



# Determination of tire wear markers in soil samples and their distribution in a roadside soil

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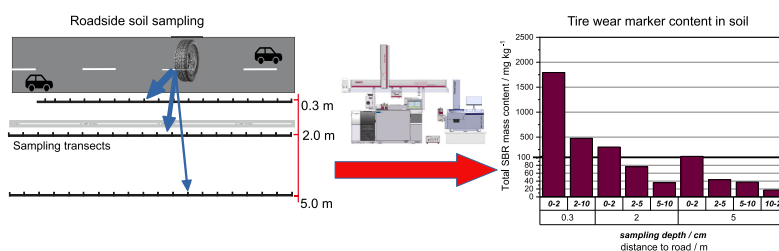
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## HIGHLIGHTS

- Determination of styrene-butadiene rubber as tire constituent using TED-GC/MS.
- Determination of zinc content as tire constituent using ICP-OES.
- Representative sampling strategy with large-volume mixed samples.
- Tire wear content is decreasing with increasing sampling depth and distance to road.
- Deposited tire wear particles are mainly present in soil fraction <100 μm.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Tire wear (TW) constitutes a significant source of microplastic in terrestrial ecosystems. It is known that particles emitted by roads can have an effect up to 100 m into adjacent areas. Here, we apply for the first-time thermal extraction desorption gas chromatography-mass spectrometry (TED-GC/MS) to determine TW in soil samples by detection of thermal decomposition products of styrene-butadiene rubber (SBR), without additional enrichment. Additionally, zinc contents were determined as an elemental marker for TW. Mixed soil samples were taken along three transects along a German motorway in 0.3, 2.0, and 5.0 m distance from the road. Sampling depths were 0–2, 2–5, 5–10, and 10–20 cm. Four fine fractions, 1 000–500, 500–100, 100–50, and <50 μm, were analyzed.

TW contents based on SBR ranged from 155 to 15 898 mg kg<sup>-1</sup>. TW contents based on zinc were between 413 and 44 812 mg kg<sup>-1</sup>. Comparison of individual values of SBR and zinc reveals SBR as a more specific marker. Results confirm that most TW ends up in the topsoil within a 2 m distance.

The sampling strategy resulted in representative data for a larger area. Standard deviations of quadruple TED-GC/MS determination of SBR were <10% for all grain size fractions. TED-GC/MS is a suitable analytical tool for determining TW in soil samples without the use of toxic chemicals, enrichment, or special sample preparation.

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## 1. Introduction

Microplastics are particles in size from 1 to 1 000  $\mu\text{m}$  (ISO/TR 21960:2020), but particles between 1 and 5 mm are often considered as well in microplastics studies. Strictly speaking, the term microplastics only includes thermoplastics and thermosets, but in the running discussion elastomers are involved as well because they can also form polymer particles (Braun, 2021).

Tire wear (TW) is generated by shear stress between tires and road surface during the driving process. The abrasion particles consist of tread material, including rubber and integrated mineral and organic particles from road wear and other road dust, and are thus referred to as tire and road wear particles (TRWP), with a TW content of about 50% (Sommer et al., 2018; Baensch-Baltruschat et al., 2020).

The mass of emitted TW is globally a challenge. It is estimated to be 1 327 000  $\text{t a}^{-1}$  for the European Union and up to 133 000  $\text{t a}^{-1}$  for Germany (Wagner et al., 2018; Baensch-Baltruschat et al., 2021). Kole et al. (2017) calculated TW emissions per capita per year ranging from 0.2 kg in India up to 4.7 kg in the US. For Germany, modeled values range from 0.7 to 1.4 kg for annual emission per capita (Wagner et al., 2018; Baensch-Baltruschat et al., 2021). Annual input rates in the environment per capita of  $0.98 \pm 0.35$  kg and  $1.8$  kg  $\text{a}^{-1}$  were modeled for Switzerland and the Seine watershed catchment in France, respectively (Unice et al., 2019; Sieber et al., 2020).

TW can be found in several environmental compartments including soils and surface waters and may affect the respective ecosystems (Baensch-Baltruschat et al., 2020; Knight et al., 2020). Previous studies, investigating road runoff treatment facilities, found contents between  $0.38$  mg  $\text{g}^{-1}$  TRWP in a settling pond and  $80$  mg  $\text{g}^{-1}$  TW in the sediment of a clarification tank (Eisentraut et al., 2018; Klöckner et al., 2019). With road runoff, TW can be transported to drainage systems and could end up finally in freshwater ecosystems. It was modeled that about 18–22% of TW is released to freshwater (Unice et al., 2019; Sieber et al., 2020), and TW was detected in sediments of surface waters, with a content  $<1$  mg  $\text{g}^{-1}$  in lake sediment and up to  $11.6$  mg  $\text{g}^{-1}$  in river sediments (Unice et al., 2013). A detailed assessment for Germany determined 75 200 to 98 400  $\text{T a}^{-1}$  non-airborne (coarse) TW emissions and calculated input of TW into soils of 58 700 to 68 190 and surface waters of maximum 8 660 to 19 770  $\text{T a}^{-1}$  (Baensch-Baltruschat et al., 2021). Though no studies about retention of TW in wastewater treatment plants are conducted yet, it is assumed that TW is removed with the sewage sludge due to its high density of at least  $1.1$  g  $\text{cm}^{-3}$ , or higher if TW is agglomerated with street abrasive particles in TRWP (Baensch-Baltruschat et al., 2020).

Estimated 5 to 10 mass percent of TRWP are transported by air and 90 to 95 mass percent with road runoff (Baensch-Baltruschat et al., 2021). Nevertheless, the main share of TW are coarse particles (Sommer et al., 2018) and remain in close vicinity to the road. However, only a few studies investigated the occurrence of TW in soils with highly variable results ranging from 200 to 158 000 mg  $\text{kg}^{-1}$  (Fauser et al., 2002; Kocher et al., 2008; Unice et al., 2013; Baensch-Baltruschat et al., 2020). Most likely, the majority of TW emission ends up in the top layer of adjacent soils (Kole et al., 2017; Sieber et al., 2020). Information about the distribution of TW with depth and distance from the road edge is not yet available. It can be expected that the distribution of TW in roadside soils follows the well-known pattern of exponential decrease with depth and distance generally found for heavy metals (Ward et al., 1977; Wheeler and Rolfe, 1979; Carrero et al., 2013; Werkenthin et al., 2014). These heavy metals can derive from TW and other traffic-related sources as brake lining, fuel additives, or oil leaking (Werkenthin et al., 2014). Furthermore, higher metal contents were found in size fractions,  $<250$   $\mu\text{m}$ , of road dust and road sediments (Ellis and Revitt, 1982; Xanthopoulos and Hahn, 1990).

For the analysis of microplastics in soil, it is common to isolate the polymer particles from the particulate soil matrix, as polymer particles have often been found to be associated with or in soil aggregates (Zhang

and Liu, 2018; Rillig and Lehmann, 2020). TW particles are known to be part of heteroaggregates including road particles and brake particles (Sommer et al., 2018; Wagner et al., 2018; Klöckner et al., 2019). Isolation of TRWP from the soil matrix using density separation is difficult, as the density of these heteroaggregates is  $1.5$ – $1.8$  g  $\text{cm}^{-3}$ . Hence, a liquid with a density of  $>1.9$  g  $\text{cm}^{-3}$  is required for the enrichment of TRWP in the light fraction, resulting in the inadvertent enrichment of clay and other particles with lower density in the light fraction as well (Klöckner et al., 2019).

Detection of TW cannot be performed by spectroscopic methods, although widely used in microplastics analysis, as the added black carbon causes total absorbance or fluorescence interferences (Wagner et al., 2018). But several analytical techniques, based on the detection of either elemental or organic markers, have already been applied to identify and quantify TW in different environmental compartments (Councell et al., 2004; Kocher et al., 2010; Unice et al., 2012; Klöckner et al., 2019; Panko et al., 2019; Knight et al., 2020; Roychand and Pramanik, 2020). As an elemental marker, mainly zinc has been considered, which is used for stabilization and material performance and accounts for approx. 1.1% of tire tread material (Kocher et al., 2010). Therefore, TW is known as a significant source of zinc in the environment (Councell et al., 2004; Kocher et al., 2010; Klöckner et al., 2019). Consequently, zinc is a suitable elemental marker for quantifying TW in environmental samples, but not completely specific for TW. Zinc can originate from other sources, e.g. zinc oxide from the corrosion of galvanized road installations and is found with a geogenic background content of 50–100 mg  $\text{kg}^{-1}$  in unpolluted soils (European Commission, 2010). Furthermore, zinc can be transported in dissolved form with the soil solution (Werkenthin et al., 2014). Therefore, TRWP should be extracted from the inorganic matrix before zinc is extracted by acid digestion. Alternatively, to the aforementioned difficult density separation of TRWP, TW can be extracted with organic solvents from the mainly inorganic soil matrix. After evaporation of the solvent, the extractable organic zinc can be redissolved as inorganic zinc in nitric acid and measured via a heated graphite atomizer (Fauser et al., 1999).

As organic TW marker *N*-cyclohexyl-2-benzothiazolamine was used in GC-MS after Soxhlet-extraction of drain sediments (Knight et al., 2020). However, the use of toxic organic solvents such as dichloromethane or toluene for chemical extraction should be minimized regarding environmental sustainability. While Pyrolysis-GC/MS does not require any solvents, the analyzed sample mass is very small. Panko et al. analyzed the fine particulate matter,  $<2.5$   $\mu\text{m}$ , of airborne emission collected at roadside locations in urban hotspots and used vinyl-cyclohexene and dipentene as a specific marker for TW in Pyrolysis-GC/MS (Unice et al., 2012; Panko et al., 2019).

TED-GC/MS can detect and quantify microplastics mass contents in environmental samples by measurement of specific decomposition products after thermal degradation of the sample (Dümichen et al., 2017; Eisentraut et al., 2018). TED-GC/MS does not require any additional sample preparation, neither the decomposition of organic matrix components by oxidation or enzyme treatment nor an enrichment by density separation. For TED-GC/MS, if the limit of detection is reached, no minimal particle size exists, and even the smallest particles are captured. The measurement time of 2.5 h is relatively short, and the analyzed sample mass, up to 1 g, is high compared to Pyrolysis-GC/MS and larger sample quantities are necessary to obtain reliable and representative analytical results.

The aim of the study was to investigate the suitability of TED-GC/MS for the detection of TW in soil samples with minimal sample preparation. For comparison, zinc as an elemental marker was quantified by ICP-OES after acid digestion of the soil samples. Samples were collected next to a highly frequented road in Germany and a focus was set on the representative sampling of the roadside area based on mixed samples from 20 single samples. The samples were divided into several horizontal layers to capture a possible vertical translocation of particles from the top-layer soil into the ground. Furthermore, samples were collected

at 0.3, 2.0, and 5.0 m distances from the road to investigate TW's horizontal transport. Four fine fractions, <1 mm, were analyzed. The obtained mass contents can improve the estimation of input quantities and transport of TW in roadside soil and thereby the assessment of soil contamination with TW.

## 2. Methods and materials

### 2.1. Sampling

The sampling location was at the German Bundesstraße B27 with the technical standard of a motorway featuring two lanes each direction, double steel safety barriers in the central reservation, and single steel safety barriers on the road shoulders (see Fig. 1). Safety barriers were galvanized to prevent corrosion. The average daily traffic (ADT) amounts to 34 000 cars and 2 000 trucks (BaSt, 2021). Samples were taken along three 80-m-transects, parallel to the road. Sampling distances from the sealed road edge were 0.3, 2.0, and 5.0 m.

Along each transect 20 single samples, every 4 m, were cut out of the grassy vegetated soil using a spade. Samples were mostly solid cubic shaped due to high silt contents. The samples were divided into different horizontal layers using a knife to display a vertical displacement in the soil. All layers of one sampling depth were combined in an aluminum tub to a mixed sample and thoroughly mixed to even out the heterogeneity of the TW contents along the transects. These mixed samples had a volume between 2 and 20 L, depending on the chosen thickness of the layer. One resulting lab sample of 1–2.5 L was taken for subsequent sample preparation and analysis.

The road bank has been constructed from local soil material and gravel and therefore does not correspond to natural pedogenesis. This results in a variable soil composition and clay content at the three transects and in the different sampling depths. A loose soil structure prevented the division into thin layers for some samples. Thus, not the same layers could be obtained at all three transects.

In total, ten mixed samples were collected and analyzed. An overview of the samples is listed in Table 1. In addition to the mixed samples, eight single samples, with volumes between 100 and 500 mL, were obtained along the transect in 0.3 m distance to show small-scale variability. At the transect points 0 m, 20 m, and 40 m, single samples of the depth 0–2 cm and 2–10 cm were obtained. In the 60–80 m range of the 0.3 m distance transect, the topsoil had recently been scraped by the road maintenance department, thus only sampling in 0–10 cm was possible at the transect points 60 and 70 m. A background sample was taken from the adjacent field at about 300 m distance from the roadside and 0–20 cm sampling depth. This sample was collected as a single sample and was not divided into different layers, as the agricultural field is plowed regularly.

All tools, including knives, spades, and containers used for sampling

**Table 1**

Overview of collected samples, the distance of the transects from the sealed road edge, and the sampled depth layers. A mixed sample consisted of 20 individual samples collected along the 80 m transect at 4 m intervals.

0.3 m distance	2.0 m distance	5.0 m distance
Mixed samples	Mixed samples	Mixed samples
0–2 cm	0–2 cm	0–2 cm
2–10 cm	2–5 cm	2–5 cm
0–10 cm	5–10 cm	5–10 cm
–	–	10–20 cm
<b>Single samples</b>	<b>No single samples</b>	<b>No single samples</b>
0–2 cm		
2–10 cm		
0–10 cm		

and sample preparation in the field, were made of stainless steel or aluminum and completely zinc-, plastic-, and rubber-free. A graphical description of the sampling strategy is found in the SI.

### 2.2. Sample preparation

The single-point soil samples were air-dried at 60 °C for three days, then sieved in five fractions: >2 mm, 2–1 mm, 1 000–500 µm, 500–100 µm, and <100 µm, using stainless steel sieves with 20 cm diameter (Retsch GmbH, 42 781 Haan, Germany) and a shaking plate for 2 h. Due to clay content soil aggregates are partly stuck together. Consequently, mixed samples - which were prepared afterward - were freeze-dried for six days to decompose soil aggregates. To avoid wet sieving, the remaining small aggregates were accepted as “realistic” grain sizes near to the natural situation in the field. The dried samples were shaken for 1 h before being sieved in six fractions >2 mm, 2–1 mm, 1 000–500 µm, 500–100 µm, 100–50 µm, and <50 µm (Braun, 2021). Masses of the fractions were recorded to obtain a particle size distribution of the samples. The fraction >1 mm was not analyzed further as optical investigation displayed no visible TW or microplastic particles. All fractions, <1 mm, of single and mixed samples, were analyzed by TED-GC/MS and ICP-OES. The samples were not grounded before analysis to avoid heat or mechanical influence on the TW components.

### 2.3. TED-GC/MS analysis

Soil samples were analyzed by TED-GC/MS, as described in the literature (Eisentraut et al., 2018; Dümichen et al., 2019). Each sample is first thermally extracted in an aluminum oxide crucible from 25 to 600 °C with a heating rate of 10 K min<sup>-1</sup> under nitrogen atmosphere in a thermal balance equipped with an autosampler (TGA2, Mettler Toledo, Gießen, Germany). During this process, organic compounds are



**Fig. 1.** Sampling site: Lee side of Bundesstraße B27 near Tübingen, southern Germany. Viewing direction south.

decomposed into volatile products, which are then transferred with a nitrogen flow to a solid-phase-adsorber, the so-called Sorb-star. After the pyrolysis, this Sorb-star is transferred to a thermal desorption unit at the GC/MS system (7890, Agilent, Palo Alto, CA) via an autosampler (MPS, Gerstel, Mülheim an der Ruhr, Germany). Desorption products then are mobilized at 200 °C and get focused by a cold injection system, previous to chromatographic separation in the GC-column. Specific decomposition products are detected in the mass spectrometer (5973 N, Agilent, Palo Alto, CA). Cyclo-hexenyl benzene was used as a specific marker for styrene-butadiene rubber (SBR). Based on the quintuple signal-noise-ratio, a limit of detection (LOD) of 0.10 µg absolute SBR per crucible was calculated. Analyzed sample masses were 20–70 mg.

Mass contents of SBR were quantified by using a matrix-free external calibration using SBR dissolved in toluene with six levels from 4 to 328 µg SBR. Due to the samples' low organic content, a competition between pyrolytic decomposition products from the soil matrix and decomposition products from TW for the sorption sites on the solid phase adsorber is low. Therefore, a matrix-free calibration is suitable. Total SBR mass content in the soil <1 mm was calculated as the sum of the contents in fine fractions multiplied with their relative proportion of the grain size distribution <1 mm (SI, Table 1) of the respective sample. Total SBR content in the complete soil was calculated by multiplying total content <1 mm with its relative proportion of the grain size distribution of the complete soil sample.

#### 2.4. Quality assurance sampling strategy and TED GC/MS

Blanks with 4 µg of deuterated polystyrene as internal standard were measured before each sequence and within a sequence after three samples to demonstrate the absence of detectable cyclo-hexenyl benzene in the TED-GC/MS system and the system's proper functioning.

To screen for possible false-positive signals from the soil matrix, a soil with a total organic carbon content of 2.52%, originating from a remote area without traffic influence, and presumably no TW content, was analyzed. Using the same soil matrix, a spiking experiment with two levels, 177 and 421 mg kg<sup>-1</sup>, was conducted to determine recoveries.

Individual measurements, with 20–70 mg sample masses, might not accommodate for possible sample heterogeneity and result in non-reproducible results. To check measurement uncertainty and sample heterogeneity of individual measurements, the four fine fractions of a mixed sample were analyzed four times each.

For transect 1, additionally to the mixed samples, three single samples were collected at 0, 20, and 40 m of the 80 m transect. An average mass content, based on measurements of three single samples, was calculated and compared to the mass content of the mixed sample to display the variability. This was done to account for the potentially inhomogeneous distribution of the TRWP along the transect to validate the representativity of the sampling strategy.

#### 2.5. Trace metal analysis

Contents of TW in soils and sediments can also be estimated by determining zinc contents. 150–300 mg of each fine fraction <1 mm of the mixed samples was digested using 2 mL 50% hydrofluoric acid (HF) and 7 mL 67% nitric acid (HNO<sub>3</sub>) in a closed microwave digester (Ethos plus 2, MLS, Leutkirch, Germany). With this method, taken slightly modified from VDI-RL 2267–14, all silica minerals are completely dissolved. Elemental analysis was performed using ICP-OES (5110, Agilent, Palo Alto, CA) with external 7-point calibration. Each sample was digested and analyzed twice to minimize the influence of sample heterogeneity due to unground soil samples. Results are displayed as an average of the duplicate determinations. The total zinc contents for <1 mm, were corrected by subtraction the background value for <1 mm. Individual fine fractions were not corrected because the grain size distribution at the background was different from the samples. The total zinc content in complete soil and TW contents were calculated based on

the corrected total zinc content in <1 mm. Two mixed samples of tire powder from a bulk product of tread recycling were analyzed to determine an average zinc content in the current tire material.

### 3. Results and discussion

#### 3.1. Quality assurance sampling strategy and TED-GC/MS

Fig. 2 shows the total SBR mass content in the analyzed fine fractions (<1 mm) along the transect at a 0.3 m distance. In the uppermost layer, a total SBR content of 1 960 ± 294 mg kg<sup>-1</sup> was calculated based on three single samples. For the mixed sample, a mass content of 2 113 mg kg<sup>-1</sup> was calculated, which is within the standard deviation of the calculated average value of the single samples. The variability in the layer beneath (2–10 cm) was higher but the value of the mixed sample (812 mg kg<sup>-1</sup>) was still within the standard deviation of the average value of the single samples (729 ± 217 mg kg<sup>-1</sup>). The results show that variability of the SBR content near the road is low and imply that the applied sampling strategy resulted in representative data for the whole sampling area. Since the single samples were only obtained at the 0.3 m transect, this statement cannot necessarily be transferred to the transects in 2 m and 5 m distance, since lower contents were determined, and TW could also be less homogeneously distributed.

To obtain measurement uncertainty (including sample heterogeneity), all fractions of one mixed sample (0.3 m distance, 0–2 cm sampling depth) were measured as quadruple. Standard deviations based on quadruple measurements were 4.7, 6.1, 9.8, and 6.6 percent for the fractions 1 000–500 µm, 500–100 µm, 100–50 µm, and <50 µm, respectively. Concerning the fact, that the sieved soil fractions were used unground, this is a satisfactory result.

A presumably TW-free soil matrix gave an SBR signal below LOD, while the content of organic matter was higher than in the background sample, which showed an SBR signal 5 times over the LOD. This highlights the specificity of SBR as a TW marker. The spiking experiment with two levels of 177 and 421 mg kg<sup>-1</sup> resulted in recoveries of 93.3 and 104.8 percent, respectively. Data are given in Table 2 in the SI.

#### 3.2. Detailed appearance of tire wear markers

Samples were taken at three different distances from the road to investigate the transport of TW orthogonal to the road. Vertical

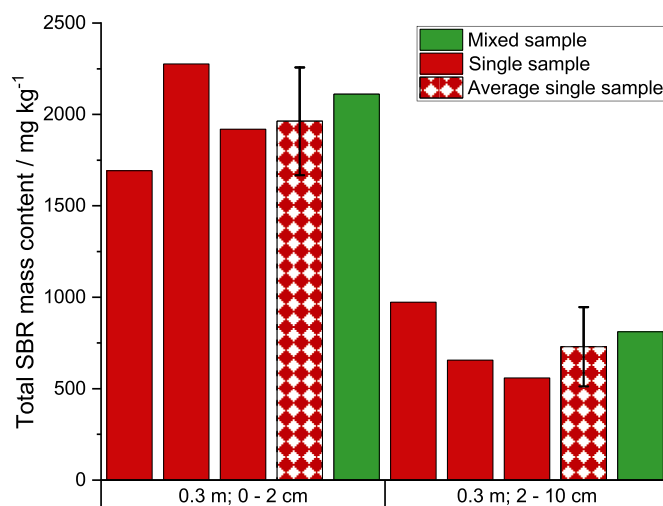


Fig. 2. Comparison of total SBR mass contents of single samples and mixed samples analyzed by TED-GC/MS. Single samples were sampled at 0, 20, and 40 m of the 0.3 m transect. Mixed samples consisted of ten single samples. The error bar shows the standard deviation of the total content in the three single samples.

transport of TW within the soil was investigated by different sampling depths. Results of SBR and zinc determination in all distances, depths, and size fractions are given in Table 2 and as figures in the SI. The background sample was collected as a single sample and was not divided into different soil horizons.

In the background sample, SBR was detected in all fractions of this sample, with an average SBR content of 14.6 mg kg<sup>-1</sup>. This indicates that part of the TW is transported over long distances and that the background content is quite high. Also, an input of TW through previous sewage sludge fertilization cannot be excluded.

With increasing sampling depth, the measured SBR content is decreasing. The maximum SBR content of 1 771–3 056 mg kg<sup>-1</sup> was found of the top layer in 0.3 m distance from the road, while the lowest value of 19.4–23.6 mg kg<sup>-1</sup> was found in more than 10 cm depth and 5 m distance to the road.

In nearly all cases (vertical and horizontal positions) SBR contents increase with decreasing particle size regarding the fractions 1 000–500, 500–100, and 100–50 µm. The particles <50 µm do not, in general, follow this pattern, here the values are often similar to the values of the 100–50 µm fraction or even lower.

The decrease of SBR in the vertical dimension is strongest in the upper layer (about a factor of 1.5–5) and lower in the deeper layers (about a factor of 1–2.5). Decrease factors are given in Tables 3 and 4 in the SI. The fraction 1 000–500 µm shows the highest relative decrease of SBR at all transects. This might result from lesser vertical transport of very large TRWP.

The decrease of SBR content in the horizontal dimension is about a factor of 5–9 in the first 2 m distance from the road (top 2 cm), but only about a factor of 0.9–3 in further distance from the road or deeper layers. Regarding the horizontal transport, no systematic trend of SBR content for different particle fractions can be observed.

Zinc contents depending on sampling depth and distance to the road are also displayed in Table 2 and Fig. 2 in the SI. In the fine fractions, the maximum zinc contents of 423–884 mg kg<sup>-1</sup> were found of the top layer

in 0.3 m distance from the road, while the lowest values of less than 100 mg kg<sup>-1</sup> were found in more than 10 cm depth and 5 m distance to the road. Zinc was also found in the background sample with a total content of 85.8 mg kg<sup>-1</sup>, which is in the range of zinc content (90th-percentile: 107 mg kg<sup>-1</sup>) typically found for agricultural soils in this region of Germany (European Commission, 2010).

In vertical and horizontal directions, the zinc contents decrease, but less than the SBR contents. As with SBR, the vertical decrease is most pronounced in the uppermost layer, although less pronounced in comparison (factor 0.9–3.5). The decrease in the horizontal dimension is about a factor of 3–8 in the first 2 m distance from road (top 2 cm), but neglectable, <1.5, in longer distance from road or deeper layers. No trend could be determined in which size fraction the highest zinc contents were found.

### 3.3. Total tire wear marker content

Results of grain size distribution are given in Table 1 in the SI. Nearly all soil samples show less than 20% of coarse sand and stones (>1 mm). Only in 0.3 m distance from the sealed road edge, the road bank material displays a coarse fraction of more than 20%, here only the upper layer 0–2 cm is similarly fine-grained as most other samples. The reason for the high content of fine material is here the high input of abraded material from road and tires. The reason for the high content of fine material in all other distances including the background sample is the natural grain size distribution of the local soil. In the coarse fraction >1 mm no TW was visible. Nevertheless, this fraction must be considered when describing the whole soil as an environmental compartment.

Fig. 3 displays the total SBR and zinc contents in soil samples collected in different depths and distances to the road. Values are listed in Table 2.

For the complete soil, the maximum SBR content of 1 796 mg kg<sup>-1</sup> was detected in the topsoil in 0.3 m distance, and the minimum content was 17.5 mg kg<sup>-1</sup> in a 10–20 cm depth in 5 m distance. The same trend

**Table 2**

Detected styrene-butadiene rubber (SBR) and zinc contents in fine fractions and the complete soil samples, including coarse fractions, based on TED-GC/MS and ICP-OES measurements as well as calculated TW mass fraction.

Transect; sampling depth		Detected SBR mass content in fine fractions / mg kg <sup>-1</sup>				Detected total SBR mass content / mg kg <sup>-1</sup>		Calculated total TW mass content / mg kg <sup>-1</sup>	
		1000–500 µm	500–100 µm	100–50 µm	<50 µm	<1 mm	Complete soil	<1 mm	Complete soil
0.3 m	0–2 cm	1 771	1 968	2 455	3 056	2 113	1 796	18 703	15 898
0.3 m	2–10 cm	360	1 029	1 565	1 673	812	525	7 183	4 648
0.3 m	0–10 m	918	409	1 250	1 091	767	575	6 788	5 084
2.0 m	0–2 cm	318	371	514	335	356	300	3 152	2 657
2.0 m	2–5 cm	60.5	130	123	108	94.7	76.1	838	674
2.0 m	5–10 cm	35.0	52.3	58.9	50.8	43.0	35.9	381	318
5.0 m	0–2 cm	102	145	169	127	120	114	1 061	1 006
5.0 m	2–5 cm	40.7	60.1	73.3	75.5	50.4	43.4	446	383
5.0 m	5–10 cm	39.4	48.0	45.2	42.2	42.6	37.6	377	333
5.0 m	10–20 cm	19.4	20.1	23.6	23.3	20.2	17.5	179	155
300 m*	0–20 cm	13.4	14.0	16.4	15.1	14.6	13.1	129	116
Transect; sampling depth		Detected zinc mass content in fine fractions / mg kg <sup>-1</sup>				Detected total zinc mass content / mg kg <sup>-1</sup>		Calculated total TW mass content / mg kg <sup>-1</sup>	
		1000–500 µm	500–100 µm	100–50 µm	<50 µm	<1 mm	Complete soil	<1 mm	Complete soil
0.3 m	0–2 cm	423	722	884	876	627	533	52 720	44 812
0.3 m	2–10 cm	121	311	343	298	143	92.8	12 058	7 802
0.3 m	0–10 m	72.2	183	246	207	73.0	54.6	6 131	4 592
2.0 m	0–2 cm	130	137	134	113	46.1	38.9	3 877	3 268
2.0 m	2–5 cm	115	108	98.8	82.3	23.7	19.1	1 993	1 602
2.0 m	5–10 cm	98.1	101	86.3	71.0	11.9	9.89	998	832
5.0 m	0–2 cm	117	112	103	95.3	27.3	25.9	2 292	2 173
5.0 m	2–5 cm	108	130	98.0	78.6	27.1	23.3	2 275	1 954
5.0 m	5–10 cm	101	105	98.0	76.3	15.5	13.7	1304	1152
5.0 m	10–20 cm	92.4	92.2	90.9	78.9	5.65	4.91	475	413
300 m*	0–20 cm	90.7	93.8	77.6	72.8	85.8	77.2	7 209	6 488

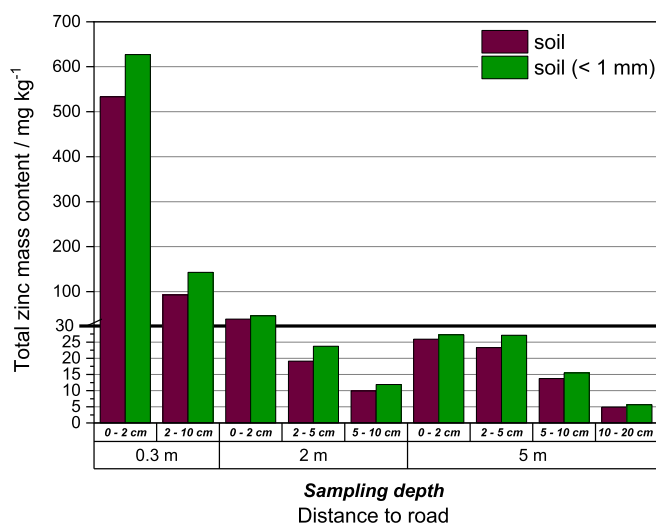
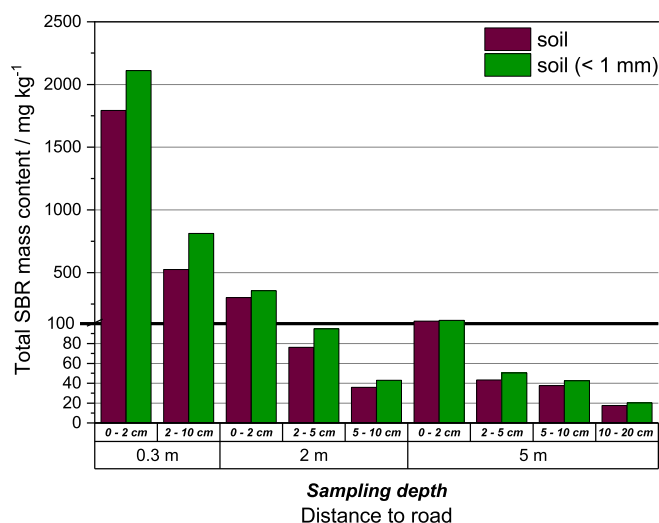


Fig. 3. Total SBR mass content detected by TED-GC/MS (left) and total zinc mass content detected by ICP-OES (right) in roadside soil samples of complete soil or soil < 1 mm.

can be seen for the fine fraction (<1 mm) with values of 2 113 and 20.2 mg kg<sup>-1</sup> respectively. The differences between the fine fractions and total soil samples' contents illustrate the variability in the coarse fractions between the different samples. At transect 1, with increasing sampling depth, the proportion of the coarse fraction >2 mm is increasing, which in turn leads to a decrease in SBR content in the complete soil.

The zinc contents, which were corrected for the background content, follow a similar pattern to the SBR contents, with a maximum of 533 mg kg<sup>-1</sup> in the topsoil in 0.3 m distance and 4.91 mg kg<sup>-1</sup> in the 10–20 cm layer in 5 m distance. It is notable, that the relative decrease from the 0–2 cm layer to the 2–5 cm layer in 2 and 5 m distance is less pronounced for zinc than for SBR. Detected zinc could be leached from TW in the upper layer and subsequently be adsorbed by soil particles in the layer beneath (Councell et al., 2004).

### 3.4. Correlation of tire wear markers

To compare SBR and zinc Fig. 4 shows the correlation of mass content of SBR and zinc of the roadside soil samples in all fractions, depths, and distances.

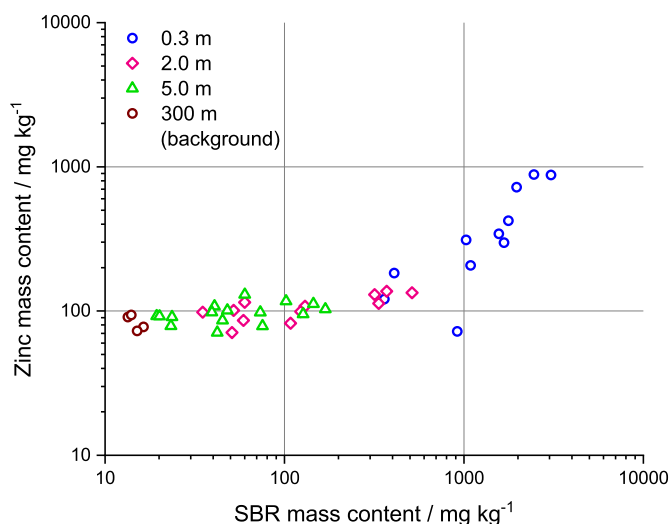


Fig. 4. Correlation of mass contents of SBR and Zinc of the roadside soil samples in all fine fractions and depths displayed for different distances. Background values are not subtracted.

and distances. Zinc values are displayed without background correction to demonstrate the superposition effect of the background contents.

In 0.3 m distance from the road edge, which is also in the direct vicinity of the crash barrier, a zinc content reaching from 72.2 to 884 mg kg<sup>-1</sup> is detected, whereas, at a distance of 2 m and more, low and quite similar zinc content of 71–137 mg kg<sup>-1</sup> near to background can be found in all grain size fractions and all depths. In comparison, SBR content shows a much wider range of values and continuously decreases from the maximum of 3056 mg kg<sup>-1</sup> directly at the road edge to 13.4 mg kg<sup>-1</sup> in 300 m distance. Variation of zinc contents is much larger for distance than for depth which shows that horizontal transport is much more dominant than vertical transport. This seems not to be the case for SBR - the variation of SBR content in size fractions and depth span a quite wide range for the same sampling distance. In 0.3 m distance, zinc and SBR values correlate because TW dominates zinc contents compared to leaching from the barrier. In 2 and 5 m distance, the influence of zinc in dissolved form increases in relation to TW, and consequently the correlation with SBR decreases.

We conclude that SBR is the most specific marker describing particle transport of TW because:

- 1) the influence of the crash barrier is clearly visible in the distribution of zinc content found at this site. The use of road safety systems is becoming more widespread, and the systems are more elaborated, consisting of more steel than older versions, which in turn could lead to increased zinc input and thus to a further overestimation of TW levels based on the zinc content.
- 2) vertical and horizontal content gradients of SBR are higher than those of zinc. This might indicate a (partly) separation of zinc from the TW particles, as zinc can be transported in dissolved form (Werkenthin et al., 2014).
- 3) SBR content gives a more differentiated impression of TW distribution in the roadside environment than zinc content due to the wider range of values. Moreover, it is less affected by other sources and by transport in dissolved form, which is found for zinc (Werkenthin et al., 2014) and other TW-markers like e.g. benzothiazoles (Kumata et al., 2002; Knight et al., 2020).

### 3.5. Conversion to tire wear

Based on worldwide production tonnages of elastomers and their share in tire production, including all different types of tires, it was estimated that general TW consists of 11.3% SBR (Eisentraut et al.,

2018).

The detected zinc content in the reference tire powder was 11.9 g kg<sup>-1</sup>, which fits well to the share of 11.3 g kg<sup>-1</sup> based on the analysis of tread material from 65 different tires (Kocher et al., 2010). Based on 11.9 g kg<sup>-1</sup> the amount of TW in the soil samples was calculated. Values were corrected for the background concentration and listed in Table 2. TW contents based on the zinc contents exceed the values determined using SBR on average by a factor of 2.5.

It becomes clear that different detection methods lead to different TW contents. Therefore, a comparison of different TW contents in soil from different studies, is not very meaningful, as, besides analytical methods, sampling distances and depths, and samples masses are variable. The emission rate, the most important factor, is strongly dependent on traffic volume and varies greatly at different study sites. Furthermore, soil structure has a significant influence on the vertical displacement of TW, as well as the meteorological conditions, since the majority of TW is transported by irregular occurring runoff during high rain intensities (Baensch-Baltruschat et al., 2020). Within 1 m distance from the road edge, road maintenance, in terms of removing the topsoil layer, has a decisive impact on TW content near the surface. In the greater distance, vegetation, soil type, and soil use should be considered in the comparison of environmental TW contents, but data are rarely completely available. For future investigations, therefore, as many as possible of these factors should be recorded to enable better comparability and thus also to gain a better understanding of TW as a soil contaminant.

#### 4. Conclusion

TED-GC/MS is well suited to detect SBR as a tire constituent in soil samples with minimal sample preparation. Additionally, zinc as an elemental marker for TW was determined employing acid digestion and subsequent ICP-OES analysis. Both methods mutually corroborate qualitatively, but not quantitatively. SBR is the more specific TW marker because zinc contents from TW are superimposed by leaching from the galvanized crash barriers and geogenic background levels.

Comparison of mixed samples and single samples resulted in similar contents and displayed that the sampling strategy resulted in representative data. The division into different layers clearly shows a decreasing SBR content with increasing sampling depth. Sampling in the distances 0.3, 2.0, and 5.0 m demonstrated the horizontal distribution of TW particles from the road. The highest SBR contents were found in the topsoil from 0 to 2 cm sampling depth in 0.3 m distance to the road. Elevated contents in the soil fractions 100–50 µm and <50 µm indicate that the majority of the deposited TW particles are <100 µm.

SBR contents, calculated for the soil samples, including the coarse fraction >1 mm without evident TW, range from 1 796 mg kg<sup>-1</sup> (converted in TW: 15 898 mg kg<sup>-1</sup>) in 0–2 cm depth and 0.3 m distance to 17.5 mg kg<sup>-1</sup> (converted in TW: 155 mg kg<sup>-1</sup>) in 10–20 cm depth and 5 m distance. In 300 m distance to the road, in 0–20 cm, 13.1 mg kg<sup>-1</sup> SBR (converted in TW: 116 mg kg<sup>-1</sup>) was detected in the soil. TW contents calculated using zinc content, exceed the SBR-based values and appear to be overestimated.

In summary, the study gives sound insight into the contents and distribution of TW in roadside soil at the lee side of a road with medium-range traffic volume. It confirms the well-known distribution hypothesis known from heavy metal input into these soils. Sampling strategy and the subsequent analysis by TED-GC/MS yield expressive information on TW mass distribution with depth and distance from the road edge. Furthermore, the method allows studies on vertical TW particle transport and degradation in soils.

#### Credit author statement

**Axel Müller:** Writing – original draft, Investigation, Visualization. **Birgit Kocher:** Writing- Reviewing and Editing, Investigation. **Korinna Altmann:** Writing- Reviewing and Editing. **Ulrike Braun:**

Conceptualization, Writing- Reviewing and Editing, Supervision.

#### Author contributions

**AM** and **BK** were responsible for sampling strategy and conducted sampling. **AM** performed TED-GC/MS measurements and data processing. **AM, BK, KA,** and **UB** drafted the manuscript. All authors edited and reviewed the manuscript. All authors approved the final manuscript.

#### 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. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2022.133653>.

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