



## Research Paper

# A novel method for the quantification of tire and polymer-modified bitumen particles in environmental samples by pyrolysis gas chromatography mass spectroscopy

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## ABSTRACT

Tire and road wear particles may constitute the largest source of microplastic particles into the environment. Quantification of these particles are associated with large uncertainties which are in part due to inadequate analytical methods. New methodology is presented in this work to improve the analysis of tire and road wear particles using pyrolysis gas chromatography mass spectrometry. Pyrolysis gas chromatography mass spectrometry of styrene butadiene styrene, a component of polymer-modified bitumen used on road asphalt, produces pyrolysis products identical to those of styrene butadiene rubber and butadiene rubber, which are used in tires. The proposed method uses multiple marker compounds to measure the combined mass of these rubbers in samples and includes an improved step of calculating the amount of tire and road based on the measured rubber content and site-specific traffic data. The method provides good recoveries of 83–92% for a simple matrix (tire) and 88–104% for a complex matrix (road sediment). The validated method was applied to urban snow, road-side soil and gully-pot sediment samples. Concentrations of tire particles in these samples ranged from 0.1 to 17.7 mg/mL (snow) to 0.6–68.3 mg/g (soil/sediment). The concentration of polymer-modified bitumen ranged from 0.03 to 0.42 mg/mL (snow) to 1.3–18.1 mg/g (soil/sediment).

## 1. Introduction

Tire and road wear particles (TRWP) are estimated to be the largest single source of synthetic polymer particles in the microscopic size range (1  $\mu\text{m}$  - 1 mm), to the environment (Boucher et al., 2020; Knight et al., 2020), often referred to as microplastic particles. A large number of studies have been published on microplastic particles over the last years, however, there is still a lack of standardization and harmonization on how to analyze, quantify and report these findings (Lusher et al., 2021). Compared to the more conventional plastic types such as polyethylene terephthalate (PET) or polystyrene (PS) which are widely used in a large variety of products, the data on concentrations of TRWP in environmental samples is very limited (Baensch-Baltrusch et al., 2020). Measurements of TRWP in such samples have been hampered by

inadequate analytical methodology. The most commonly applied analytical method for microplastics today is visual analysis coupled to a chemical analysis step, such as Fourier transform infrared spectroscopy (FTIR). However, as tire particles contain black pigment (carbon black), the infrared light is absorbed and FTIR analysis is unable to identify the rubber content (Baensch-Baltrusch et al., 2020). A recent study has also demonstrated the potential for under-reporting of microplastics when only visual techniques such as FTIR are applied (Ribeiro et al., 2021).

Thermal methods, such as pyrolysis gas chromatography mass spectrometry (Py-GC/MS) (Unice et al., 2012; ISO, 2017a, 2017b, 2017c; Goßmann et al., 2021) and thermal extraction and desorption gas chromatography mass spectroscopy (TED GC/MS) (Eisentraut et al., 2018; Klöckner et al., 2019) are becoming more common, as these

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methods use the products of the thermal decomposition as markers to identify and quantify polymers and rubbers. Such methods can be used to potentially a) identify specific tire and asphalt markers present in TRWP and b) based on those numbers, assess the amount of rubber released into the environment.

A recent study raised questions over the selection of markers used for quantifying tire rubber and how these are extrapolated to a derivation of tire-mass (Rauert et al., 2021). This included the use of 4-vinylcyclohexene (4-VCH) as a marker as specified in the ISO technical specifications for soil and sediments (ISO, 2017a) and for air (ISO, 2017c). In Rauert et al. (2021), two additional pyrolysis marker compounds were tested, the SB hybrid dimer and SBB hybrid trimer. Both showed a large and inconsistent variability in the calculated %rubber content in analyzed reference tires ( $n = 39$ ) and were not recommended as viable single markers. This is contradictory to studies by Eisentraut et al. (2018) and Goßmann et al. (2021) which suggested using SB dimer for the quantification of SBR in personal vehicle tires.

Tires contain a wide range of substances, such as rubber materials, fillers, softeners, vulcanization agents and other additives (Baensch-Baltruschat et al., 2020; Sommer et al., 2018). Each type and brand of tires contain different amounts of these components. Thus, tires are a complex mixture to analyze. Two main types of rubber can be found in tires; natural rubber (NR, polyisoprene) and synthetic rubbers, which includes styrene butadiene rubber (SBR) and butadiene rubber (BR). Previous studies have reported that the total percentage of rubber in tire tread is 50% (w/w), of which SBR+BR contribute 44% in personal vehicle tires (PV), and NR contributes 45% in heavy vehicle tires (HV) (Unice et al., 2012). The rest of the tire consists of additional rubbers and other components, as described by Sommer et al. (2018). Another study has reported that PV tires has a total rubber content of 41%, in which SBR contributes 30% and BR 20% (Grigoratos and Martini, 2014). Thus, the total contribution of SBR+BR would be 20% (12 +8% of the tire mass). Other studies have reported smaller contributions of SBR+BR in PV tires, e.g. 20–30% of the total mass of the tire, with a 60:40 ratio between SBR and BR (Vogelsang et al., 2018). Another study used the global market share of rubber in PV tires to state that tires contain 11% SBR (Eisentraut et al., 2018). For heavy vehicles, previous studies have reported that HV tires contain mainly NR, even up to 100% NR. However, this has been disputed in the recent study of Rauert et al. (2021), which showed that SBR and BR products were present in all HV tires and even in higher concentration than some of the PV tires. The use of the NR component to measure the amount of tire has also been shown to be difficult, as the thermal decomposition of NR and plant material both will result in the presence of dipentene (polyisoprene) in an environmental sample (Eisentraut et al., 2018). SBR contains both a styrene and a butadiene component and can be formulated either as solution styrene butadiene rubber (SSBR) or emulsion styrene butadiene rubber (ESBR). SBR can also have a wide range of styrene content (16–45%) according to different polymer manufacturers (SI-1 Table S1). Tires made with SSBR are especially subject to variable styrene content as the solution process is difficult to perform consistently (ANON, 1996). A lack of knowledge on the variability of SBR+BR and NR content in both PV and HV tires is a challenge for quantifying TRWP in samples and need to be addressed.

Another potential source of microplastic particles to the environment is polymer-modified bitumen (PMB) (Vogelsang et al., 2018; Sundt et al., 2014) used in road asphalt. PMB usually constitutes 5% of the total road asphalt and is only used in the top layer of the road surface. Several countries including Australia, China, Denmark, Norway, Russia, Sweden and the United Kingdom (ANON, 2018), add PMB to their road surfaces to increase resistance to cracking and deformation (rutting) of the road surface (S. et al., 2012). In Norway, the annual release of microplastics from roads is estimated to be approximately 5000 metric tons (mt), in which PMB asphalt and tires are estimated to contribute 28 mt and 4500 mt, respectively (Vogelsang et al., 2018; Sundt et al., 2014, 2016). PMB can be manufactured using different polymers, such as styrene

butadiene styrene (SBS), styrene ethylene butadiene styrene (SEBS), low-density polyethylene (LDPE), ethylene vinyl acetate (EVA), polypropylene (PP) and styrene isoprene styrene (SIS) (Polacco et al., 2005, 2006; Giavarini et al., 1996; Panda and Mazumdar, 1999; Sengoz et al., 2009; M et al., 2003; Chen et al., 2002). In Norway, PMB asphalt makes up approximately 6% (3282 km) of the total state and county road network (Vegvesen, 2020; Kjølengender, 2019), however, it is used mainly in and around the largest cities and on roads where the traffic densities and speed is the highest. Thus, there is a potentially important source of rubber associated with PMB asphalt. SBS is the only polymer used in Norway, contributing 5% of the mass of PMB (NVF, 2013).

The SBS used for PMB bitumen is a block copolymer, made of blocks of polystyrene and polybutadiene (ANON, 2021), with a styrene content of 30% (w/w). When pyrolyzed at the same temperatures, SBR and SBS form the same pyrolysis products, but at different intensities (Tsuge et al., 2011). This is due to the different ratio of styrene and butadiene in the two polymers. For all pyrolysis products related to butadiene rubber, BR (Tsuge et al., 2011) will also produce the same pyrolysis products as SBR and SBS. As recently discussed in Rauert et al. (2021), the marker compounds and the conversion from rubber to tire described in current Py-GC/MS methodologies do not account for variability in tire composition of synthetic rubber. These methods also incorrectly assume that the SBR pyrolysis products are selective. This study aims to address these challenges.

Our study is aimed at quantifying the total mass of SBR+BR+SBS in environmental samples using pyrolysis products previously not explored as markers for SBR and SBS, as well as combining multiple pyrolysis products for the quantification in order to compensate for individual differences between types of tires. Further, the total mass of SBR+BR+SBS is used to calculate the mass of tire and PMB in a sample using different calculation approaches based on available traffic data and the measured SBR+BR content in reference tires relevant for the sample locations and sample time. The non-specificity of the SBR and SBS pyrolysis products in tire and environmental samples was also tested and can be found in [supplementary Information \(SI-10\)](#).

## 2. Experimental details

### 2.1. Chemicals and reference material

The reference standard SBR used in this study was SBR-1500 (Polymer Source Inc., Canada), a non-vulcanized SBR with 23.5% styrene content. The reference standard SBS polymer was Kraton D, a standard SBS (30% styrene) added to PMB in Norway and provided by the bitumen company Nynas AB (Drammen, Norway). Deuterated poly(1,4-butadiene-d6) (d6-PB, Polymer Source, Inc., Quebec, Canada) was used as an internal standard, as described in the method by Unice et al. (2012), ISO (2017a, 2017b). All standards were dissolved in chloroform (CHCl<sub>3</sub>, Sigma Aldrich). SBR and SBS were prepared in three different concentrations: 100 µg/mL, 500 µg/mL and 1000 µg/mL, and d6-PB was prepared at 2.5 mg/mL.

### 2.2. Sample collection and processing

Reference tire samples were collected from 31 unused tires using knives with disposable ceramic blades (Slice TM), or with tapping knives (Ironsides TM), using separate blades for each tire. The tire samples were donated from two major tire manufacturers, Bridgestone and Continental, and one tire import company, Starco Norge. Various environmental samples (snow, soil, gully-pot sediment) were collected from sites with high average annual daily traffic (AADT), and where PMB-asphalt was applied. Snow samples were collected in February (2019) at two sites; Skullerud (SK, Oslo, Norway, 71 250 AADT, 59°51'39.5"N 10°49'51.7"E) and Storo (ST, Oslo, Norway (50 950 AADT, 59°56'37.6"N 10°46'47.2"E). Snow cores were collected at 0 m, 1 m and 3 m distance from the road at Skullerud and 0 m from the road at Storo.

The length of the snow cores for each sample were measured and then packed in zip-lock bags (made of polyethylene, PE) and kept in freezer ( $-20\text{ }^{\circ}\text{C}$ ) until processing. The frozen snow sample was weighed and then melted in the zip-lock bag in room temperature. The volume of melt water was recorded and then transferred to pre-cleaned glass beakers using 1 mm sieves to remove large items. The samples were stirred by hand-shaking the beakers for 20 s before 16 mL subsamples were transferred to glass jars, that had been pretreated in the muffle furnace (Nabertherm, Germany) at  $550\text{ }^{\circ}\text{C}$  in order to remove any contamination. The subsamples were frozen ( $-20\text{ }^{\circ}\text{C}$ , 24H) and freeze dried (3–4 days, Leybold Heraeus Lyovac GT2). Dried snow material was then put directly into the pyrolysis cup by weight. Soil samples (SK-sed) from Skullerud (Oslo, Norway, 71 250 AADT,  $59^{\circ}51'39.5''\text{N}$   $10^{\circ}49'51.7''\text{E}$ ) were sampled August 27th and 28th (2018). They were collected as mixture samples at 0–1.5 m, 1.5–3 m and 3–4.5 m distance from the road, using Multi-increment sampling (MIS, > 30 subsamples of > 0.5 kg for each sample location). The samples were sieved with 1 mm sieves and placed in small glass jars (pre-treated in muffle furnace) for storage. The samples were then put directly into the pyrolysis cup by weight. Gully-pot sediment sample (SF) were sampled from the Smestad tunnel (Oslo, Norway, 44 060 AADT,  $59^{\circ}56'10.4''\text{N}$   $10^{\circ}40'47.7''\text{E}$ ). The gully-pot samples were collected from three different gully-pots inside the tunnel, collected during two tunnel wash events (5th of November 2018 and 21st of April 2020). The sediment samples were taken using a small Van Veen grab sampler and collected in disposable aluminum foil baking pans. Subsamples were collected with a pre-cleaned metal spoon (RO-water) and stored in small glass jars (pre-treated in muffle furnace). The glass jars were then frozen and freeze-dried as described for the snow samples. Dried sediment material was then put directly into the pyrolysis cup by weight. All samples were analyzed in triplicates (technical replicates) except for SK-0 m, which was analyzed in nine replicates and the (2018) samples of SF, which were single samples.

The proposed method focuses on samples where it is expected to find high concentrations of road contamination, low concentration of other synthetic polymers than tire and PMB-rubber, and low concentration of organic matter. This includes tunnel wash water, road-runoff, road dust, gully-pot sediments and in some cases also road-side soil. When analyzing these samples, it is recommended as a cost-benefit measure to analyze samples directly, either on glass-fiber filters or as freeze-dried material. However, if it is expected that the concentrations of tire and PMB in the sample are low and/or it is expected to find higher concentrations of other polymers or organic matter, it is recommended to include different steps of pre-treatment to minimize influence on pyrolysis marker compounds from competing sources. Such steps should be customized to each sample based on sample type and sampling location. For example, if analyzing urban road dust from larger cities, it could be expected that the samples also contain a large proportion of microplastics that is not related to tire and PMB, such as PET and PVC (O'Brien et al., 2021). In these cases, density separation (Klößner et al., 2019) targeting the tire and PMB fractions could be applied. For samples with high concentrations of organic matter, the organic matter can cause large background noise. This will make it more difficult to analyze low concentrations of tire and PMB, as well as influencing the marker compounds for tire and PMB with competing sources. To reduce the interference from organic matter, treatment with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) or Fenton's reagent could then be applied (Hurley et al., 2018). Another option would be to use a thermal desorption step to remove volatile compounds before pyrolyzing the sample (Okoffo et al., 2020a).

### 2.3. Pyrolysis gas chromatography-mass spectrometry

Samples were analyzed with a multi-shot pyrolyzer (EGA/PY-3030D) equipped with an auto-shot sampler (AS-1020E) (Frontier lab Ltd., Fukushima, Japan) coupled to a GC/MS (5977B MSD with 8860 GC, Agilent Technologies Inc., CA, USA). Samples were weighed (1–14 mg d.w. for environmental samples and 0.05–0.15 mg for tire samples)

into each pyrolysis cup. All samples were analyzed in triplicates. Internal standard (d6-PB) was added to the cup and the pyrolysis cup was placed in the auto-sampler of the pyrolysis unit. Blank samples were analyzed to assess potential contamination during sample preparation. These included empty pyrolysis-cups, cups with internal standard (10  $\mu\text{L}$ ) and cups with chloroform (30  $\mu\text{L}$ ) + internal standard (10  $\mu\text{L}$ ). Cups used for Pyrolysis GC/MS were new. Blank runs (with no cups) were performed between successive batches to avoid carry-over between samples. Standard solution samples of 25–30  $\mu\text{g}$  SBR were included as quality control samples (QC) and analyzed in between sample runs.

The samples were pyrolyzed with single-shot mode at  $700\text{ }^{\circ}\text{C}$  for 0.2 min (12 s). Injections were made using a 50:1 split and with a pyrolyzer interface temperature at  $300\text{ }^{\circ}\text{C}$ . Further details on the Py-GC/MS setup are given in SI-2 Tables S3–3.

### 2.4. Total SBR+BR+SBS quantification

To mitigate the issue associated with the chemical complexity of tires and the inadequate availability of standards for the identification of the individual components, a total SBR, BR, and SBS concentration approach was adopted. For this purpose, the total ion chromatogram (TIC) of both SBR1500 and SBS was thoroughly investigated by manual inspection, employing MZmine 2 (Pluskal et al., 2010). The peaks that showed the least difference in peak height between SBR and SBS, were selected and investigated further as potential markers. Using different combination of possible markers, the best fit for quantifying both SBR and SBS in the same sample was determined by the marker combinations with the lowest standard deviation when applied to SBR1500 + SBS. The selected markers consisted of  $m/z$  78 Da for benzene,  $m/z$  118 Da for  $\alpha$ -methylstyrene,  $m/z$  117 Da for ethylstyrene and  $m/z$  91 Da for butadiene trimer (first trimer in the TIC) (SI Table S2). A set of calibration curves were prepared for three different ratios of SBR and SBS (20:80, 40:60 and 80:20). Masses of 1  $\mu\text{g}$ , 2  $\mu\text{g}$ , 5  $\mu\text{g}$ , 25  $\mu\text{g}$ , 100  $\mu\text{g}$  and 150  $\mu\text{g}$ , were inserted into pyrolysis cups ( $n = 3$ ) and spiked with 25  $\mu\text{g}$  d6-PB as internal standard. The summarized peak height of all marker compounds is normalized against the peak height of d6-PB and then plotted against the mass of SBR+SBS at each calibration level to form the calibration curve ( $R = 0.99$ ,  $p < 0.05$ , Fig. S1).

### 2.5. Calculation of tire and PMB

The concentration of tire and PMB in the sample is calculated via a set of equations based on the available data in each case. The flow chart presented in Fig. 1 explains which equations to use in different scenarios.

The first step in the calculation process is to determine if PMB particles are expected in the sample. If so, the next step is to determine if traffic data for the sample location can be collected. The traffic data needed is the annual average daily traffic (AADT), the ratio between personal vehicles (PV) and heavy vehicles (HV) for each road stretch and the use of studded tires or non-studded tires. The second input are sets of emission factors (EF) for tire and road wear. Emission factors are representative values that relates a quantity of a pollutant to a specific activity that leads to the release of this pollutant (Agency, 2021). For example, by measuring the tire loss in mass from driving a personal vehicle in different conditions such as highway and urban driving, previous studies have derived the mass of tire particles (mg) per kilometer driven by a personal vehicle (v/km). For tire wear, the proposed emission factors from Klein et al. (2017) were used. For highway driving, the EFs for personal vehicles (PV) is 0.104 g per vehicle kilometer driven (g/vkm) and 0.668 g/vkm for heavy vehicles (HV). For urban driving, the EFs are higher; 0.132 g/vkm for PV and 0.850 g/vkm for HV (Table S5). For road wear, the central bureau for statistics in the Netherlands (Anon, 1998), reported EFs for low density vehicles (personal vehicles, PV) at 7.9 g/vkm and for high density vehicles (heavy vehicles, HV) at 38 g/vkm. Roughly 5 times higher emissions are

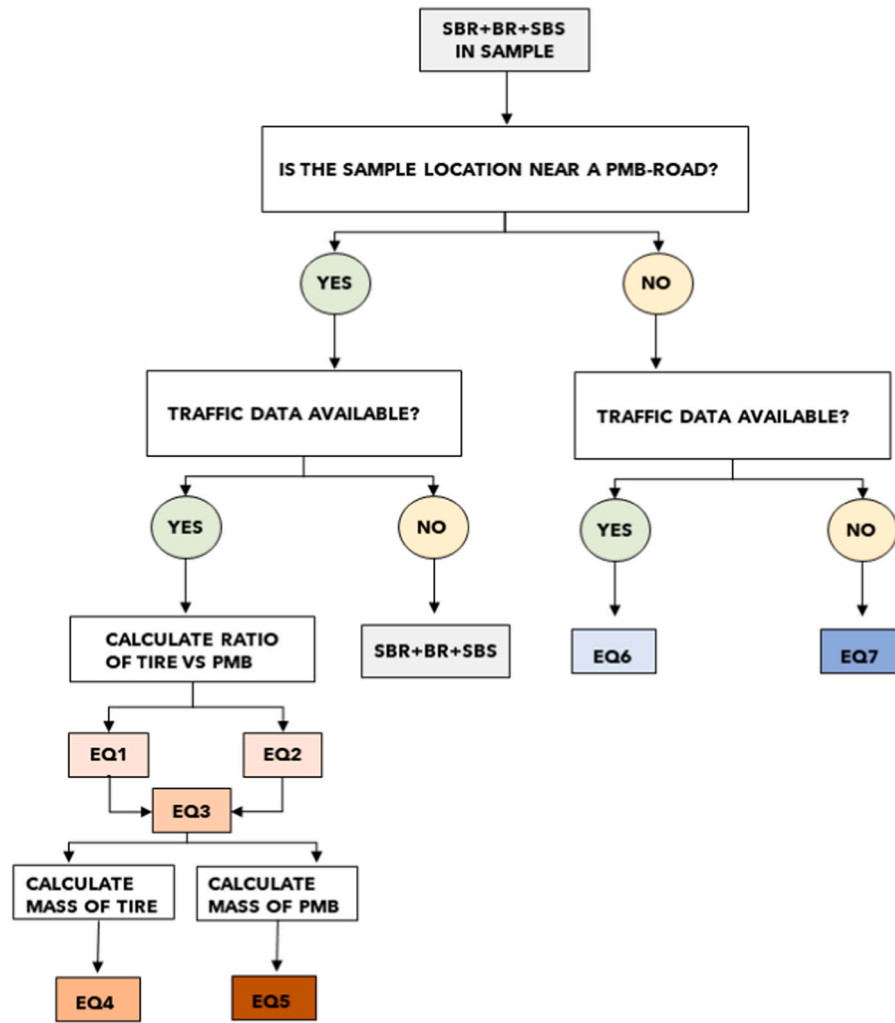


Fig. 1. Flowchart guiding the selection of the most appropriate calculation (equation) dependent on the scenario and available data.

expected from HV compared to PV. In Norway, the use of studded tires is extensive, thus a lot of the work on road wear has been focused on the use of studded tires. The term SPS is used for “specific studded tire road wear”, which is estimated to be 5–10 g/vkm for PV (NVF, 2013) and roughly 5 times higher for HV. In the national estimations of PMB, Vogelsang et al. (2018) used 7.5 g/vkm as the EF for road wear. However, the use of studded tires varies in different locations due to climate and legislation. The correct percentage of studded tires at each location needs to be applied in order to calculate the emission of road wear at a specific site. For this study, three levels of EFs for road wear with studded tires (5, 7.5 and 10 g/vkm) were used in order to reflect the variation in EFs reported by different studies. It is assumed that the road wear from non-studded tires is insignificant when compared to studded tires (Sörme and Lagerkvist, 2002). For non-studded tires, the Norwegian Public Roads Administration reports that the road wear from non-studded winter tires and summer tires are 40 times lower than the wear from studded tires (Snilsberg, 2020). This corresponds to similar values reported from New Zealand, where road wear EFs for non-studded tires (PV) are reported to be 0.44 g/vkm when the asphalt has 50% bitumen and 0.09 g/vkm for 10% bitumen (Kennedy et al., 2002). The EFs are therefore corrected for the ratio of studded tires used at the sample location (Table SI-5). With this information, it is possible to estimate the mass of tires and PMB produced over a given time at any site (Eq. 1, based on road specific tread emission from Vogelsang et al. (2018)). These estimates are used to determine the expected ratio between tire and PMB, which then gives the expected ratio between

SBR+BR and SBS in a sample.

$$EM_T = (L_r * N_{v,r,t} * ((R_{PV} * EFT_{PV}) + (R_{HV} * EFT_{HV}))) \quad (1)$$

$$EM_A = L_r * N_{v,r,t} * (((R_{PV-st} * EFA_{PV-st}) + (R_{PV-nst} * EFA_{PV-nst}) * R_{PV}) + ((R_{HV-st} * EFA_{HV-st}) + (R_{HV-nst} * EFA_{PV-nst}) * R_{HV})) \quad (2)$$

Where:

- $EM_T$  is estimated mass of tire in a sample (mg);
- $EM_A$  is the estimated mass of asphalt in a sample (mg);
- $L_r$  is the length of the particular road stretch  $r$  (km);
- $N_{v,r,t}$  is the number of vehicles that have travelled the particular road stretch  $r$  during the given time period  $t$ ;
- $EFT_{PV}$  is the emission factor for personal vehicle tires (mg/vkm);
- $EFT_{HV}$  is the emission factor for heavy vehicle tires (mg/vkm);
- $R_{PV}$  is the ratio of personal vehicles at the sampling location;
- $R_{HV}$  is the ratio of heavy vehicles at the sampling location;
- $EFA_{PV-st}$  is the emission factor for asphalt based on studded personal vehicle tires (mg/vkm);
- $EFA_{PV-nst}$  is the emission factor for asphalt based on non-studded personal vehicle tires (mg/vkm);
- $EFA_{HV-st}$  is the emission factor for asphalt based on studded heavy vehicle tires (mg/vkm);
- $EFA_{PV-nst}$  is the emission factor for asphalt based on non-studded heavy vehicle tires (mg/vkm);

$R_{PV-st}$  is the ratio of personal vehicles (PV) with studded tires at the sampling location, compared to all PV vehicles;

$R_{PV}$  is the ratio of personal vehicles (PV) at the sampling location compared to all vehicles;

$R_{HV-st}$  is the ratio of heavy vehicles (HV) with studded tires at the sampling location, compared to all HV vehicles;

$R_{HV}$  is the ratio of heavy vehicles (HV) at the sampling location, compared to all vehicles.

As the asphalt contains 5% bitumen and the bitumen contains 5% SBS, the estimated mass of SBS in the sample is found by applying the conversion factor ( $CF_{SBS}$ ) of 0.0025 to the mass of asphalt. The mean SBR+BR concentration of reference tires (PV and HV combined,  $SBR+BR_{RT}$ ) is used to convert the estimated mass of tires to estimated mass of SBR+BR. The ratio of SBS can then be established for each sample location by the following Eq. 3.

$$R_{SBS} = \frac{(EM_A * CF_{SBS})}{(EM_T * SBR + BR_{RT}) + (EM_A * CF_{SBS})} \quad (3)$$

where

$R_{SBS}$  is the estimated ratio of SBS from the total SBR+BR+SBS concentration;

$EM_A$  is estimated mass of asphalt in a sample (mg);

$CF_{SBS}$  is the conversion factor for asphalt to SBS (0.0025);

$EM_T$  is estimated mass of tire in a sample (mg);

$SBR + BR_{RT}$  is the measured SBR+BR concentration in reference tires ( $\mu\text{g}/\text{mg}$ ).

Using the estimated ratio of SBS for each sample location, the expected mass of tire ( $M_T$ ) and PMB ( $M_{PMB}$ ) in that sample can be calculated, using Eqs. 4 and 5. The variables  $S_{PV}$  and  $S_{HV}$  are the mean mass of SBR+BR measured in personal vehicle (PV) tires and heavy vehicle (HV) tires, respectively. These values are obtained from analyzing the reference tire samples.

$$M_T = \frac{M_S - (M_S * R_{SBS}) * Sc}{(S_{PV} * R_{PV}) + (S_{HV} * R_{HV})} \quad (4)$$

$$M_{PMB} = \frac{(M_S * R_{SBS})}{C_{PMB}} \quad (5)$$

where

$M_T$  is the mass of tire in a sample (mg);

$M_{PMB}$  is the mass of PMB in a sample ( $\mu\text{g}$ );

$M_S$  is the mass of SBR+BR+SBS in a sample ( $\mu\text{g}$ );

$R_{SBS}$  is the estimated ratio of SBS from the total SBR+BR+SBS concentration for each location;

$Sc$  is the conversion factor for styrene content in standards vs tires;

$S_{PV}$  is the mass of SBR+BR in personal vehicle tires ( $\mu\text{g}/\text{mg}$ );

$R_{PV}$  is the ratio of personal vehicles at the sampling location;

$S_{HV}$  is the mass of SBR+BR in heavy vehicle tires ( $\mu\text{g}/\text{mg}$ );

$R_{HV}$  is the ratio of heavy vehicles at the sampling location;

$C_{PMB}$  is the conversion factor for SBS to PMB, based on the percentage SBS in PMB (0.05).

The variable  $Sc$  is applied if the styrene content of the standards used for the calibration curve differs from the expected styrene content in tires. The styrene content differs between different types of tires, based on the ratio of SBR to BR, as well as the type of SBR used in each tire (Table S1). SBR has on average 27.4% styrene and BR has 0% styrene. According to Unice et al. (2012), the average ratio of SBR to BR is 65–35%, which means that most tires will have a styrene content of 17.8% ( $0.274 \times 0.65 = 0.178$ ). SBS used in PMB has an average styrene content of 30%. For each environmental sample location, the expected styrene content of the sample can be calculated using the ratio of SBS ( $R_{SBS}$ , Eq. 5). As an example, the  $R_{SBS}$  at Skullerud is 5.4%. This means that in the samples from Skullerud, the expected the styrene content from tire and PMB together will be 19.4%.

( $0.178 + (0.30 * 0.054) = 0.194$ ). The calibration curve used in this

method contains on average 27% styrene (Table SI-4). To correct for this difference, the correction factor ( $Sc$ ) is calculated as:  $(1 - 0.27) / (1 - 0.194) = 0.91$  for Skullerud samples. This approach is then applied to all sample locations to correct for styrene differences.

Using Eqs. 4 and 5, the mass of tire and PMB in the sample will be obtained from the measured SBR+BR+SBS values. As both the ratio of SBS in PMB bitumen (Vogelsang et al., 2018; NVF, 2013; Anon, 1998) and the SBR+BR mass in PV and HV tires display a large variation of values (Rauert et al., 2021), only applying the mean value of SBS and SBR+BR to calculate PMB and tire would lead to large uncertainties. As an attempt to deal with this, a Monte Carlo prediction model (100,000 simulations, Crystal Ball in Excel (Oracle)) is used to calculate the predicted mean value of tire and PMB and predicted standard deviation. The Monte Carlo simulation predicts what the tire and PMB values in the sample will be based on the SBR+BR values found in the reference tires of this study and the emission factors for road wear, as described above.

If the sample is expected to contain PMB-particles, but no traffic data is available, then it will not be possible to apply Eqs. 1–5. For these locations, reporting the combined concentration of SBR+BR+SBS will give information on the amount of rubber present in the sample, although the separation between the rubber types will not be possible.

If the sample is collected near a location where PMB is not applied to the asphalt, then it can be expected that SBS is not present in the sample, thus the four chosen markers will give the total mass of SBR+BR. Simplified versions of Eq. 4 can then be applied to obtain the mass of tire in the sample. If traffic data for the location is obtained, then Eq. 6 is applied. If there is no traffic data available, Eq. 7 can be applied. For this approach, a calibration curve based on SBR1500 alone can be applied and the  $Sc$  is calculated based on the styrene content of SBR1500 and tires alone.

$$M_T = \frac{M_{SB} * Sc}{(S_{PV} * R_{PV}) + (S_{HV} * R_{HV})} \quad (6)$$

$$M_T = \frac{M_{SB} * Sc}{S_V} \quad (7)$$

where

$M_T$  is the mass of tire in a sample (mg);

$M_{SB}$  is the mass of SBR+BR in a sample ( $\mu\text{g}$ );

$Sc$  conversion factor for styrene content in standards vs tires;

$S_{PV}$  is the mass of SBR+BR in personal vehicle tires ( $\mu\text{g}/\text{mg}$ );

$R_{PV}$  is the ratio of personal vehicles at the sampling location;

$S_{HV}$  is the mass of SBR+BR in heavy vehicle tires ( $\mu\text{g}/\text{mg}$ );

$R_{HV}$  is the ratio of heavy vehicles at the sampling location;

$S_V$  is the average mass of SBR+BR in vehicle tires ( $\mu\text{g}/\text{mg}$ ).

## 2.6. Statistical analysis

The statistical analysis and modelling were performed using RStudio 1.3.1093 (Team, 2020), R version 4.0.4 (2021–02–15). Following packages were used for the analysis: ggplot-package (Lai et al., 2016) (ggplot2\_3.3.3).

The uncertainty analysis was performed by using Excel Monte-Carlo Add-In Crystal Ball (Team, 2021). Using the crystal ball applications, both Eqs. 4,5 and 6 were simulated 100'000 times, and the application provides statistics for the simulation in order to obtain the mean value and standard deviation of each analyzed sample.

## 3. Results and discussion

### 3.1. Total concentration of SBR+BR+SBS

#### 3.1.1. Accuracy and precision of the method

None of the marker compounds were detected in any of the blank cups or the solvent blanks tested. The limit of detection (LOD,  $3xS/N$ ) for the four markers was between 1 and 2  $\mu\text{g}$  of SBR+SBS (SI-6, Table S6)

and the limit of quantification (LOQ, 10xS/N) was between 1 and 5 µg.

Method accuracy (%) was determined via standard addition of SBR and SBS (alone and in combination) into environmental samples and one tire reference sample. Accuracy was 85–151% (SI-7, Tables S7-S10). The calculation of recovery is explained in SI-7. Poorer precision was observed in the lowest concentrations approaching the LOQ, which is expected. This is due to observed heterogeneity in concentrations of SBR+BR in the tire itself, and due to signal-noise levels approaching the LOD (Vogelsang et al., 2018).

### 3.1.2. Concentration of SBR+BR+SBS in reference tires

SBS is not present in the reference tires as confirmed by one of the largest tire manufacturers (Bridgestone and Rødland, 2020). Thus, the results from using the SBR+BR+SBS-method on pure tire samples can be considered to contain only SBR and BR. The concentration of SBR+BR measured in the reference tires using the mixture markers showed a large range of values (115–682 µg/mg, n = 31), with an average SBR+BR concentration of  $319 \pm 127$  µg/mg (average  $\pm$  standard deviation) for all tires (Table 1, Fig. 2). However, to demonstrate that the proposed marker combinations are more suitable for the Norwegian reference tires than previously proposed markers (4-VCH, SB dimer, SBB trimer), all reference tires have been quantified using different markers. As seen in Table 1, the % standard deviation (standard deviation compared to the average value), shows that the variation in SBR+BR concentrations is lower when using the proposed mixture of *benzene*,  *$\alpha$ -methylstyrene*, *ethylstyrene* and *butadiene trimer* for quantification compared to the other markers. This is supported by several studies, showing that the use of multiple markers can give more reliable results, and are less impacted by possible interference compared to single markers (Okoffo et al., 2020b; Ribeiro et al., 2020; Breerton, 2007).

The reference tires can also be grouped in two major groups; by car type (PV vs. HV) and by season (summer vs winter, all-year), however, none of these groups were significantly different to each other (see SI-8 for boxplot and statistical analysis). When calculating the mass of tires based on the measured mass of SBR+BR, both Eqs. 4 and 6 is designed to use SBR+BR values for PV and HV tires for the seasonality relevant for the samples. For example, for snow samples, the PV and HV values for winter tires were applied. Using Eq. 7, the average SBR+BR for all tires can be applied.

All the proposed markers (*benzene*,  *$\alpha$ -methylstyrene*, *ethylstyrene* and *butadiene trimer*) displayed higher variability in the HV tires compared to the PV tires. The marker *benzene* is the most stable marker for both types of tires, showing a st.d. of 22% in PV and 44% in HV (SI Table S10). The marker  *$\alpha$ -methylstyrene* is the least stable marker, with a 96% standard variation across all tires, which illustrates the difficulty of measuring different tires with different rubber contents. However,  *$\alpha$ -methylstyrene* has the lowest percentage standard deviation when used in a combination of SBR and SBS, thus it is needed for environmental samples where it is expected to find tires and PMB-particles in a mixture. For all the sample types included in the study, the contribution ratio (%) of each marker is tested using Kruskal-Wallis test (Table S11). The results show that the ratios of *benzene*,  *$\alpha$ -methylstyrene*, *ethylstyrene* and *butadiene trimer* were significantly different between the sample types tested (SI Fig. S6). Samples that contain a balanced mixture of SBR and SBS have a lower percentage of *benzene* and higher percentage of  *$\alpha$ -methylstyrene*

**Table 1**

The table compares the average concentration and % standard deviation of SBR+BR in reference tires (n = 31) using the mixture markers (*benzene* +  *$\alpha$ -methylstyrene* + *ethylstyrene* + *butadiene trimer*), the 4-vinylcyclohexene (4-VCH), the SB dimer and the SBB trimer for quantification.

	<i>benzene</i> + <i><math>\alpha</math>-methylstyrene</i> + <i>ethylstyrene</i> + <i>butadiene trimer</i> (µg/mg)	4-VCH (µg/mg)	SB (µg/mg)	SBB (µg/mg)
PV mean	311.1	93.6	364.1	193.9
PV std. %	26.5	44.8	68.0	66.7
HV mean	329.5	144.9	335.5	266.4
HV std. %	51.0	62.1	89.8	92.8
All tires mean	319.1	116.0	351.6	225.6
All tires std. %	39.7	61.8	77.1	85.3

and *ethylstyrene*. Looking at the average *benzene* percentage, the gully-pot samples from Smestad were slightly lower compared to the snow samples and the soil samples. Gully-pots are expected to only retain minor fractions of tire particles and mainly particles above 50 µm (Vogelsang et al., 2018). The knowledge on PMB-particles is limited, however, as these contain a very small fraction of rubber (5%) and mainly mineral components, it should be expected that PMB particles have a higher density than tire particles. It is therefore more likely that a larger fraction of PMB compared to tire particles are retained in gully-pots. This could potentially explain the difference in the *benzene* percentage observed for the Smestad gully-pot samples, as the PMB particles would contribute to a higher percentage of the styrene-related markers. As described in chapter 2.2, the present proposed method is optimized for samples where it is expected that SBR+BR+SBS are the main microplastic component. For example, a recent study by Goßmann et al. (2021) showed that TWP was the main microplastic component of road dust, with 5 g/kg TWP compared to just 0.3 g/kg of other microplastics components (d.w.). Additional method preparation steps including density separation (Klößner et al., 2019) may be required if samples are expected to contain significant amounts of interfering polymer types, such as polyvinyl chloride (PVC), polyethylene terephthalate (PET), acrylonitrile-butadiene-styrene copolymer (ABS) and polystyrene (PS). PVC and PET share *benzene* as a pyrolysis product, while ABS and PS will produce  *$\alpha$ -methylstyrene* which are also produced by TRWP pyrolysis.

Although there are significant differences between marker ratios of different sample types, the average contribution of each marker is stable and can be used to verify that the samples are not substantially influenced by compounds other than SBR, BR and SBS. Differences in the marker ratios can in fact contribute to better understanding of the samples, and additionally to determine whether additional sample preparation steps are needed or not, and finally to have an assumption of how influenced the sample is from SBS.

### 3.2. Calculation of Tire and PMB in environmental samples

The use of the calculation method (Eqs. 4 and 5) is demonstrated on the environmental samples analyzed, Skullerud snow (SK), Skullerud soil (SK-sed) and Smestad tunnel gully-pot sediment (SF) (Table 2). The SBR+BR+SBS concentration for each individual sample can be found in Table S9-S10. The SK and SF samples were collected during winter, so the winter tire concentrations (PV, HV) were applied. For the SK-sed samples, the average SBR+BR for summer and winter tires combined was applied. Using the Monte Carlo simulations, the average predicted tire and PMB concentration in each sample was calculated. It needs to be pointed out that the calculation will not be able to predict how the actual transport pattern between tire and PMB might change with distance, due to differences in size or density. This calculation assumes that the ratio between tire and PMB is constant at all distances analyzed in this study. The assumptions apply for the SK and SK-sed samples. The highest concentration of tire particles was found in gully-pot samples (SF). One of the gully-pots (SF1) was sampled both in 2018 and 2020, and the concentrations found in 2020 were significantly higher ( $66.3 \pm 184$  mg/g, predicted average  $\pm$  standard deviation using 100,000 Monte Carlo simulations), compared to 2018 ( $12.2 \pm 33.8$  mg/

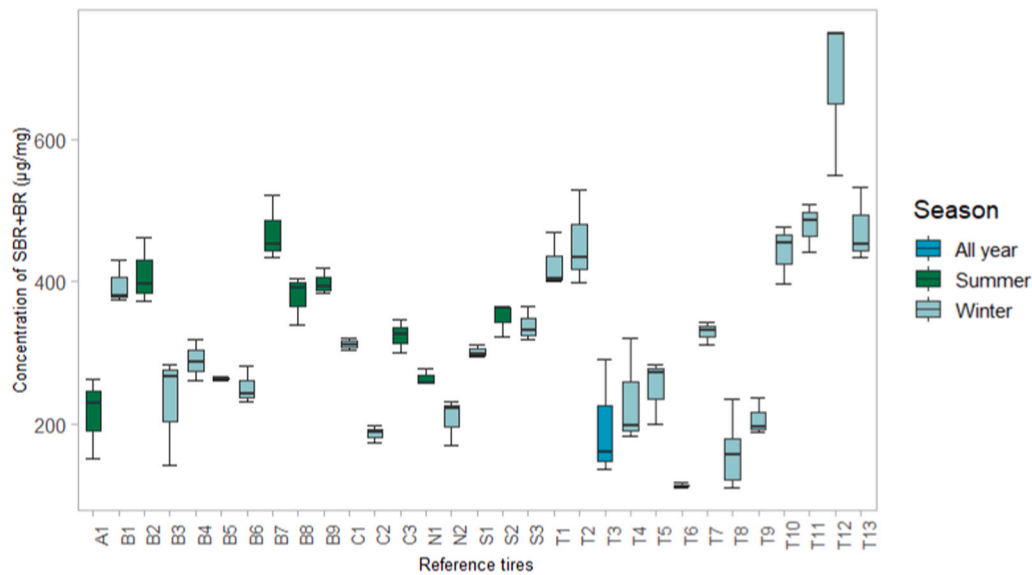


Fig. 2. Concentration of SBR+BR (µg/mg) in reference tires. Tires A1-S3 are personal vehicle tires (PV) and T1 to T13 are heavy vehicle tires, all analysed in triplicates? (n = 3). Type of tire is depicted by color.

Table 2

The table summarizes the results from using Eq. 4, where the input variables  $R_{SBS}$ ,  $S_{PV}$  and  $S_{HV}$  (in yellow) have a distribution assumption fitted to the values and the variables  $M_S$ ,  $S_C$ ,  $R_{PV}$  and  $R_T$  (in white) are constant. The output value  $M_T$  (in blue) is then predicted with 100,000 Monte Carlo simulations, which gives an average  $M_T$  and the standard deviation for each sample. The average  $M_T$  and standard deviation for all SK and SF samples is calculated based on the predicted average  $M_T$ .

Sample	Output values	Input variables							Predicted values	
	$M_T$ (mg/g, mg/mL)	$M_S$ (µg/g, µg/mL)	$R_{SBS}$	$S_C$	$S_{PV}$ (µg/mg)	$S_{HV}$ (µg/mg)	$R_{PV}$	$R_{HV}$	Average $M_T$ (mg/g, mg/mL)	Standard deviation (mg/g, mg/mL)
SK-0m	1.7	494.7	0.054	1.00	278.6	318.0	0.88	0.12	1.7	3.6
SK-1m	1.6	490.3	0.054	1.00	278.6	318.0	0.88	0.12	1.7	3.6
SK-3m	0.10	30.0	0.054	1.00	278.6	318.0	0.88	0.12	0.11	0.22
SK-sed-0m	4.9	1614.2	0.054	1.00	311.1	329.5	0.88	0.12	4.9	0.04
SK-sed-1.5m	4.8	1601.2	0.054	1.00	311.1	329.5	0.88	0.12	4.8	0.04
SK-sed-3m	3.7	1211.8	0.054	1.00	311.1	329.5	0.88	0.12	3.7	0.03
SF1-2018	10.7	3351.8	0.048	1.00	278.6	318.0	0.92	0.08	12.2	33.8
SF1-2020	62.9	18606.3	0.048	1.00	278.6	318.0	0.92	0.08	66.3	184.0
SF2-2020	5.6	1664.5	0.048	1.00	278.6	318.0	0.92	0.08	5.9	16.5
SF3-2020	8.7	2564.7	0.048	1.00	278.6	318.0	0.92	0.08	9.1	25.4

g). The main reason for this could be the time of sampling, as the 2018 samples were collected in November, just before the winter season and the 2020 samples were collected in April, just after the winter season. As winter tires, both studded and non-studded are used in Oslo, it is expected to find higher concentrations of tire and road wear particles after the winter season compared to before. The concentration of tire found in the other two gully-pots were significantly lower than SF1 (Table 2). The reason for these differences may be that the gully-pots have not been emptied at the same time, or SF1 received more tire and PMB-particles, being the gully-pot closest to the tunnel inlet. The concentrations of tire found in the SK-sed soil at 0 and 1.5 m distance from the road were similar ( $4.9 \pm 0.04$  and  $4.8 \pm 0.04$  mg/g). At 3 m distance, the predicted tire concentration was lower ( $3.7 \pm 0.03$  mg/g). Same concentrations were found for both 0 m and 1 m distance from the road in the SK snow samples ( $1.7 \pm 3.6$  mg/mL). At 3 m distance, a significantly lower predicted concentration was found ( $0.11 \pm 0.22$  mg/mL). The results using the Monte Carlo simulations also show that there is a large standard deviation in the predicted concentrations. This is related to the

large variations of SBR+BR-values found in the reference tires, as explained in chapter 3.2.2. A comparison of the SF gully-pot sediment and the SK-sed soil samples shows that the retention found in the road-side soil is comparable to the retention in gully-pots. This confirms that soil retention could be an important step in retaining tire particles from further dispersion from the road system. The results found in this study are comparable to other studies using Py-GC/MS methods to measure the amount of tire particles in environmental samples. Previous studies have reported findings of 9100 µg/g of TRWP in roadside soil (average value, range 200–20,000 µg/g d.w.) (Unice et al., 2013). However, the method applied by Unice et al. assumes that a TRWP particle contains 50% tire tread and 50% minerals (or other road components), as well as a fixed 25% rubber content in all tire tread particles. A recent study by Klöckner et al. (2021) reported a possible 75% tire tread in the TRWP in their study, showing that a fixed 50% tread content does not apply to all TRWPs. As the proposed method presented here calculates tire tread and PMB concentrations separately, and not TRWP, comparisons with other studies need to take this into account. No comparable gully-pot samples

analysed with Py-GC/MS were found. However, three studies using TED-GC-MS have analyzed sludge samples from road treatment systems and found between 16 and 150 mg/g TRWP, based on 50% tread content (Eisentraut et al., 2018; Klöckner et al., 2019). Mengistu et al. (2021) studied gully-pot sediments in Norway using simultaneous thermal analysis (STA), Fourier transform infra-red (FTIR) and parallel factor analysis (PARAFAC). Concentrations of tire particles were found to be between 1 and 150 mg/g (Mengistu et al., 2021), which is comparable to the present study. However, as the sampling sites in the study by Mengistu et al. (2021) were from municipality roads with a substantially lower AADT (417 – 2608 AADT) compared to the Smestad tunnel (44 060 AADT), it was presumed that the gully-pot sediments would show a larger difference in tire concentrations compared to what was found. This potentially confirms the importance of emptying the gully-pots for sediment regularly. The gully pots in tunnels are frequently emptied as part of the regular tunnel cleaning, while gully pots along smaller roads may accumulate sediment for longer periods before emptying, or even not emptied at all (Lindholm, 2015). The concentrations found in the gully-pots confirms that tire particles are retained in gully-pots and that high concentrations of tire particles can be found along roads with both low and high traffic densities. It also shows that the concentrations found are comparable to other road treatment systems, thus the potential of gully-pots as simple retention measures for TRWP should be further explored. Unfortunately, there is no information available on the presence of any PMB bitumen in the sample sites used for comparison. If PMB bitumen is used at these locations, this present study shows that the concentrations of TRWP reported are likely overestimations due to the presence of SBS in road samples.

Furthermore, the use of the PMB calculation (Eq. 5), gives the average predicted mass of PMB ( $M_{PMB}$ ) (Table 3), based on the expected ratio of SBS for each location. Being a ratio based on the SBR+BR+SBS concentration, the results from the PMB calculations are proportional to the results of the tire calculations, so the variations within and between sites described for tire particles will be the same and therefore not described in detail here. All calculations can be found in Table 3 and supplementary (S15).

### 3.3. Method Potentials and limitations

The presented method shows great potential in measuring the total mass of SBR+BR+SBS in environmental samples, and subsequently the possibility to calculate the mass of both tire and PMB particles in these

samples. The method can be applied to samples with or without the presence of PMB, and it can be used with or without traffic data input for samples without PMB. This flexibility makes it a novel and robust method which can be applied to most sample sites and most relevant road matrices, such as soil, sediment and snow as demonstrated by this study. It should also be applicable to other relevant matrices such as road dust, road-runoff and tunnel wash water, and should be explored further in future studies. The presented method proposes to use reference tires that are relevant for each study, i.e. considering geographically and seasonal differences. Alternatively, a large sample set of tires from across the globe and for different purposes such as winter or summer, may be useful in order to compare measurements from different studies. A reference database may also contribute to understand the variability in tires caused by the different geometric isomers that SBR can exist in. Studies have shown that the marker compound VCH is affected by the ratio of the different butadiene isomers present (Choi, 2002; Choi and Kwon, 2014, 2020), and it is a possibility that such a variation would also occur in other SBR-related marker compounds.

The preferred pathway for this method (Fig. 1) is dependent on the availability of high-resolution traffic data for each location where samples are collected, such as AADT, ratio of PV and HV, ratio of studded tires and the polymer type used for PMB. As this data may be difficult to obtain in some countries, modified equations to apply where traffic data is lacking, is provided. Some countries also use rubber granulate from discarded tires in the polymer-modified asphalt (Bouman et al., 2020) instead of adding single polymers to the bitumen. In these cases, the tire contribution from the PMB will be added to the total tire concentration for the location, as it will not be possible to distinguish between the two sources of tire. There are currently no studies available that have measured the contribution of tire particles from rubber granulate PMBs, or if the road abrasion factors will be the same for PMB asphalt with tire and SBS. This should be addressed in future studies.

## 4. Conclusions

The present study aimed to improve the methods for determining concentration data of tire and road wear particles in environmental samples. Opposed to the current methods (ISO, 2017a, 2017b), the present method utilised multiple pyrolysis marker components to both determine the content of tires as well as the so far neglected content of polymer-modified bitumen in road wear. Quantification with the combined pyrolysis marker components proposed in this study (benzene,

**Table 3**

The table summarizes the results from using Eq. 5, where the input variables  $R_{SBS}$  (in yellow) have a distribution assumption fitted to the values and the variables  $M_S$  and  $C_{PMB}$  (in white) are constant. The output value  $M_{PMB}$  (in blue) is then predicted with 100 000 Monte Carlo simulations, which gives an average  $M_{PMB}$  and the standard deviation for each sample. The average  $M_{PMB}$  and standard deviation for all SK and SF samples is calculated based on the predicted average  $M_{PMB}$ .

Sample	Output values	Input variables			Predicted values	
	$M_{PMB}$ (mg/g, mg/mL)	$M_S$ ( $\mu$ g/g, $\mu$ g/mL)	$R_{SBS}$	$C_{PMB}$	Average $M_{PMB}$ (mg/g, mg/mL)	Standard deviation (mg/g, mg/mL)
SK-0m	0.53	494.7	0.054	1.00	0.54	0.085
SK-1m	0.53	490.3	0.054	1.00	0.54	0.084
SK-3m	0.032	30.0	0.054	1.00	0.033	0.0051
SK-sed-0m	1.7	1614.2	0.054	1.00	1.8	0.28
SK-sed-1.5m	1.7	1601.2	0.054	1.00	1.8	0.27
SK-sed-3m	1.3	1211.8	0.054	1.00	1.3	0.21
SF1-2018	3.2	3351.8	0.048	1.00	3.3	0.53
SF1-2020	17.7	18606.3	0.048	1.00	18.1	2.9
SF2-2020	1.6	1664.5	0.048	1.00	1.6	0.26
SF3-2020	2.4	2564.7	0.048	1.00	2.5	0.40



*α-methylstyrene, ethylstyrene and butadiene trimer*) showed high recovery percentages (83–104%) in the performed tests and displayed lower variability in reference tires than previously proposed markers. The presented method has also a new and improved step of calculating the amount of tire and road wear in a sample based on the measured rubber content and site-specific traffic data for each location. Using site-specific data may in many situations be more useful for local road and environmental management compared to using global statistics and tire values from different parts of the world. Tires have been shown to have a large variation in content, likely to accommodate for different driving styles and weather conditions found in different parts of the world. Our study shows that there are large differences between different brands and/or types of tires. Using fixed rubber concentrations to calculate the mass of tires in environmental samples, as commonly used in previous methods, is therefore contributing to large uncertainties. These uncertainties are important to communicate when presenting results of tire concentrations in environmental samples. Our study proposes to combine large datasets of tires with a Monte Carlo prediction simulation. Predicting the possible tire values based on the variation in rubber content gives us a predicted mean value and a predicted standard deviation of that mean. This both decreases uncertainty as well as communicates that tires are a difficult matrix to measure. Also, using locally adapted values could give higher resolution data which is relevant both for environmental research and for planning measures in current and future road projects.

#### CRedit authorship contribution statement

**Elisabeth S. Rødland:** Conceptualization, Methodology, Data curation, Formal analysis, Visualization, Writing – original draft, Writing – review & editing. **Saer Samanipour:** Methodology, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. **Cassandra Rauert:** Investigation, Writing – original draft, Writing – review & editing. **Elvis Okoffo:** Writing – original draft, Writing – review & editing. **Malcolm Reid:** Conceptualization, Writing – original draft, Validation, Writing – review & editing. **Lene Heier:** Conceptualization, Writing – original draft, Writing – review & editing. **Ole Christian Lind:** Conceptualization, Writing – original draft, Writing – review & editing. **Kevin Thomas:** Writing – original draft, Writing – review & editing. **Sondre Meland:** Conceptualization, Writing – original draft, Writing – review & editing, Funding acquisition, Project administration.

#### 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.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2021.127092](https://doi.org/10.1016/j.jhazmat.2021.127092).

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