$) (Table S2). A substantial improvement in r^2 values was obtained when using the sum of the integrated peak areas from all six markers (denoted as sum of peak areas, SPA) instead of the peak areas of individual markers (Figure S10).

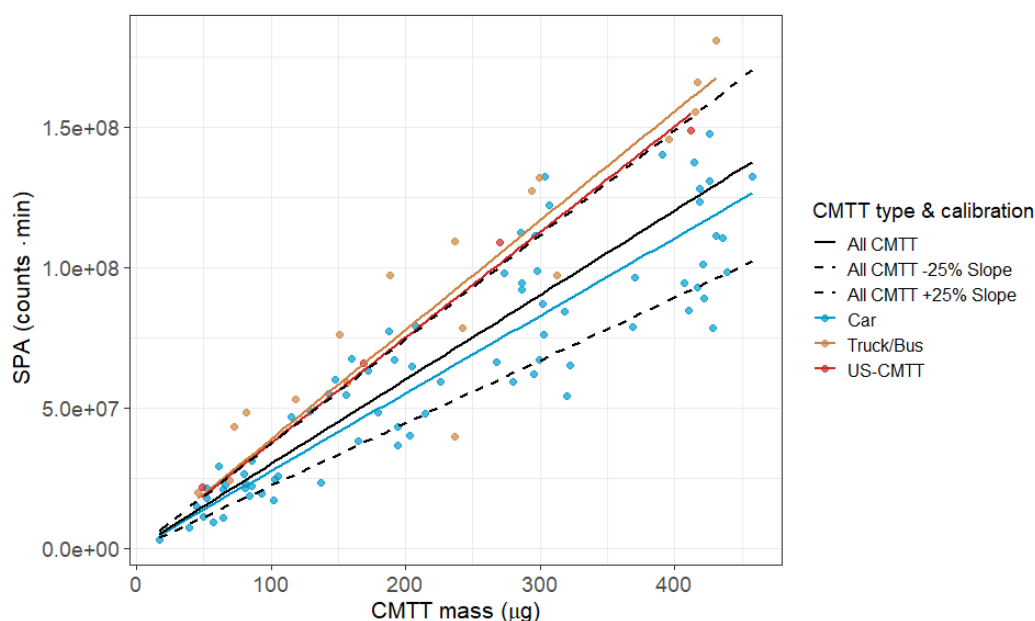
Linear regressions of SPA against CMTT mass were calculated for US-CMTT, CMTT samples from each vehicle category separately, and for all CMTT samples from car and truck/bus tires together. The intercepts of all these linear regressions were not significantly different from zero. Therefore, linear regressions were calculated in a second step with intercepts set to zero (Figure 4). The slope of the truck and bus tires was larger than that of the passenger car tires. The higher total response of the sum of the six pyrolysis markers per mass of truck/bus tire material compared to CMTT from passenger car tires is due to the higher contributions from isoprene and limonene (Figure 3), which results from the higher NR content in tires for trucks and buses. A similar slope was also observed for the US-CMTT, which represents a mixture of tires with a high fraction of truck/bus tires (USTMA, 2026).





290 **Figure 3. Measured peak area for the individual pyrolysis markers versus the mass of the cryo-milled tire tread (CMTT) samples from used tires. The CMTT samples from passenger cars and trucks/buses were grouped according to the vehicle category. The linear regression lines are shown separately for the different types of CMTT and for all CMTT samples together. The coefficients of determination (r^2) refer to the relationship between the peak area and all CMTT (Car & Truck/Bus) samples. The r^2 values separately for cars and trucks/buses are listed in Table S2 in the SI.**

Linear regression of SPA against the mass of all CMTT samples from car and truck/bus tires used in this study yields a slope
295 of 297'311 per μg of CMTT (standard error of 8'324 μg^{-1} , $r^2=0.93$). This slope can be used to quantify tire tread material based on Py-GC-MS analysis and will be used as the reference throughout this study and as the calibration constant for the conversion of SPA measured in CMTT samples and in atmospheric deposition samples into the mass of tire tread material.



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Figure 4. Sum of the peak areas (SPA) of the six pyrolysis markers versus the mass of CMTT samples from old tires for passenger cars and for trucks and buses, as well as for a mixture of new tires (US-CMTT). Linear regressions for the different CMTT types and for all measured CMTT samples (All CMTT) are also shown (intercepts forced to be zero). The estimated slope of the linear regression on all data $\pm 25\%$ covers most of the observed variation of the measured values.

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It is important to note that TWPs in the environment are always a mixture of tire tread from various tires, and that this mixture of tires is unknown. We, therefore, assumed that the SPA obtained from analysis of CMTT from the 23 tire types was representative of the tires available on the market and that the spread of the SPA in Figure 4 covers the variability of all different tires. Consequently, it is to be expected that the SPA corresponding to a certain mass of TWP in environmental
310 samples lies within the vertical scatter defined by the SPA determined for the individual tires at the respective mass (Figure



4). We, therefore, derived a calibration constant, essentially corresponding to the slope of the regression line calculated for all tire tread materials (All CMTT in Figure 4), to convert the measured SPA into a mass of TWP.

Despite the varying rubber mixtures of the different tire types, a $\pm 25\%$ range of the above-mentioned slope (or calibration constant) encompasses the variation observed in the individual CMTT samples. Assuming that the true conversion factor lies within the above mentioned $\pm 25\%$, the percentage systematic uncertainty or systematic error for the calculated TWP mass lies between -20% ($1 - \frac{1}{1.25}$) and $+33\%$ ($1 + \frac{1}{0.75}$). Applying the obtained calibration constant to an environmental sample that is dominated by truck tires, e.g., like the mixture of the US-CMTT, will result in a systematic overestimation of TWP mass by about 20%. On the other hand, the mass of TWP in environmental samples that are dominated by passenger car tires is likely to be underestimated.

3.2 Data processing of the Py-GC-MS method

The response of the Py-GC-MS instrument varied over time, caused by the buildup of contamination in the GC column and in the transfer lines and due to instrumental drift of the MS detector. Linear deuterated polymers are therefore often used as internal standards to correct for these variations (Anon, 2017; ISO/TS 20593:2017(E), 2017). However, linear deuterated polymers essentially made up of C-C backbones show a different (pyrolytic) degradation kinetic compared to cross-linked tire rubber. Pyrolysis of the latter involves the fragmentations of C-C (~ 346 kJ/mol), C-S (~ 272 kJ/mol), and S-S (~ 226 kJ/mol) bonds distributed in a complex cross-linked network (Wang et al., 2024). Therefore, the use of deuterated polymers to correct for signal fluctuations associated with the analysis of rubber material might not be representative. As deuterated tire materials were not commercially available, we used CMCTT-6 as an external calibrant to correct for signal variations of the GC-MS instrument. To that end, 5 samples containing increasing amounts of CMCTT-6 were measured as external controls along with each series of environmental samples. The data from CMCTT-6 used for method calibration (Figure S11, Table S3) served as the reference and all subsequent measurements of CMCTT-6 were related to these reference measurements. This approach allowed us to correct instrumental fluctuations of the Py-GC-MS instrument. Specifically, the linear regression parameters (intercept and slope) were calculated for each pyrolysis marker determined in CMCTT-6 from both the method calibration dataset and the external control measurements. The intercepts for all six markers and for both the calibration measurements and the external control measurements used in this study did not deviate from zero (95% confidence level). VCH was an exception in the calibration dataset, where a small intercept deviated from zero, as the measured peak areas for the different masses of CMCTT-6 lay on a straight line ($r^2=1.00$). However, no offset correction was generally needed and the correction for variation in the sensitivity of the Py-GC-MS was derived in a second step from linear regressions with the intercept forced to be zero, and thus, from the ratio of the resulting slopes for the external controls and the method calibration measurements. The applied signal correction, thus, corresponds to a projection of the Py-GC-MS signals recorded during the measurement of individual CMCTT-6 onto the signals obtained for the CMCTT-6 material during the reference (method calibration)



measurement. More details about data processing and the uncertainty involved in the applied correction for varying instrument sensitivity can be found in Annex A.

3.3 Recovery

345 The recovery of TWP was determined by analyzing $n=12$ test samples. These test samples consisted of a mixture of a known amount of CMTT (CMCTT-5 was used for this purpose), and sand (50:50 mass ratio) that was muffled at 600°C for 12h to remove potential organic contaminants. The test samples were treated and analyzed in the same way as the atmospheric deposition samples. The recovery ratio (r) was calculated by dividing the recovered amount of CMTT by the known amount of CMTT in the samples. The average recovery ratio (r) was 0.685, with a standard deviation of $\sigma_r = 11.9\%$. The quantifications
350 of TWP from measurements of the environmental samples, were corrected for incomplete recovery as described in Annex A.

3.4 Measurement uncertainty

As described in section 3.1, the calibration constant determined in this study, which is used to convert the measured SPA into mass of TWP (see equation 8 in Annex A), could be systematically incorrect by between -20% and +33%. This range of potential systematic error is expected to cover all plausible calibration constants and can therefore be approximated by a bias
355 u_b ranging from -10.0% to 16.5%.

Other main components of uncertainty are the sensitivity correction with a standard uncertainty $u_s = 8.1\%$ (Annex B) and the incomplete recovery with $\sigma_r = u_r = 11.9\%$ (section 3.3). For the quantification of the mass deposition rate of TWP using a passive sampling setup as used in this study, the sampling position additionally affects the amount of TWP collected. Therefore, an uncertainty component covering the representativeness of the sampling point should be considered. Air quality monitoring
360 networks use similar passive sampling containers for the measurement of the atmospheric deposition of total dust (VDI, 2012). Based on measurements of total dust deposition within the Swiss National Air Pollution Monitoring Network, the standard deviation from duplicate side-by-side measurements was $u_d = 22.8\%$ (Ashta et al., 2026). Here, u_d represents the difference between samples collected at locations only a few meters apart. We assume that similar differences apply to atmospheric deposition of TWP collected in this study and that u_d describes the influence of the position of the sampling container on the
365 result. When other sampling methods are used, or when the analytical method is applied to other environmental samples (e.g., active sampling of airborne TWP), the uncertainty component u_d should be adapted accordingly. For applications where only the amount of TWP in a collected sample is of interest, the uncertainty component u_d is not even needed. The uncertainty components u_r , u_s , and u_d were considered as random. The combined expanded uncertainty for the quantification of TWP mass and mass deposition rate from the mean of n samples can then be expressed as (Magnusson and Ellison, 2008)

370

$$U = 2 \cdot \sqrt{\frac{u_s^2 + u_r^2 + u_d^2}{n} + u_b^2} \quad (1)$$



The coverage factor of 2 leads to a confidence level of 95%. For a single sample ($n=1$), the ranges of the combined expanded uncertainties for the quantification of TWP ($u_d = 0\%$) and for the mass deposition rate of TWP are $[-35\%$ to $44\%]$ and $[-58\%$ to $63\%]$, respectively. The combined expanded uncertainties decrease when the mean TWP mass or mass deposition rate is calculated from an increasing number of samples and converge with increasing n towards the systematic error of the calibration constant used.

3.5 Limit of detection

The limit of detection (LOD) and limit of quantification (LOQ) of the described method were determined based on $n=7$ procedural blanks, i.e., sampling containers that were not exposed to atmospheric deposition but otherwise treated in the same way as the environmental samples. These sampling containers contained neither the target analytes nor the environmental matrix, e.g., mineral dust and biological particles. The signals of the six pyrolysis markers from the blank samples were processed analogously to those from the environmental samples; CMCTT-5 served as an external control. The mean mass of CMTT determined in the blank samples was $\mu_B = 0.08\ \mu\text{g}$, and the standard deviation was $\sigma_B = 0.02\ \mu\text{g}$. We interpret the signals from the blank measurements as noise, as the qualifier ions were not detected. However, there is a small contribution to the signal of the quantifier ions of the pyrolysis markers.

At low masses of CMTT and correspondingly small signal intensities, the measurement uncertainty is probably dominated by the uncertainty related to the correction of the Py-GC-MS sensitivity. The associated standard uncertainty u_s was 8.1% (section 3.4 and Annex B) and the measurements of blank values and external controls with the lowest CMTT mass indicate that this relative uncertainty is also applicable at very low amounts of CMTT (Figure B2) and $\sigma_B = 0.02\ \mu\text{g}$ is also a reasonable representation of the standard deviation of measurements at masses of CMTT in the range of the detection limit, denoted as σ_D . We therefore calculated the limit of detection (LOD) of the analytical method following an approach described by Currie (1968), which was also applied to an analytical chain for atmospheric microplastics (Ashta et al., 2026; Currie, 1968). In this approach, a critical level L_C is defined, as the threshold above which a measured signal is very likely due to the presence of the quantity being measured, here tire tread material. L_C is therefore the threshold at which false positive decisions are minimized; it is $L_C = \mu_B + 2 \cdot \sigma_B = 0.12\ \mu\text{g}$. The limit of detection is then the threshold at which the risk of false negative decisions is acceptable (here, the 95% confidence level). Finally, the LOD can be specified as

$$LOD = L_C + 2 \cdot \sigma_D = 0.16\ \mu\text{g} \quad (2)$$

4 TWP in environmental samples

As part of a larger measurement campaign, we collected samples of atmospheric bulk deposition at several sites in Switzerland on a four-weekly basis over a period of one year. The results of the full measurement campaign are beyond the scope of this



paper and will be published elsewhere. Here, we apply the developed analytical method to selected atmospheric deposition samples from that larger study as proof of principles. The selected atmospheric bulk deposition samples were collected in parallel for four weeks (30.01.2025 to 27.02.2025) at two sites (DUET and DUE). DUET represents a suburban traffic site next to a busy road and DUE a nearby suburban site without direct influence of road traffic. At both locations, duplicate samples were taken, which were processed and analyzed in pairs (DUET A, DUE A, and DUET B, DUE B) on different days in the laboratory. The samples were filtered, processed, and measured as described in section 2 and CMCTT-6 was used as an external control.

The mass of TWP in all four samples as calculated from the measured SPA was well above the limit of detection and within the calibration range. Table 1 lists the mass of TWP and the derived mass deposition rates (MDR) for the individual samples. Furthermore, the corresponding mean values of the two duplicate measurements, and the associated range of plausible values expressed as the 95% confidence intervals are provided.

Sample		TWP (μg)	95%-CI TWP (μg)	MDR ($\mu\text{g m}^{-2} \text{ day}^{-1}$)	95%-CI MDR ($\mu\text{g m}^{-2} \text{ day}^{-1}$)
DUET	A	172.8	73.4-282.0	928.3	394.5-1514.9
	B	141.4	60.1-230.7	759.6	322.8-1239.7
	<i>mean</i>	<i>157.1</i>	<i>89.4-236.3</i>	<i>843.9</i>	<i>480.2-1269.3</i>
DUE	A	48.6	20.7-79.3	261.2	111.0-426.3
	B	45.7	19.4-74.6	245.5	104.3-400.7
	<i>mean</i>	<i>47.2</i>	<i>26.8-70.9</i>	<i>253.4</i>	<i>144.2-381.1</i>

Table 1. Determined mass of tire wear particles (TWP) and calculated atmospheric bulk mass deposition rate of TWP (MDR) in duplicate samples (A and B) collected in parallel at two sites DUET and DUE on a four-weekly basis (30.01.2025 to 27.02.2025). The range of plausible values expressed as the 95% confidence interval (95%-CI) and the corresponding values for the mean mass of TWP mass and mean mass deposition rates at the two sites are also listed.

The TWP mass of the atmospheric deposition samples and the corresponding MDR were at the site close to a busy road (DUET) higher than at the DUE site that is further away from roads (Figure 5). The uncertainties of the individual samples are considerable, consequently, the differences between the TWP mass determined for i) the samples from the same site and ii) the samples from the two different sites are statistically not significantly different.

The uncertainties of the mass deposition rates (MDR) of tire wear particles reduce to -43 % to +50 %, when the mean values of the duplicate determinations from both locations are calculated using equation 1. In that case the differences between the



MDR of the two sites DUET and DUE were significant. The mean mass deposition rate of TWP at DUET was $843.9 \mu\text{g m}^{-2} \text{ day}^{-1}$ compared to $253.4 \mu\text{g m}^{-2} \text{ day}^{-1}$ at the DUE site (Table 1).

The measured peak areas of the six pyrolysis markers in atmospheric deposition samples can be projected onto the plane spanned by the first two principal components derived from PCA of the CMTT samples. The composition of the pyrolysis markers in the atmospheric deposition samples from DUET and DUE project closer to the CMTT samples from car tires than to those from truck and bus tires (Figure S12). This suggests that the TWP at these two sites were dominantly influenced by emissions from passenger cars. This also suggests that the lower range of the systematic error of the calibration constant, which was chosen to cover a mix of tires in the environment that is dominated by truck and bus tires, is too conservative for these specific sites and u_b is likely smaller than assumed.

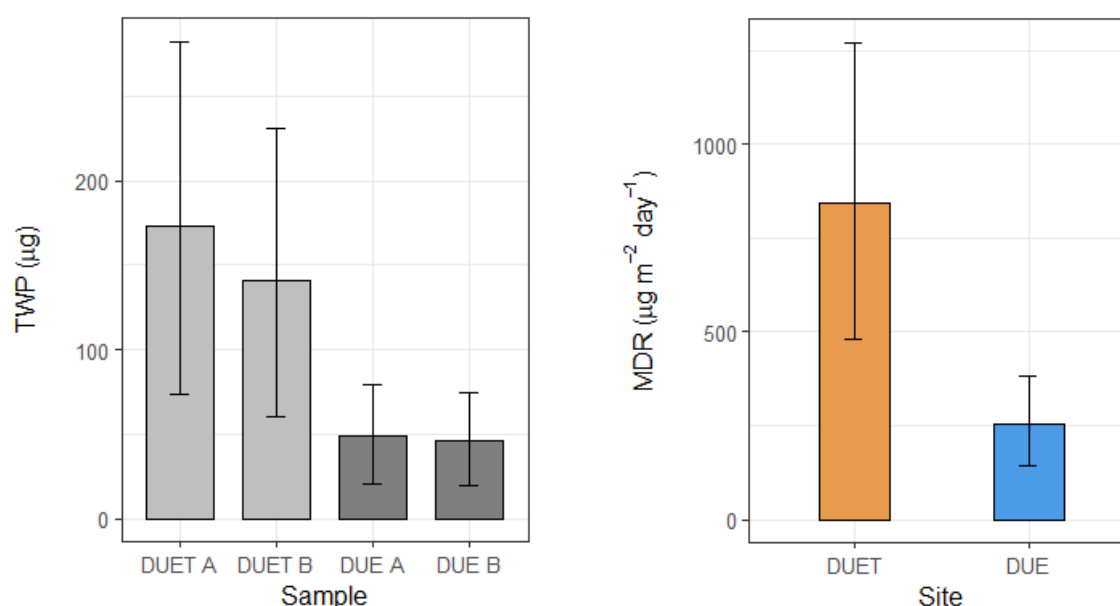


Figure 5. Comparison of the mass deposition rates of TWP at a site close to a busy road (DUET, brown) and a nearby site 200 m distance from roads (DUE, blue) calculated from atmospheric bulk deposition collected from 30.01.2025 to 27.02.2025. The left panel shows the mass of tire wear particles (TWP) determined in the duplicate samples (A and B) collected at the two sites (DUET and DUE). The mean mass deposition rates calculated from the duplicate samples for both sites are shown in the right panel. The error bars represent the expanded measurement uncertainties (95% confidence level).

The TWP masses in the environmental samples presented and the derived MDR represent a snapshot of atmospheric deposition of tire wear at two sites and should, therefore, be interpreted with care. Nevertheless, our values can be compared to those from literature to assess the plausibility of our data. In a recent study, scanning electron microscopy – a particle based method – was applied to determine the MDR of TRWP collected at increasing distances to a highway in Germany (DTV $\approx$ 100'000-



460 120'000) (Weinbruch et al., 2025). The MDR of TRWP was at a distance of 20 m from the highway 4'781 $\mu\text{g m}^{-2} \text{ day}^{-1}$
(calculated using the data provided in 40). Assuming that 50% of the TRWP mass is tire wear, the MDR at a 20 m distance
from the German highway reduced to 2'391 $\mu\text{g m}^{-2} \text{ day}^{-1}$, which is 2.5 times higher than the MDR we determined for DUET,
the site located 20 m from a road with a DTV of 19'000. Another study determined the MDR of tire wear particles at two urban
background sites in Oslo and Trondheim (Norway) using Py-GC-MS (Herzke et al., 2026). Unfortunately, the analytical
465 method used in this Norwegian study was not described in detail, which makes a quantitative comparison of the results with
our analyses of samples from Switzerland difficult. However, the mean MDR of TWP in Oslo and Trondheim were 557 $\mu\text{g m}^{-2} \text{ day}^{-1}$
and 191 $\mu\text{g m}^{-2} \text{ day}^{-1}$, respectively, which is comparable to the MDR of TWP at DUE, the suburban site considered
in this study. Comparisons with literature data are currently generally difficult because there is no widely accepted reference
method and various methods are used. Nevertheless, we conclude that the application of the analytical method developed in
470 this study leads to plausible values for TWP masses in atmospheric depositions and the derived MDR.

5 Conclusion

We propose a mass-based analytical method for the quantification of tire wear particles (TWP) in atmospheric deposition
samples. The method combines targeted sample pretreatment, including density separation and removal of matrix
interferences, with Py-GC-MS analysis of six characteristic pyrolysis products of tire rubber, namely butadiene, 4-
475 vinylcyclohexene, isoprene, limonene, styrene, and α -methylstyrene. The use of multiple pyrolysis markers originating from
the major rubber types used in tire manufacturing (NR, SBR, and BR) makes the method more robust against variations in tire
composition than approaches relying on only one or two markers.

Analysis of cryo-milled tire tread material from a selection of passenger car and truck/bus tires demonstrated that the sum of
the peak areas of the six selected markers is strongly correlated with tire tread mass. The applied calibration approach yielded
480 a coefficient of determination of 0.93 across all investigated tire types and allowed the quantification of TWP masses down to
a limit of detection of 0.16 μg . Application of the method to atmospheric deposition samples showed that the measured TWP
masses were well within the calibration range and resulted in deposition rates that are consistent with expectations based on
site characteristics and literature data.

An important feature of this work is the separate treatment of the different components of uncertainty and the calculation of
485 the total measurement uncertainty. The dominant source of uncertainty arises from differences in rubber composition among
tires and the unknown composition of tire mixtures present in environmental samples. This challenge is inherent to mass-based
marker methods and cannot be fully eliminated. However, the comparison of patterns of the six pyrolysis markers in
environmental samples with those measured in a broad range of tire materials provides a means to assess and constrain the
associated bias.

490 The proof-of-principle application further demonstrated elevated atmospheric deposition of TWP at a site located near a busy
road compared with a nearby suburban background location, confirming the suitability of the analytical approach for detecting



spatial differences in atmospheric TWP deposition. The presented approach is not restricted to atmospheric deposition. With appropriate adaptations of the sample preparation procedure, the approach should also be applicable to other environmental matrices, including airborne particulate matter, road dust, soils, sediments, and surface waters.

495

Appendix A Data Processing

A.1 Measurement of CMTT and Py-GC-MS sensitivity correction

The peak area of each pyrolysis marker for every measurement of a CMTT sample of mass x (in μg) is denoted as $PA_{i,c}(x)$ and $PA_{i,s}(x)$, depending on whether the measurement stems from method calibration or from external controls carried out in conjunction with the measurement of atmospheric deposition samples. The index i denotes the pyrolysis marker, i.e., butadiene, isoprene, VCH, styrene, α -methylstyrene, and limonene ($i = 1, \dots, 6$). Figure A1 shows the peak areas $PA_{i,c}(x)$ and $PA_{i,s}(x)$ for CMCTT-6 measured during method calibration ($PA_{i,c}(x)$) and the external controls ($PA_{i,s}(x)$) that are always measured together with the atmospheric deposition samples.

For all measurements of CMTT samples, linear regressions of $PA_{i,c}(x)$ and $PA_{i,s}(x)$ against the mass of CMTT x were calculated, $a'_{i,c}$ and $a'_{i,s}$ are the corresponding slopes of the regression lines describing the sensitivity of the measurement (change in peak area per μg of CMTT), and $b_{i,c}$ and $b_{i,s}$ are the intercepts representing possible offsets (peak area in the absence of CMTT).

$$PA_{i,c}(x) = a'_{i,c} \cdot x + b_{i,c} \quad (3)$$

$$PA_{i,s}(x) = a'_{i,s} \cdot x + b_{i,s}$$

All $b_{i,c}$ and $b_{i,s}$ obtained in this study did not deviate from zero (95% confidence). VCH was an exception in the calibration measurements, where a small intercept deviated from zero, as the measured peak areas for the different masses of CMCTT-6 lay on a straight line ($r^2=1.00$), see Figure S11. Table S3 shows the values for $a'_{i,c}$, $b_{i,c}$, $a'_{i,s}$ and $b_{i,s}$, including the corresponding p values and coefficients of determination (r^2) for the measurement of CMCTC-6 used for method calibration and on the days when the atmospheric deposition samples from DUET and DUE were analyzed. Since the intercepts $b_{i,c}$ and $b_{i,s}$ were negligible, the slopes were recalculated ($a_{i,c}$ and $a_{i,s}$), this time with the intercepts set to zero, i.e.



$$PA_{i,c}(x) = a_{i,c} \cdot x$$

$$PA_{i,s}(x) = a_{i,s} \cdot x$$

(4)

Changes in the sensitivity of the Py-GC-MS at the measurements of atmospheric deposition samples compared to the state
520 during the calibration measurements can be compensated by a correction factor $c_{i,s} = a_{i,c}/a_{i,s}$, and the projection of the Py-
GC-MS sensitivity behavior onto the sensitivity behavior during the calibration measurement can be written as follows

$$PA_{i,s}^p(x) = PA_{i,s} \cdot c_{i,s}$$

(5)

with $PA_{i,s}^p(x)$ the projected (or corrected) response (or peak area) for pyrolysis marker i when a mass x of CMTT sample s is
analysed.

525

A.2 Measurement of atmospheric deposition

The measured peak areas of the six pyrolysis markers in atmospheric deposition samples ($PA_{i,AD,s}$ with $i = 1, \dots, 6$) were
corrected based on the external controls that were measured with each series of atmospheric deposition samples. To account
for sensitivity changes of the Py-GC-MS, the measured peak areas were multiplied with the corresponding correction factors
530 $c_{i,s}$ of equation (3), i.e.

$$PA'_{i,AD,s} = PA_{i,AD,s} \cdot c_{i,s}$$

(6)

If the measurement of external controls and application of equation 3 were to result in a significant intercept, an offset
correction could be performed by using the estimated parameters from equation 3. However, this was not necessary in this
study. The sum of peak areas is then calculated as

535

$$SPA_{AD,s} = \sum_{i=1}^6 PA'_{i,AD,s}$$

(7)

The sum of peak areas in individual atmospheric deposition samples can be converted to the mass of TWP (in μg) by

$$TWP_{AD,s} = \frac{SPA_{AD,s}}{r \cdot c_f}$$

(8)



with $c_f = 297311 \mu g^{-1}$ the calibration constant derived from the analysis of all available CMTT samples (CMCTT-1 to CMCTT-18 and CMTTT-1 to CMTTT-5) as explained in the main text, and $r = 0.685$ the mean recovery of tire wear for the applied analytical method. Finally, the mass deposition rate MDR (in $\mu g \cdot m^{-2} \cdot day^{-1}$) is calculated as

$$MDR_{AD,s} = \frac{TW P_{AD,s}}{A \cdot t} \quad (9)$$

where A is the area of the inlet of the glass container used for sample collection ($0.00866 m^2$), and t is the sampling time (28 days).

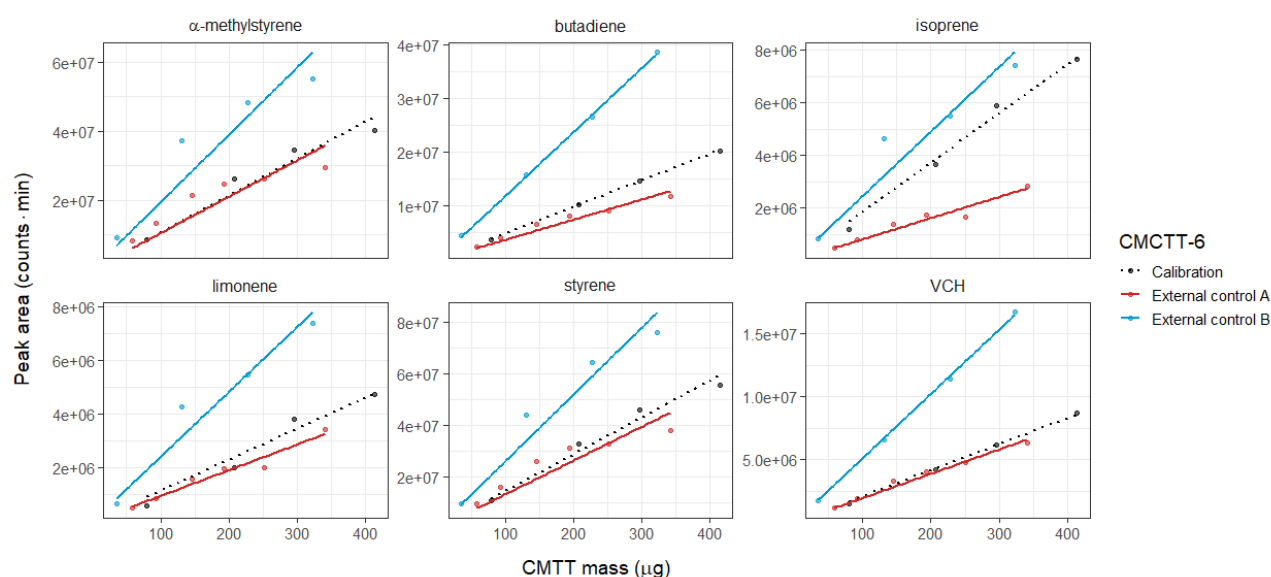


Figure A1. Peak area of the six pyrolysis markers against the mass of CMCTT-6 in the method calibration dataset and the two external controls used for data correction of the atmospheric deposition samples included in this study (DUET A, DUE A, DUET B, and DUE B).



Appendix B Uncertainty of Py-GC-MS sensitivity correction

555 The correction for changes of the Py-GC-MS sensitivity over time is not perfect. The calculated slopes ($a_{i,s}$) used for the correction have uncertainties which are, however, available as the standard errors of the regression analyses. These standard errors can be regarded as random and independent and are combined when the responses of all six pyrolysis markers are summed. The sensitivity corrected sum of peak areas from CMTT samples measured as external controls can be written as

$$SPA_s(x) = \sum_{i=1}^6 PA_{i,s}^p(x) \quad (10)$$

560

The corresponding absolute standard uncertainty $u_s(x)$ of $SPA_s(x)$ for the correction of a measurement of a CMTT sample s can be calculated as

$$u_s(x) = \sqrt{\sum_i u_{i,s}^2(x)} \quad (11)$$

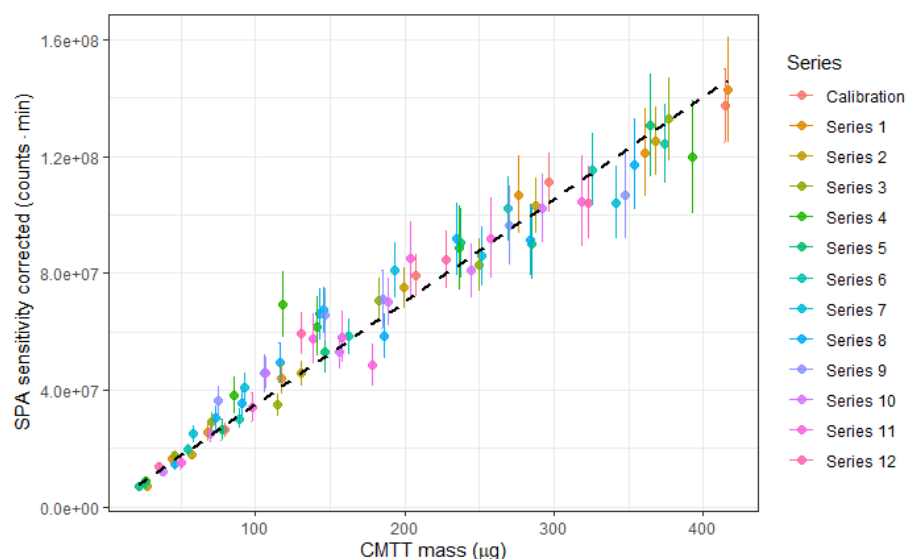
565 with $u_{i,s}(x)$ the absolute standard uncertainty for pyrolysis marker i . Note that $u_s(x)/x$ is constant and the standard uncertainty for $SPA_s(x)$ can also be expressed as a relative standard uncertainty σ_s . We measured thirteen series of CMCTT-6 in total, each on different days spanning a one-year period and each consisting of typically five different and known sample masses. The measurements of external controls allow the estimation of u_s . Figure B1 shows the sensitivity corrected sum of peak areas for all measurements of CMCTT-6 including the expanded uncertainty due to sensitivity correction, i.e. $\pm 2 \cdot u_s(x)$.

570 The range of the relative standard uncertainties for all thirteen series was $u_s = 4.6 - 8.1 \%$, we consider the upper value of 8.1 % as a conservative and realistic estimate for the uncertainty introduced by sensitivity correction.

The measured $SPA_s(x)$ of measurements can be converted to the corresponding CMTT mass using the relationship (or slope) of the measured sum of peak areas and CMTT mass in the calibration data set as the reference and proceed as outlined in sections A.1 and A.2.

575

580



595 **Figure B1.** Sensitivity corrected sum of peak areas of the six pyrolysis markers for the analysis of CMTT samples of known and
 variable mass (all CMCTT-6). The measurements shown are those of the calibration data set and the measurements of external
 controls, which were carried out in twelve series over a period of one year. The broken line indicates the linear regression of the
 measurements in the calibration data set, i.e. the measurements that served as the reference for the applied sensitivity correction.
 The error bars indicate the uncertainty of the sensitivity correction at 95% confidence level. Most measurements overlap with the
 600 regression line, indicating a realistic estimation of $u_s(x)$, the absolute standard uncertainty associated with the sensitivity correction.

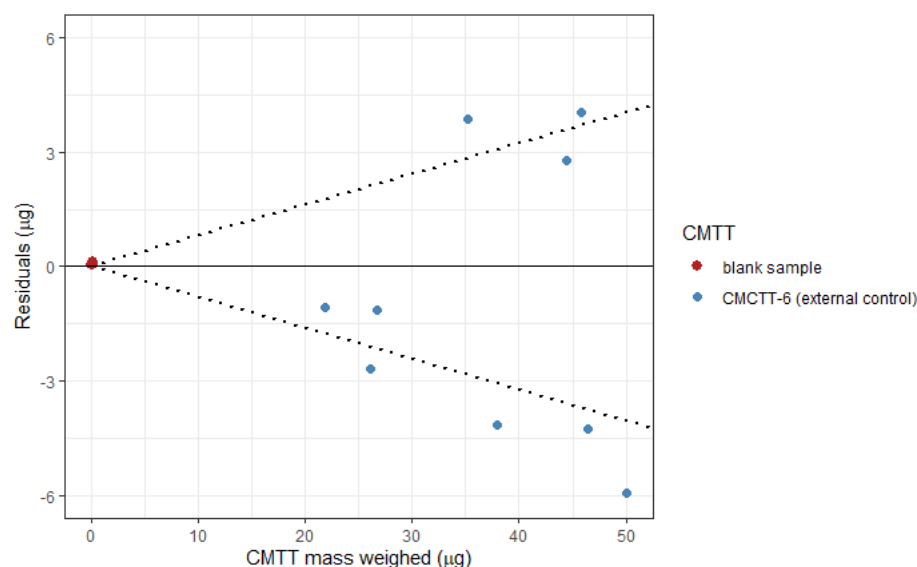


Figure B2. Difference of CMTT mass derived from sensitivity corrected SPA and the (*true*) weighed mass of CMTT for the available
 measurements of blanks and CMTT at low masses (denoted as residuals). The measurements of the seven blank samples (red dots)
 615 appear at this scale of the y-axis on top of each other. The CMTT measurements of CMCTT-6 are those shown in Figure B1 with
 CMTT masses below 50 µg. The dotted lines indicate the relative uncertainty of u_s of ± 8.1 %.



Code and data availability

The data and the code for data processing and generation of figures and tables are made available upon request.

Supplement link

620 The link to the supplement will be included by Copernicus.

Author contributions

All three authors (MAR, RK and CH) conceptualized the scientific ideas and shared the writing of the manuscript. MAR performed the measurements. MAR and CH did the data curation and the formal data analysis. RK and CH acquired funding and provided supervision.

625 Competing interests

The contact author has declared that none of the authors has any competing interests.

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Review statement

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