Characterization of tire and road wear particles from road runoff indicates highly dynamic particle properties

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Keywords: TWP, density separation, microplastic, SBR, rainfall, urban

Abstract

Tire and road wear particles (TRWPs) are heteroagglomerates of tire rubber and other particles deposited on the road surface and one of the main contributors to non-exhaust emissions of automobile traffic. In this study, samples from road environments were analyzed for their TRWP contents and concentrations of eight organic tire constituents. TRWP concentrations were determined by quantifying Zn in the density fraction <1.9 g/cm³ and by thermal extraction desorption-gas chromatography-mass spectrometry (TED-GC/MS) and the concentrations ranged from 3.7 to 480 mg TRWP/g. Strong and statistically significant correlations with TRWPs were found for 2-hydroxybenzothiazole and 2-aminobenzothiazole, indicating that these substances may be suitable markers of TRWPs. The mass distribution of TRWPs in road dust suggests that the main mass fraction formed on roads consists of coarse particles (>100 µm). Data for a sedimentation basin indicate that the fine fraction (< 50µm) is preferentially transported by road runoff into receiving waters. The size distribution and density data of TRWP gathered by three different quantitation approaches also suggest that aging of TRWPs leads to changes in their particle density. An improved understanding of the dynamics of TRWP properties is essential to assess the distribution and dissipation of this contaminant of emerging concern in the environment.

Abbreviations

TRWP, tire and road wear particle; TP, tread particle; PM, particulate matter; PM10, particulate matter <10 µm; TED-GC/MS, thermal extraction desorption-gas chromatography-mass spectrometry; BT, benzothiazole; MBT, 2-mercaptobenzothiazole; OBS, 2-morpholinothiobenzothiazole; MTBT, 2-methylthiobenzothiazole; OHBT, 2-hydroxybenzothiazole; ABT, 2-aminobenzothiazole; 6PPD, N-(1,3-dimethylbutyl)-N′-phenyl-1,4-phenylenediamine; DPG, 1,3-diphenylguanidine; SBR, styrene butadiene rubber; ICP-MS,

inductively coupled plasma mass spectrometry; UPLC-MS, ultra-performance liquid chromatography mass spectrometry; LOQ, limit of quantification; SPT, sodium polytungstate; PCA, principal component analysis; NCBA, N-cyclohexyl-2-benzothiazolamine; 24MoBT, 2-(4-morpholinyl)benzothiazole.

1. Introduction

Non-exhaust emissions result from wear of vehicle parts and contribute 35 – 55% to total traffic emissions (Gon et al., 2013; Grigoratos and Martini, 2015). One of the main components with up to 30% of non-exhaust emissions (Simons, 2016) are tire and road wear particles (TRWPs), which are heteroagglomerates consisting of tread particles (TP) and particles that are deposited on the road surface (Kreider et al., 2010; Wagner et al., 2018). The share of non-exhaust emissions to total particulate matter (PM) is expected to become even higher with growing traffic volume and a reduction in exhaust emissions due to technological advancements in combustion technology (Rexeis and Hausberger, 2009). For the European Union, emissions of TP were estimated to be as high as 1330 $x10^3$ t/a based on registered cars in 2014 (Wagner et al., 2018) and per capita emission estimates range from 0.2 kg/cap*a (India) up to 5.5 kg/cap*a (USA; Kole et al., 2017). With increasing traffic volume, also the emissions of TRWPs will increase. The fate of this contaminant of emerging concern after emission, however, is a matter of ongoing research. While modelling studies aim at predicting the distribution of TRWPs in the environment (Sieber et al., 2020; Unice et al., 2019), the particle properties on which these models are based on are largely uncertain (Unice et al., 2019) and data on environmental concentrations for model calibration are scarce. By modelling, the share of TRWPs reaching surface water was estimated to be up to 25%, while the

proportion remaining at the roadside and in the soil near the road ranges between 50 and 80% (Kole et al., 2017; Sieber et al., 2020; K.M. Unice et al., 2019; Wagner et al., 2018).

Uncertainties regarding TRWP properties include the size distribution of TRWPs generated under environmental conditions, the density of TRWPs and the influence of biofilm formation on size, density and shape of TRWPs (Unice et al., 2019). Knowledge on the size distribution of TRWPs is fragmentary and sizes from <0.1 µm up to >100 µm have been reported. The airborne PM10 fraction of TRWPs was analyzed in several studies (Grigoratos and Martini, 2014). In contrast, coarse particles > 10 µm have rarely been analyzed and information is limited to particles collected during on-road driving where presence of other particles affecting the measured size distribution could not be excluded (Dannis, 1974; Kreider et al., 2010), particles generated by road simulators (Chang et al., 2020; Kreider et al., 2010) and 'super-coarse' airborne particles (10 - 80 µm; Sommer et al., 2018). The size of TRWPs, however, is of high relevance for their environmental fate and transport (Unice et al., 2019) and effects in the ecosystem: in the aquatic environment, coarse particles (e.g. 100 µm) settle faster compared to finer particles of similar density, while particles below 10 µm may even remain dispersed in the water column (Besseling et al., 2017).

Quantitative analyses of TRWPs in the environment are still scarce (Wagner et al., 2018). Tire rubber is a complex and heterogeneous mixture and formulation varies between tire model and manufacturer (Wagner et al., 2018; Wik and Dave, 2009). A large diversity of compounds, amongst which are for example substances belonging to the group of persistent mobile organic contaminants, may be released from tire rubber and could be identified in environmental samples (Seiwert et al., 2020). The quantification of TRWP heteroagglomerates with mass spectrometric methods is challenging and can be achieved by quantification of tire specific marker substances (Wagner et al., 2018). Markers can be tire constituents or degradation products of the rubber polymers generated during analysis (for example by using thermal extraction desorption-gas

chromatography-mass spectrometry, TED-GC/MS (Eisentraut et al., 2018)). An example for an elemental marker is particulate Zn in the density fraction <1.9 g/cm³, which was found suitable for TRWP quantification in samples from road environments (Klöckner et al., 2019).

Benzothiazole (BT, CAS 95-16-9) and its derivatives are common organic tire constituents and have been identified in tire particles as well as in environmental samples (Kumata et al., 2002; Spies et al., 1987; Wik and Dave, 2009; Zhang et al., 2018). Among these are for example the vulcanization agents 2-mercaptobenzothiazole (MBT, CAS 149-30-4) or 2-morpholinothiobenzothiazole (OBS; CAS 102-77-2) and transformation products of MBT such as 2-methylthiobenzothiazole (MTBT, CAS 615-22-5), 2-hydroxybenzothiazole (OHBT, CAS 934-34-9) or 2-aminobenzothiazole (ABT, CAS 136-95-8) (Zhang et al., 2018). Other common tire ingredients are the antiozonant N-(1,3-dimethylbutyl)-N′-phenyl-1,4-phenylenediamine (6PPD, CAS 793-24-8) and the vulcanization accelerator 1,3-diphenylguanidine (DPG, CAS 102-06-7) (Unice et al., 2015).

To study properties of TRWPs found in the environment, highly concentrated samples would provide easiest access to TRWP. A number of samples from the vicinity of hotspots, i.e. from road environments were selected in this study, together with a lake sediment with low expected TRWP concentration for comparison. Apart from reporting the occurrence of TRWP in environmental samples, the aims were to assess the suitability of Zn analysis in the density fraction <1.9 g/cm³ and organic tire constituents as quantitative markers for TRWP in various environmental samples. Furthermore, the particle size distribution of TRWPs in road dust samples and sediments of a road runoff treatment system were investigated. Knowledge about the particle size distribution of TRWPs would be highly beneficial for removal strategies for road runoff, transport prediction in surface waters and the assessment of exposure to aquatic organisms.

2. Materials and Methods

2.1. Sampling

A total of three road dust samples were taken in Leipzig (Germany) on 8th April 2019 at the facility of the communal road cleaning service (Straßenreinigung Leipzig). These samples are denoted with "SK". Samples from sweeping cars coming from different regions of the city were taken (SK_North, SK_West and SK_South). The swept distances were 38.0 km, 29.4 km and 32.9 km of urban roads for SK_North, SK_South and SK_West, respectively. The sweeping cars were vacuum assisted wet sweepers, namely a Faun Viajet 6 Streamline (SK_North, SK_West) and a Bucher-Schörling Cityfant 60 (SK_South). During sweeping, water spray was added to the road for increased collection efficiency. Samples were taken after the content of the dust container of the sweeping car was dumped and before sweeping water was drained (see also Figure S1). Sampling was performed witha shovel and stored in plastic buckets.

Two sediment samples from a technical sedimentation basin treating highway runoff from highway 100 in Berlin, Germany, were taken on 6th December 2018 (18HAL) and 25th March 2019 (19HAL). The treatment system consists of a silt trap, a sedimentation basin and a consecutive artificial wetland (Figure S2). Hydraulic surface charge was ≤10 m/h (determined by operating facility after construction in 2007). The basin is cleared in irregular intervals by pumping the content to the local wastewater treatment plant. This is the only time when the water level is lowered. The volume is 14.3 m^3/ha impervious catchment area, an assessment of the retention capacity can be found in the supporting information. The underground construction prevents exposure of the basin contents to sunlight. Samples were obtained by scooping 5 – 10 times with an angular beaker attached to a telescope rod (Bürkle, Bad Bellingen, Germany) on the ground of the basin. Collected sediments were transferred into plastic buckets.

Four sediment samples from an open settling pond system treating highway runoff from highway 38 close to the city of Leipzig, Germany, consisting of two ponds in series (S1 and S2) were taken from the inlet (S1In, S2In) and outlet (S1Out, S2Out) of each settling pond (see also Figure S3) on 10th October 2018. The ponds are designed as wet ponds with constant water level. The volume of the main pond is 93.8 m³/ha impervious catchment area. Surface areas of the ponds are approximately 516 m² and 2640 m² for S1 and S2, respectively. Further assessment is provided in the supporting information. In contrast to the technical sedimentation basin, the ponds are exposed to sunlight, wind and changes in ambient temperature. Sampling was performed with an angular beaker attached to a telescope rod (Bürkle, Bad Bellingen, Germany) from the shoreline or by walking into the pond with waders (Figure S4). Sediments were then transferred into plastic buckets.

One sample of lake sediment was obtained from Lake Tegel (TGL) and was in a previous analysis shown to be free of TRWPs (Klöckner et al., 2019). Lake sediment was obtained by dredging on June 28, 2016 (GPS 52°34‘24.6’’N 13°15‘10.2’’E).

A tire rubber composite sample (TP_{mix}) was obtained from PVP Triptis (Triptis, Germany). TP_{mix} consisted of used shredded car tires, where metal wire and textiles were removed. Particles were sieved to a size of 250 – 315 µm.

An overview of the samples and the number of subsamples taken for each analysis is shown in Table S3.

2.2. Size fractionation

Environmental samples were freeze-dried and then dry sieved to <500 µm using a vibratory sieve shaker (AS200, Retsch, Haan, Germany) to remove large particulate matter and increase homogeneity. Samples from the open settling ponds were oven-dried before sieving to <500 µm.

In addition, four samples of two different sample types were size-fractionated by wet-sieving using a vibratory sieve shaker (AS200, Retsch, Haan, Germany) and tap water. These samples were road dust (SK_North, SK_West) and sediments from the technical sedimentation basin (18HAL, 19HAL). The following size fractions were obtained: <20 µm, 20 – 50 µm, 50 – 100 µm, 100 – 250 µm, 250 – 500 µm. Samples were freeze dried after wet-sieving. The fraction <20 µm was centrifuged first and overlaying water was decanted before freeze drying. Size fractions were analyzed for their TRWP content based on Zn in the density fraction <1.9 g/cm³ (see also 2.3 & 2.4) and for organic tire constituents (see also 2.5, 2.6).

2.3. Density separation and $TRWP_{Zn}$ quantification

Of each whole sample, subsamples (n=3) were analyzed for their TRWP concentration by particulate Zn analysis in the density fraction <1.9 g/cm³ (Klöckner et al., 2019). In addition, a subsample (n=1) of each size fraction obtained by wet-sieving was analyzed for TRWP. For this, 1-2 g of samples were weighed into a 50 mL centrifugation tube (Nunc™, Thermo Scientific, Waltham, USA). Sodium polytungstate (SPT) solution of density 1.9 g/cm³ was added (TC-Tungsten Compounds, Grub am Forst, Germany). Samples were shortly vortexed (Reax 2000, Heidolph Instruments, Schwabach, Germany), placed in an ultrasonic bath for 15 min (Bandelin Sonorex Digitec) and vortexed again for 10 min at 2000 rpm (Multi Reax, Heidolph Instruments, Schwabach, Germany). Then followed centrifugation (3000 rpm, rcf = 1952 g, 15 min, Rotanta 460, Hettich, Tuttlingen, Germany) and freezing at -73 °C. The buoyant fraction was rinsed out from the frozen tube with ultrapure water and filtrated with a 1.0 µm cellulose nitrate membrane filter (47mm diameter, GE Healthcare, Chicago, USA). Samples were washed with 100 mL ultrapure water during filtration to remove leftover SPT. By this procedure, Zn in the density fraction >1.9 g/cm³ (i.e. minerals) and soluble Zn can be removed. The remaining Zn is considered

to derive from TRWPs (Klöckner et al., 2019). The obtained fraction was analyzed for Zn content as described in chapter 2.4. The TRWP concentration of the whole sample was calculated based on the determined particulate Zn concentration in the density fraction <1.9 g/cm³, , a median concentration of 8.7 mg Zn/g in TP and a 50% TP contribution to TRWPs (Klöckner et al., 2019; Kreider et al., 2010). TRWP concentrations obtained by this method are denoted with $TRWP_{Zn}$.

2.4. Microwave digestion and elemental analysis

Approximately 500 mg of dried samples were digested with 6 mL HNO_3 (Chemsolute, superpure grade, 67-70%, Th. Geyer, Renningen, Germany) and 2 mL H_2O_2 (Suprapur®, 30%, Merck, Darmstadt, Germany) in a microwave digestion system (Multiwave, Rotor 8NXF100, Anton Paar, Graz, Austria). Microwave power, temperature and pressure in the digestion vessels were automatically adjusted during digestion to maximum 900 – 1500 W, 260 °C and 60 bar. Samples were diluted to a final volume of 50 mL by addition of ultrapure water (Milli-Q integral, Merck, Darmstadt, Germany) before being analyzed with inductively coupled plasma-mass spectrometry (ICP-MS; iCAP Q S, Thermo Scientific, Waltham, USA) using a micro-flow nebulizer and cyclonic spray chamber and the following measurement conditions: RF power: 1548 W, nebulizer gas flow: 0.95 L/min, sample flow rate: 0.395 mL/min, collision gas flow: 5mL/min, cooling gas flow: 14 L/min, auxiliary gas flow: 0.8 L/min.

2.5. Extraction of organic tire constituents from environmental samples and preparation of leachates

Of each whole sample and of each size fraction obtained by wet-sieving, subsamples (n=3) were analyzed for organic tire constituents. Freeze dried samples (see also chapter 2.2) were extracted with ultrasound-assisted solid–liquid extraction. 100 mg sample (50 mg in case of TP_{mix}) were extracted with 10 mL 2-propanol (ULC-MS - CC/SFC grade, Bisolve Chimie, Dieuze, France).

Samples were placed in an ultrasonic bath (Sonorex Digitec DT 255 H, Bandelin instruments, Berlin, Germany) for 60 minutes before being centrifuged for 10 minutes at 1000 rpm (Rotanta 460, rcf = 217 g, Andreas Hettich, Tuttlingen, Germany). Overlaying solvent was decanted into an evaporation vial with 1 mL end point and evaporated to dryness under N_2 stream in a 40 °C water bath (Excel-Vap®, Biotage, Uppsala, Sweden). Analytes were then re-dissolved by addition of 1 mL solution of 50:50 (v/v) methanol (SupraSolv grade, Merck, Darmstadt, Germany) in ultrapure water (Milli-Q) with the use of 5 minutes of ultrasonic bath. Extracts were then transferred to a syringe (Injekt Solo, 2 mL, B. Braun, Melsungen, Germany) and filtered through a 0.22 µm PTFE syringe filter (Membrane Solutions, Plano, Texas, USA) into a 2 mL screw neck vial (ND8, Labsolute, Th. Geyer, Renningen, Germany). Samples were stored at 8 °C until analysis. Aqueous leachates of TP_{mix} were prepared similar to the extracts but with ultrapure water (Milli-Q integral, Merck, Darmstadt, Germany) instead of 2-propanol and with only 50 mg sample. After centrifugation, methanol (SupraSolv grade, Merck, Darmstadt, Germany) was added to a filtered (0.22 µm) aliquot of the supernatant to a final concentration of 50% (v/v) methanol.

2.6. UPLC-MS analysis

Extracts were analysed with an ACQUITY UPLC-System using an HSS T3 column (100 x 2.1 mm, 1.7 µm) and XEVO XS Q-TOF-MS (Waters GmbH, Eschborn, Deutschland). Flow rate was 0.45 µL/min, column temperature was 45 °C. The mobile phase consisted of A) water with 0.1% formic acid and B) methanol with 0.1% formic acid. The solvent gradient was: 0 min 2% B, 12.25 min 99 % B, 15.00 min 99 % B; 15.10 min 2 % B, 17.00 min 2 % B. Capillary voltage was 0.7 kV (positive ion mode). Source temperature was 140 °C, desolvation temperature was 550 °C, sampling cone voltage was 20 V and source offset was 50 V. Nitrogen was used as cone gas, while argon was used as collision gas. Desolvation gas flow was 950 L/h, scanned mass range was 50 –

1200 m/z and scan time was 0.15 s. Collision energy was 4 eV for molecular ions and 15 – 35 eV for fragment analysis. TargetLynx was used for quantitative analysis and exact mass accuracy had to be <5 ppm. Quantification of analytes was performed by external quantification using a dilution series of analytical standards (see also Table S2). Limit of quantification (LOQ) was defined as the tenfold signal to noise ratio and was obtained from a dilution series of prepared standard mix. Details can also be found in the supporting information.

2.7. TED-GC/MS analysis and $TRWP_{TED}$ quantification

A subsample from each environmental sample (n=1) was analyzed for the total TRWP content by means of TED-GC/MS. In addition, density separation was performed (as described in chapter 2.3) on a subsample (n=1) of each environmental sample and the fraction <.19 g/cm³ was analyzed by TED-GC/MS. Details of the TED-GC/MS analysis can be found elsewhere (Eisentraut et al., 2018). In short, dry samples were cryogenically ground, weighed into crucibles and thermally extracted in a temperature range of 25 – 600 °C under nitrogen atmosphere using a thermogravimetric analyzer (TGA2, Mettler/Toledo, Gießen, Germany). Decomposition products passed through a heated coupling device (Gerstel, Mülheim, Germany and BAM, Germany) attached to the outlet of the TGA2 and absorbed to a solid-phase consisting of polydimethylsiloxane (SorbStar, Mercury Instruments, Karlsfeld, Germany). The loaded solid phase was transferred to a thermodesorption unit (TDU, Gerstel) where the decomposition products were mobilized again (50 – 200 °C), cryo-focussed (-100 °C, CIS, Gerstel), inserted into a gas chromatograph (7890, Agilent, Palo Alto, CA, USA) and detected in a mass spectrometry system (5973N, Agilent). The SBR degradation product 3-phenylcyclohexene was used for TRWP quantification. 20 mg of unseparated dry sample or 1 mg of density separated dry sample (<1.9 g/cm³) were used. TRWP concentration was calculated

246 based on the SBR concentration in the dry sample, a SBR content of 11.3% in TP and a 50%
247 contribution of TP to TRWPs (Kreider et al., 2010). TRWP concentrations obtained by this method
248 are denoted with $TRWP_{TED}$.

249 **2.8. QA/QC**

250 For organic analyses, subsamples were extracted in three replicates to account for sample
251 heterogeneity and random errors in sample preparation. Procedural blanks and solvent blanks
252 accompanied each measurement. Quantification of organic tire constituents was performed by
253 external calibration with 7 calibration points ranging from 0.01 – 300 ng/mL. Calibration with fresh
254 standard solution (<3 d) was performed with every measurement to account for differences in
255 instrumental sensitivity and to achieve comparable signals.
256 For $TRWP_{Zn}$, subsamples were analyzed in triplicate. SPT solution was filtered with 1.0 µm
257 cellulose nitrate membrane filters to prevent particle contamination. SPT density was confirmed
258 by pipetting 1000 µL and recording the weight (3 replicates). Single-use falcon tubes were used
259 for the separation process. Zn quantification was achieved by external calibration using a dilution
260 series of multi-element standard solutions 1, 2A (SPEX CertiPrep, Metuchen, NJ, USA) and VI
261 (Merck, Darmstadt, Germany). Indium (Spex CertiPrep, Metuchen, NJ, USA) was added to each
262 sample digest and was used as internal standard.
263 Quantification of $TRWP_{TED}$ was performed with external calibrations by spiking a sample with
264 deuterated polystyrene and SBR standards at four to six concentration levels, respectively. This
265 was done for the unseparated as well as the density separated samples. The sample matrix used for
266 spiking was selected based on the average mass loss in TGA.

During sampling, all sampling equipment was rinsed with ultrapure water before use. Large sample volumes of ≥ 5 L were obtained at each site and thoroughly mixed to increase sample homogeneity when taking subsamples.

2.9. Statistical analysis

Median and standard deviation were calculated for concentrations of each sample, if triplicate analyses were performed. Correlations between $TRWP_{Zn}$ ~ $TRWP_{TED}$, $TRWP_{Zn}$ ~ SBR <1.9 g/cm³, $TRWP_{Zn}$ ~ organic tire constituents and $TRWP_{TED}$ ~ organic tire constituents were obtained by a Pearson product-moment correlation. A principal component analysis (PCA) was performed on concentration data from all analyses. For PCA, values below LOQ were replaced with 0.5*LOQ, data was centered by subtracting the column mean and scaled by dividing the centered column with the standard deviation. In addition, k-means clustering was performed on the coordinates of the individuals obtained by PCA in order to better differentiate between clusters. PCA was performed using Rstudio (Version 1.1.414) and the packages FactoMineR (v. 1.42) and factoextra (v. 1.0.5), while k-means clustering was performed using the stats package (v. 3.6.1).

3. Results and Discussion

3.1. Comparison of TRWP concentrations in near road environments as determined by two independent methods: $TRWP_{Zn}$ and $TRWP_{TED}$

TRWP content was determined by two independent methods in samples from road environments and in lake sediment in order to compare method performance and to obtain concentrations in traffic related environments. Quantification of TRWPs was achieved by particulate Zn content in the fraction <1.9 g/cm³ and by TED-GC/MS. TED-GC/MS uses specific degradation products of the tire rubber; hence no separation of TRWP from the matrix is required before analysis and the bulk sample can be directly analyzed. On the contrary Zn is not sufficiently specific for tire rubber and TRWP were separated from the particulate matrix by density separation before Zn analysis.

In the studied samples, TRWP concentrations ranged from 0.17 mg/g up to 480 mg/g (Figure 1). TRWP concentrations were highest in the sediments collected in the technical sedimentation basin (HAL) , while those of road dust (SK) and the open settlings ponds (S1, S2) were one order of magnitude lower. For lake sediment (TGL), quantification of TRWPs by Zn resulted in a concentration of 40 mg TRWP/g, whereas 0.17 mg TRWP/g were found by TED-GC/MS analysis.

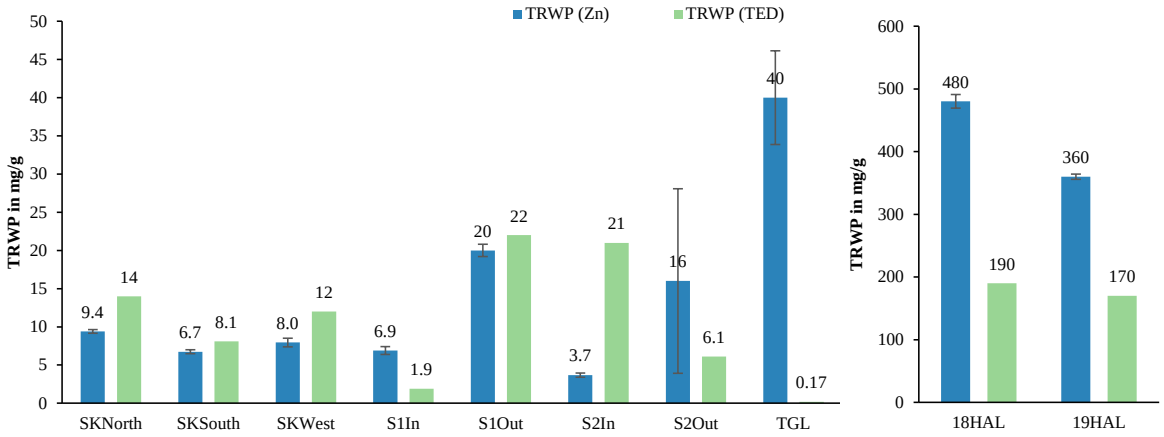

Figure 1: Comparison of determined TRWP concentrations by Zn in density fraction <1.9 g/cm³ via ICP-MS (n = 3) and by SBR in whole samples via TED-GC/MS (n = 1). Values were rounded to two significant digits. Error bars show one standard deviation for the values determined by Zn. Samples: road dust (SK_North, SK_South, SK_West), sediments from the inlets and outlets of consecutive open settling ponds (S1In, S1Out, S2In, S2Out), a lake sediment (TGL) and sediments from a technical sedimentation basin (18HAL, 19HAL).

Only few studies are available that quantified TRWP in environmental samples. Recently, a review study estimated TP concentrations by using concentrations of the organic tire constituents N-cyclohexyl-2-benzothiazolamine (NCBA) and 2-(4-morpholinyl)benzothiazole (24MoBT) that had previously been determined in environmental compartments and tires (Bänsch-Baltruschat et al., 2020). The concentrations estimated for road dust collected from road surfaces outside of tunnels ranged from 1.4 – 37 mg TP/g (Bänsch-Baltruschat et al., 2020), which would be equivalent to 3 – 75 mg TRWP/g assuming a 50% contribution of TP to TRWP (see also chapter 2.3 and 2.4). Sediments from road runoff detention systems were estimated to contain up to 10 mg TP/g, i.e. 20 mg TRWP/g (Bänsch-Baltruschat et al., 2020). These estimates agree well with the TRWP contents in road dust (SK) and in the open settling ponds (S1, S2) presented in this study, whereas the concentrations as high as in the technical sedimentation basin (HAL) could not be confirmed by literature data.

317 Agreement and differences between the TRWP concentration data obtained by the two methods
318 deserve a more thorough consideration. The correlation coefficient between $TRWP_{Zn}$ and
319 $TRWP_{TED}$ for the whole set of 10 samples was r = 0.986 ($p = 1.89*10^{-7}$; see also Figure S8),
320 indicating a good agreement between the methods. This high correlation, however, was in part due
321 to the high values of the technical sedimentation basin; without these two samples, no correlation
322 was found (Figure S9). For the subset of the road dust samples (SK), however, the two methods
323 deviated by only 20% and a correlation could again be obtained (Figure S10). Pronounced
324 differences between the two methods were found for the sediments from the open settling ponds
325 (S1, S2) and the lake. These differences may be a result from errors in $TRWP_{Zn}$ determination such
326 as (a) an incomplete enrichment of TRWPs in the density fraction <1.9 g/cm³, (b) or leaching of
327 Zn from TRWPs, both leading to an underestimation of TRWP, (c) the presence of particulate Zn
328 from other sources in the density fraction <1.9 g/cm³, leading to an overestimation of TRWP. Or
329 they may results from errors in $TRWP_{TED}$ determination, such as disturbances in SBR
330 quantification by sample matrix. While the latter cannot be addressed in this study, possible
331 interferences in the $TRWP_{Zn}$ determination may be discussed in more detail.
332
333 The efficiency of the density separation was determined by comparing the SBR content in the
334 whole sample to the SBR content in the density fraction <1.9 g/cm³ (Figure 2, Table S4). This also
335 allows a confirmation of the assumed density of TRWP and an assessment on the TRWP in the
336 density fraction >1.9 g/cm³. As would be expected, SBR enrichment was high for the samples
337 where the two methods provided good agreement in TRWP quantification, i.e. in road dust samples
338 (SK) and sediments from the technical sedimentation basin (HAL).
339 The lake sediment (TGL) posed an extreme example. While the $TRWP_{TED}$ concentration in the
340 unseparated lake sediment was close to LOQ and accuracy might have been hampered, density

separation increased the TRWP concentration and probably allowed a more accurate quantification of SBR. This led to a (theoretical) SBR enrichment of 200% in the density fraction <1.9 g/cm³ (see also Table S4).

The open settling pond sediments showed variable results: for the samples from the first settling pond (S1), SBR quantification in the density fraction <1.9 g/cm³ indicated that approximately half of the TRWP had a density >1.9 g/cm³ (Figure 2, Table S4). The sample from the inlet of the second settling pond (S2In) had an even lower SBR enrichment in the density fraction <1.9 g/cm³ (34%), while for the outlet (S2Out) the enrichment of SBR in the fraction <1.9 g/cm³ was high (81%). A reason for the high variability in enrichment of TRWPs may be aging processes that lead to changes in the density of TRWPs. Road simulator studies have shown that TRWPs directly after their generation consist of tread rubber and mineral particles from the road surfaces (Kreider et al., 2010). In this study, these kind of TRWPs are referred to as “young” TRWPs. When the particles are exposed to environmental conditions, aging processes such as heteroagglomeration with other particles or biofilm growth may increase density (Besseling et al., 2017). Particles that may have undergone such changes are referred to as “aged” TRWP in this study. Best agreement between the two methods and highest enrichment in density separation was generally found for samples expected to contain young TRWPs (road dust) and with comparatively high concentrations (technical sedimentation basin). Reduced agreement between $TRWP_{Zn}$ and $TRWP_{TED}$ was observed for the open settling ponds and may, among other reasons which are discussed further below, originate in aging processes that lead to an increase in density and a reduced enrichment of TRWP by the density fractionation.

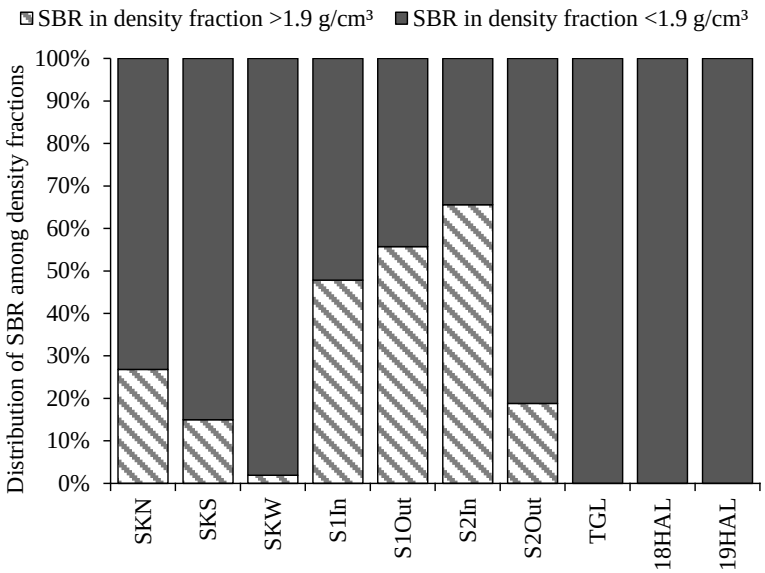

Figure 2: Distribution of SBR in the density fractions <1.9 g/cm³ and >1.9 g/cm³. SBR in density fraction >1.9 g/cm³ was not determined by TED-GC/MS but calculated as the difference between total SBR and SBR <1.9 g/cm³. Quantities of >100% (18HAL: 140%, 19HAL: 120%, TGL: 200%) were adjusted to 100% for illustration purposes.

The quantification of TRWPs via density separation and Zn analysis may overestimate TRWPs if particulate Zn from other sources is present in the density range <1.9 g/cm³. Such sources could for example be Zn bound to or contained within organic particles of low density. This may have been the case for two of the four samples from the open settling ponds (S1In, S2Out), for the sediments from the technical sedimentation basin (18HAL, 19HAL) and for the lake sediment. The lake sediment, however, represents a worst case sample as its total Zn concentration (0.86 mg Zn/g) was much higher than in usual sediments together with a high concentration of particulate organic matter (16.5% dw), to which the Zn may have been adsorbed, while the traffic impact was presumably low (Klöckner et al., 2019).

TRWP quantification by the Zn method could underestimate the true TRWP concentration if Zn was leached during aging. This would be visible by a high SBR enrichment and an underestimation

with the Zn method. Such combination could not clearly be identified. However, the difference between TRWP quantification by Zn and TED-GC/MS for one of the samples of the open settling pond samples (S2In) may be due to a combination of low enrichment and leaching of Zn. $TRWP_{Zn}$ in the road dust samples is always slightly lower than $TRWP_{TED}$ and leaching of Zn could also occur on the road surface when TRWPs are in contact with rain water. Such small differences, however, could also result from deviations in the assumed average Zn and SBR content of TRWPs and an associated systematic under- or overestimation in TRWP quantification.

It has to be noted that also SBR quantification by TED-GC/MS may be prone to errors, for example due to the matrix that may interfere with the formation of 3-phenylcyclohexene as decomposition product of SBR or due to variability in the portion of SBR in TRWPs (Eisentraut et al., 2018). It is also unclear how differences in generation conditions and associated chemical changes in TRWP composition may influence instrumental sensitivity or if high organic matter contents affect quantification. Furthermore, the deviation of TED-GC/MS analyses cannot be assessed since only single measurements were performed. Given the uncertainties associated with both methods, an agreement by a factor of two as in the case for the technical treatment system (HAL) can be considered acceptable. However, further analyses of different sample types would be beneficial. For the assessment of the correlation of the two methods, samples with TRWP concentrations in the intermediate concentration range would be required.

3.2. Presence of organic tire constituents in near road environments

As mentioned above, organic tire constituents such as the benzothiazole derivatives NCBA or 24MoBT have been used to assess the amount of tire material in aquatic and road environments

(Bänsch-Baltruschat et al., 2020). In order to examine if organic tire constituents show a similar distribution as TRWPs in different environments and can thus serve as markers for TRWPs or whether they occur independently, extracts of the 10 samples from road environments (chapter 3.1) were screened for the presence of eight organic compounds (Table S1). All these substances have been determined in tire rubber before (Table S5), but their suitability as marker substances for TRWP has been questioned (Wagner et al., 2018).

The concentrations of the eight organic compounds (Table S6) were compared with the $TRWP_{Zn}$ and $TRWP_{TED}$ data using PCA. Four clusters of samples were obtained (Figure 3a). Interestingly, the two samples from the technical sedimentation basin (HAL) were clearly distinguished one from the other, meaning that they showed a different composition compared to the other samples but were relatively similar to each other. A third group comprised the two samples from the first open settling pond (S1), while all other samples formed a single cluster. In this cluster, also the TGL sample was contained, which showed presence of most organic analytes although $TRWP_{TED}$ was at least one order of magnitude lower (0.17 mg TRWP/g) than all other samples. This indicates that either emission sources of the organic tire constituents other than TRWP or leaching of substances from tires and transport in the aqueous phase contributed to the measured concentrations (Kumata et al., 2002; Unice et al., 2015) or degradation of SBR in the lake led to an underestimation of $TRWP_{TED}$.

The high correlation between $TRWP_{Zn}$ and $TRWP_{TED}$ is reflected by the small angle between the vectors in the loading plot (Figure 3b). TED-GC/MS results showed a lower loading, since only single measurement results were available, whereas other values were determined in triplicates. Similar correlations were obtained with ABT, OHBT, MTBT and OBS, whereas MBT, 6PPD, DPG and BT did not correlate. A PCA on a subset of analytes excluding the compounds that were

frequently < LOQ (6PPD, OBS, MTBT and BT) indicated similar correlations between variables but a slightly different clustering of individuals (Figure S11).

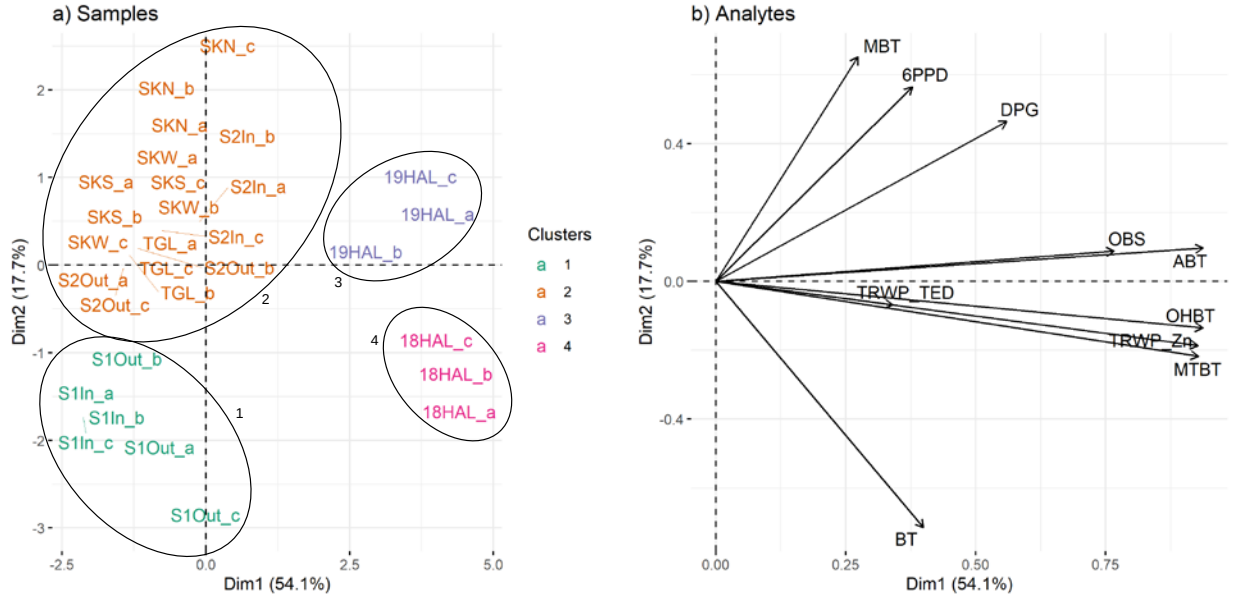

Figure 3: Results of PCA on concentrations of organic tire constituents, $TRWP_{Zn}$ and $TRWP_{TED}$. Values below LOQ were replaced with 0.5*LOQ. A k-means clustering was conducted on the coordinates of the individuals for an easier identification of clusters.

Strong and statistically significant correlations were obtained for OHBT ($r = 0.94$, $p = 4.0 \times 10^{-5}$), ABT ($r = 0.99$, $p = 5.8 \times 10^{-6}$) and MTBT ($r = 0.94$, $p = 0.020$) with $TRWP_{Zn}$, while correlation of OBS ($r = 0.67$, $p = 0.071$) was strong but not significant (see also Figure S12). Correlation of organic tire constituents with $TRWP_{TED}$ were similar to those with $TRWP_{Zn}$ (Figure 3b, Figure S14, and Table S8).

Physicochemical properties of the analytes, such as their octanol-water partitioning coefficient (log P) or water solubility, were not decisive for the correlations (Table S1). This could be an indication that the substances were not solely adsorbed to particulate matter, but that they were still fixed in the rubber matrix of TRWPs and only available to dissolution by an organic solvent. Since MTBT was <LOQ in 50% of the analyzed samples, OHBT and ABT seemed to be most suitable to indicate presence of TRWPs.

As in the case of the correlation between $TRWP_{Zn}$ and $TRWP_{TED}$, the correlations between these substances and $TRWP_{Zn}$ were caused by the extremely high concentrations in the samples from the technical sedimentation basin (see also Figure S14). However, even without the extreme samples a correlation of OHBT and ABT with $TRWP_{TED}$ could be obtained (Figure S15). This correlation was significant for ABT with $r = 0.86$ and $p = 0.028$, but no longer for OHBT ($r = 0.69$, $p = 0.059$). In order for a substance to serve as a TRWP marker, the following criteria should ideally be met (Wagner et al., 2018): the substance should be present in comparable concentrations among different tires and in a high concentration compared to the surrounding matrix, be amenable to analytical methods, be specific for tires (i.e. have few other sources), provide a high environmental stability when contained within TRWP and not leave TRWP due to leaching when exposed to aqueous media. While not all these criteria can be examined in this study, the leaching behavior is particularly interesting since ABT and OHBT are quite polar and highly water soluble (S_w: 1480 mg/L (ABT) - 2350 mg/L (OHBT) (US EPA, 2019)). Concentrations of OHBT and ABT in the isopropanol extract of shredded car tires (TP_{mix}) were compared with an aqueous leachate obtained by sonication of TP_{mix} in ultrapure water. The leachate contained only 7% of the OHBT and 16% of the ABT extracted with isopropanol (Table S7). It seems that even though the solubility of OHBT and ABT in water is high, their availability for leaching from the tire matrix is limited. Moreover, the stability of OHBT and ABT in aqueous environment is also limited (Kloepfer et al., 2005; Reddy and Quinn, 1997). However, OHBT has been found in the dissolved phase of street runoff (Kloepfer et al., 2005). A rapid degradation after dissolution would be beneficial for a TRWP marker, as this would avoid to detect the marker independent from the presence of TRWPs. The low leaching potential and the high correlation with the $TRWP_{TED}$ concentrations both in the 10 samples as well as without the extreme samples (HAL) renders OHBT and ABT promising candidates as TRWP markers.

The determination of organic TRWP markers would provide a third approach to quantify TRWPs in environmental samples, but this needs further investigation. For example, parallel application of all three methods to a larger set of samples would be required to validate the suitability of OHBT and ABT as TRWP markers in different matrices. It would also be necessary to check if other quantitatively relevant sources for these compounds in the environment exist.

3.3. Mass distribution of TRWPs and organic tire constituents throughout grain size fractions

Knowledge about the size distribution of TRWPs is essential to predict their transport. Therefore, four of the samples were size-fractionated: two road dust samples (SK) and the two samples from the technical sedimentation basin (HAL). The road dust samples are close to the source of emission, while the sediment samples were expected to represent material washed off the road and transported with road runoff towards aquatic environment. The distribution of $TRWP_{Zn}$, ABT and OHBT among the different grain size fractions was determined. The particle size distribution of the four analyzed samples is shown in the supporting information (Figure S16). In the road dust samples (SK), the size fraction >100 µm dominated total particulate matter, while the sediments of the technical sedimentation basin (HAL) were much finer with 60 – 85% of the mass in the fractions <100 µm. This indicates that the sedimentation basin receives most of the sediments during low flow conditions that allow the settling of fine particles, whereas at high flow conditions of up to 10 m/h hydraulic surface load, fine particles would likely not settle (see also Figure S5).

$TRWP_{Zn}$ was not evenly distributed over the five size fractions: in the road dust samples, 65% – 75% of the TRWP mass was found in the size fractions 50 - 500 µm (Figure 4a, b). Contrary to the road dust, the TRWPs found in the sediments of the sedimentation basin were dominated by finer particles with 50 - 80% of their mass in the range <50 µm (Figure 4c, d). The same is true for the

two potential organic markers ABT and OHBT, and size distributions of the three parameters do well agree for all four samples (Figure 4). This underlines the possible use of OHBT and ABT as indicators of TRWPs in particulate samples from road environment.

While these samples provide only a snapshot of the multitude of road environments, it seems as if the majority of TRWPs in road dust is >50 µm, whereas the particle sizes in the treatment system are the result of a fractionation process.

The shift towards finer TRWPs from the road (SK) to the sedimentation basin (HAL) may be due to different processes: a) coarse particles may have been washed off the road less effectively by the surface runoff than finer ones, or b) coarser particles may have settled already in the silt trap that precedes the sedimentation basin or c) coarser particles disintegrated due to mechanical forces during transport with runoff water. The sediment of the silt trap was not investigated for TRWPs.

Possible aging processes on the road that may have affected the size distribution of TRWPs could be photo-oxidation (Romero-Sánchez et al., 2003) and thermo-oxidation (Carli et al., 2012), while in water leaching of softeners (Halle et al., 2020) could lead to an embrittlement of the rubber compounds and associated reduction in stability causing mechanical degradation.

Differences in the particle size distributions between the two samples from the sedimentation basin may be explained by the fact that one of the samples (19HAL) was taken after the basin had been cleared and while fresh rain water was entering the basin. Fine particles (<20 µm) may therefore not have settled at the time of sampling. They would rather settle after the rain event when the flow rate in the basin approaches zero.

The limited presence of fine particles in road dust may also be due to other reasons: the fraction <10 µm may under dry conditions be transferred into atmosphere (Grigoratos and Martini, 2014) or under wet conditions be bound to and transported with water. Furthermore, road sweeping cars were not designed for representative sampling of road dust, like for example the wet dust sampler

(Lundberg et al., 2019) and the collection efficiency of road sweepers for particles <10 µm may be limited (Amato et al., 2010). This aspect would require more attention for a final assessment of the size distribution of TRWP on roads.

Particle loss due to the wet-sieving step can be excluded since the total TRWP concentrations calculated from the size fractions matched the total concentrations shown in Figure 1. For SK_North and SK_West, concentrations of 9.5 and 6.3 mg TRWP/g, while for 18HAL and 19HAL concentrations of 410 and 360 mg TRWP/g were obtained, respectively.

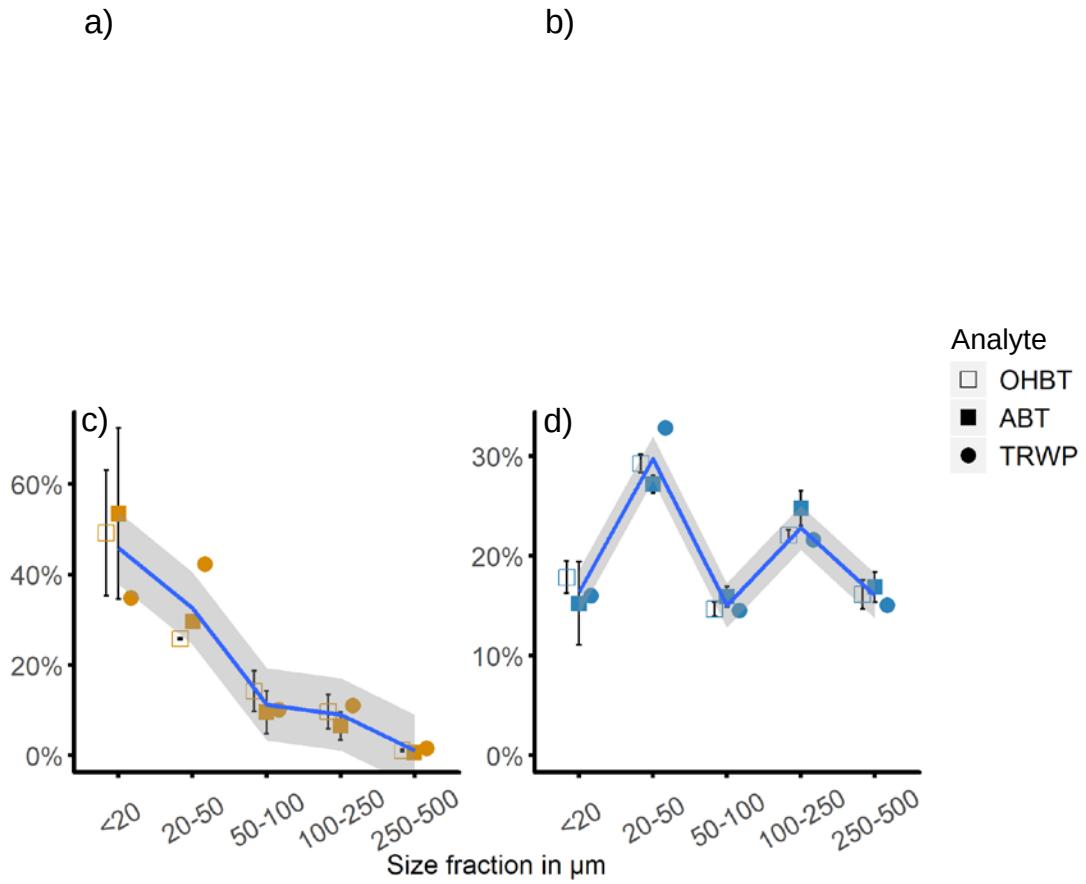

Figure 4: Distribution of TRWPs, OHBT and ABT in the size fractions of four samples from road environment. a) SK_North, b) SK_West, c) 18HAL, d) 19HAL. For TRWP, single values were obtained. Organic tire constituents were determined in triplicate, error bars indicate one standard deviation. The solid line depicts a trend line, while the grey area shows the 95% confidence interval.

527 It should be noted, that Figure 4 shows mass distributions of TRWPs. The TRWP number
528 distribution would be much more clearly dominated by fine particles in all four samples. Assuming
529 a spherical form for TRWPs, 125 particles of 20 µm diameter would correspond in mass to only
530 one TRWP with 100 µm in diameter.
531 Comparing the determined TRWP size distributions in the samples from road environment with
532 literature data is complicated since most previous studies focused on the airborne PM10 fraction.
533 TRWPs of up to 350 µm in size were determined in a road simulator, with a predominating size of
534 75 – 100 µm (Kreider et al., 2010). Recently, the influence of parameters such as road roughness
535 or humidity on the TRWP size distribution generated in a road simulator was assessed and also
536 revealed particles up to 400 µm in size (Chang et al., 2020). These results are in agreement with
537 the data for the road dust determined in this study (Figure 4a, b). Total particulate matter in road-
538 runoff has been reported to be dominated by fine particles <100 µm or even <50 µm (Charters et
539 al., 2015; Kayhanian et al., 2012; Wang et al., 2017). The dominance of TRWPs in this size range
540 in the sedimentation basin (Fig. 4c, d) is, thus, plausible.
541
542 **4. Conclusions**
543 Zn analysis in the density fraction <1.9 g/cm³ and the analysis of organic tire components both
544 were suitable to determine the TRWP size distribution in samples from road environment and can
545 therefore be considered valuable tools for TRWP research. The correlation between TRWP
546 determined by TED-GC/MS and by Zn in the density fraction <1.9 g/cm³, and two organic tire
547 components (OHBT and ABT) is promising to establish a set of potential marker compounds for
548 the quantification of TRWP. For a profound assessment of these correlations, additional research
549 would be required, in particular regarding the correlations at further concentration levels and for

different sample types as well as concerning the influence of aging processes on the quantification methods.

Although the particle size distribution between road dust samples differs, the dominant mass fraction (>60%) of the TRWP may be emitted as coarse particles with a size of >50 µm. The decrease of the particle size distribution between road dust and sediments from the technical sedimentation basin indicates that TRWPs of smaller size are transported preferentially. It is reasonable to assume that the same is true for the transport of TRWPs from road to surface waters. On the contrary, coarser particles tend to be retained in near road environments. And with them also the majority of TRWP mass would remain in near road environments. Any aging process, however, that would lead to disintegration of coarser TRWPs into finer ones would facilitate their subsequent transport into aquatic environment and over large distances.

Besides size, particle density also affects TRWP transport. The assumption that TRWP density is below 1.9 g/cm³ could be verified for relatively young TRWPs but not for aged ones, which seem to reach densities above 1.9 g/cm³. The processes leading to these alterations in density are yet unknown. Thus, also changes in TRWP density must be taken into account in the assessment of TRWP transport.

This study outlines that the properties of TRWPs generated on roads are subject to change. The extent of these changes as well as the processes leading to these changes need to be known better. Only then can the emissions of TRWPs, the extent to which they are distributed in the environment and the compartments in which they eventually remain be adequately assessed.

Funding Sources

This study was funded by the Federal Ministry of Education and Research Germany (BMBF) through the MiWa project (“Microplastic in the water cycle – sampling, sample treatment, analysis, occurrence, elimination and assessment”, reference number 02WRS1378H, funding

measure RiSKWa). The funding source had no involvement in the study design, in the collection, analysis and interpretation of data, in the writing of the report or in the decision to submit the article for publication.

Disclosure

The authors declare no competing interest.

Acknowledgement

The authors thank Berliner Wasserbetriebe, Straßenreinigung Leipzig and Autobahnmeisterei Leipzig for provision of road environment samples, Robert Ladwig (Leibniz-Institute of Freshwater Ecology and Inland Fisheries) and Aki Sebastian Ruhl (Technische Universität Berlin) for sampling in Lake Tegel, Mirko Albrecht (Chemnitz University of Technology) for the provision of the TP_{mix} sample, Josephine Karte, Jürgen Steffen and Ines Volkmann (all UFZ) for instrumental analysis, and Robby Rynek, Viviane Stelzner and Sebastian Fehse (UFZ) for help in sample preparation.

Contributors

PK performed the sampling, sample preparation, data evaluation and statistical analyses. BS performed UPLC-MS analyses and data evaluation. PE and UB performed TED-GC/MS analyses and data evaluation. PK interpreted the results with contributions from SW and TR. PK, TR and SW prepared the manuscript. SW and TR supervised the project. All authors have given approval to the final version of the manuscript.

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