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Tire and road wear particles in road environment – quantification and assessment of particle dynamics by Zn determination after density separation

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1. Introduction

Tire and road wear particles (TRWP) are suspected to be an important environmental pollutant, due to their high abundance, occurrence in air, water and sediment, heavy metal contents, and their persistence (Kole et al., 2017; Spies et al., 1987; Wagner et al., 2018; Wik and Dave, 2009). The term TRWP describes heteroaggregates of abraded tire material with road material and other particles deposited on the road (Kreider et al., 2010). Without inclusion of other particles, abraded tire material is denoted as tread particles (TP).

The quantity and quality of TRWP emitted from road traffic can be expected to be highly variable since they are depending on local factors such as traffic conditions, road material and surface, mineral and organic deposition and weather (Gustafsson et al., 2008; Lee et al., 2013). While tire rubber has a density of approximately 1.2 g/cm³ (Degaffe and Turner, 2011), the densities of particles collected from roads were reported to range from 1.5 to 2.2 g/cm³ (Kayhanian et al., 2012). The density of mineral particles is assumed to be close to the density of quartz (2.65 g/cm³; Lide, 2008). Approximately 50% of the mass of TRWP generated in a road-simulator were reported to originate from road wear (Kreider et al., 2010). Consequently, the density of TRWP is expected to fall between that of TP and quartz and recently a density of 1.8 g/cm³ was estimated (Unice et al., 2019). However, measured data on the density of TRWP generated on streets are not available yet.

In microplastics research, density separation is commonly used to isolate plastic particles from other particulate matter, e.g. minerals, based on their density. This approach was first applied by Thompson et al. (2004) and was further developed since then (e.g. Imhof et al., 2012). A recent adaptation and overview of existing methods was given by Coppock et al. (2017). In principal, a solution of high density, of sodium chloride, zinc chloride or sodium polytungstate leads to flotation of particles with lower density, allowing a separation of plastic particles from denser matrix components.

Even though the emissions of TRWP are enormous (1.33 x 10^5 t/a in Europe (Wagner et al., 2018)) knowledge on environmental concentrations of TRWP is limited (Unice et al., 2019). This may at least partially be due to limitations in the analytical methods available for their determination. Furthermore, the lack of (certified) TRWP reference materials hampers validation of analytical methods as only TP is readily available. Since TRWP are a mixture of chemicals, use of a marker is a promising approach for quantification in environmental samples. An ideal marker would be selective, permanent (not leaving the particle), stable (not degrading) and easily detectable (Wagner et al., 2018). For instance, benzothiazoles have been used as marker substances to estimate the presence of TRWP in sediments and soils already in 1987 (Spies et al., 1987). Due to their water solubility and reactivity, benzothiazoles are not suitable for the quantification of TRWP (Kumata et al., 2002; Wik and Dave, 2009; Zhang et al., 2018). Vinylcyclohexene and dipentene were considered TRWP specific breakdown products in pyrolysis-GC-MS (Unice et al., 2013), while cyclohexenylbenzene was recently used in thermal desorption-gas chromatography-mass spectrometry (TED-GC-MS) (Eisentraut et al., 2018). S and Zn have been used as markers to detect single TRWP (Adachi and Tainosho, 2004).

Furthermore, Zn was used to determine influence of traffic emissions on soils and aquatic environments (Councell et al., 2004; Hjortenkrans et al., 2007) and has a certain potential to serve as a marker due to its high concentration in tires. However, total Zn is not a good indicator for TRWP as other sources exist in urban environments, such as galvanized street furniture and car bodies (Blok, 2005; Councell et al., 2004; Wagner et al., 2018). The use of organo-Zn complexes as tire indicator was proposed by Fauser et al. (1999). However, the selectivity of this approach was questioned later (Unice et al., 2013). Further potential indicator elements of tires are Al, As, Cd, Cr, Cu, Fe, Mo, Na, Ni, Pb, Sb, and V (Kocher et al., 2010), but no proof of their suitability has been provided yet, while other sources of these elements obviously exist (see also appendix, Table A1). Conclusively, elemental markers may be suitable to detect TRWP in environmental matrices only if matrix components are removed prior to analysis.

This work aims at identifying an elemental marker suitable for the determination of TRWP in environmental samples and to combine its quantification with a subsequent density separation procedure (adjusted from Thompson et al., 2004) that separates TRWP from other particulate metal species. Elemental determination is conducted in digests of the separated fractions. Theoretical calculations and analyses of road runoff sediment as internal reference material support the improvement of the density separation procedure, which is then verified with TED-GC-MS as independent method. The developed method is exemplarily applied to samples from road environment.

2. Materials and methods

2.1. Samples

2.1.1. Tire samples

20 used passenger car tires from different vehicle classes have been collected. Tire tread was obtained using an electric multi-tool (Fein MultiMaster Start), resulting tread pieces were cut with a ceramic knife and partly milled using a cryogenic mill (Retsch Cryomill). In addition, one composite sample obtained from a rubber recycling company (PVP Triptis GmbH, Triptis, Germany) was analyzed. Here, ground passenger car tires are shredded under ambient temperature and textiles and metal wires are removed. This composite sample TP_{mix} was used for method optimization.

2.1.2. Environmental background sample

Lake sediment (obtained from Lake Tegel in Berlin (28 June 2016, ca. GPS 52°34’24.6”N 13°15’10.2”E), Germany by dredging from a boat) was used for method optimization. The sediment was dried in the oven at 100 °C and homogenized using pestle and mortar. Lake

Tegel is an urban lake characterized by historic eutrophication. Most of the inflowing water is treated since the 1990s by precipitation, flocculation and filtration, reducing its nutrient and total particulate matter content (Heinzmann and Chorus, 1994). The lake is surrounded by forest and residential areas.

2.1.3. Field samples

Samples were taken on 10 November 2017 at a road runoff treatment facility in Berlin Halensee, Germany (52°29'49.7"N 13°16'56.0"E). Here, road runoff is pre-treated in a sedimentation basin (HAL_SED) before being distributed over a soil retention filter (HAL_SRF). Sampling was conducted with a stainless steel beaker and a stainless steel cylinder (47 mm inner diameter, sharpened rim) to a depth of ca. 15 cm, respectively. Two SRF samples were taken: close to the inlet (HAL_SRF1) and on the opposite side of the filter area (HAL_SRF2).

Samples from two consecutive settling ponds treating highway runoff (LE_S1, LE_S2) were taken in Leipzig, Germany on 13 March 2018 at the Highway A 38 (51°16'29.1"N 12°29'31.5"E) with an Ekman dredge. After treatment the water enters a nearby trench.

All samples were filled in 1 L glass bottles, stored in a refrigerator, sieved (500 µm; Retsch GmbH, Haan, Germany), dried (100 °C) and homogenized in a mortar prior to analysis.

2.2. Sample digestion

Samples were digested using microwave assisted acid digestion (Multiwave, Rotor 8NXF100, Anton Paar, Graz, Austria). 6 mL HNO_3 (Chemsolute, superpure grade, 67-70%, Th. Geyer, Renningen, Germany) and 2 mL H_2O_2 (suprapure, 30%, Merck KGaA, Darmstadt, Germany) were added, according to a protocol for rubber digestion provided by the manufacturer. For digestion of tire tread samples, approximately 400 mg were used. For the analysis of density separated fractions from environmental samples, net weight in microwave digestion was 380 mg (8-1111 mg) on average, depending on the mass of the respective fraction. Microwave power was 900 – 1500 W, maximum temperature was 220 – 240 °C, and maximum pressure was 60 bar. After digestion, samples were filled up to 50 mL with ultrapure water (Milli-Q, Merck KGaA, Darmstadt, Germany) and centrifuged at 4000 rpm for 10 minutes.

2.3. Instrumental analyses

2.3.1. Elemental analysis

Elemental analysis was conducted using inductively coupled plasma mass spectrometry (ICP-MS; iCAP Q S, Thermo Scientific, Waltham, USA) and inductively coupled plasma optical emission spectroscopy (ICP-OES; ARCOS, Spectro, Kleve, Germany). Details can be found in the appendix.

2.3.2. TED – GC-MS

Chromatograms were obtained using the TED-GC-MS system described in literature (Eisentraut et al., 2018). Quantification was done via external calibration using SBR and an internal standard of deuterated polystyrene. A decomposition product of SBR, 3-phenylcyclohexene, was used amongst others as specific marker compound for the elastomer. The calibration curve for the TED-GC-MS method can be found in Figure A3. Further details can be found in the appendix.

2.4. Separation of TP and TRWP from particulate samples

A density separation setup consisting of a 50 mL volumetric flask with beaded rim (DURAN, Class A, Hirschmann, Eberstadt, Germany) and an attached PVC tube (flexible) was used (15 mm inner diameter, 170 mm length, Guttasyn, Witten, Germany). Sample mass was approximately 1 g for environmental samples, while for method development 500 mg (testing of working range and selectivity) and 250 mg (testing of different densities) were used. For separation of the floating fractions, a Hoffmann type pinch cock (Bochem, Weilburg, Germany) was used. The resulting fractions were filtered (Whatman cellulose nitrate membrane filter, 47 mm diameter, 0.1 µm nominal pore size, GE Healthcare, Chicago, USA) and dried at 70 °C. The separation solution was produced from sodium polytungstate (SPT)

(Carl Roth, Karlsruhe, Germany) dissolved in ultrapure water (Milli-Q). Further details can be found in the appendix (Scheme A1, Figure A1).

2.5. Calculation of particle sedimentation rate

Sedimentation speed of particles can be calculated using a transformation of Stokes' law (equation 1).

Equation 1: $$v_p = \frac{2}{9} * \frac{r^2 g\ (\rho_p - \rho_f)}{\eta}$$

where v_p is the sedimentation speed of the particle, r is the particle radius, g is the gravitation constant (9.81 m/s²), ρ_p is the density of the particle at 25 °C, ρ_f is the density of the fluid at 25 °C (1.9 g/cm³) and η is the dynamic viscosity of the fluid at 25 °C (0.00227 Pa*s). For the buoyant velocity of particles, the negative sedimentation speed was used. Time needed for a particle to rise from the bottom of the tube to the light fraction was calculated on a basis of 16 cm total distance (see section 2.4).

2.6. Selectivity towards TP

Selectivity of the density separation was assessed by spiking 500 mg sediment with 1 mg zinc oxide (ZnO, ≥ 99%, Carl Roth, Karlsruhe, Germany), 2 mg zinc chloride ($ZnCl_2$, EMSURE®, Merck KGaA, Darmstadt, Germany), 2 mg zinc sulfide (ZnS, 99.99%, Chempur, Karlsruhe, Germany), 4 mg zinc sulfate ($ZnSO_4$, 99.5 – 103%, Fluka Chemie AG, Büchs, Switzerland) and 100 mg TP_{mix}. The Zn content of added TP_{mix} was approximately 1.4 mg while the Zn amount of the spiked species was approximately 4.0 mg.

3. Results and discussion

3.1. Elemental composition of tire samples

To select possible marker elements, 20 tire tread samples and one mixed sample were analyzed for their elemental concentration and variation thereof (Table 1). The most abundant elements in TP are S and Zn at concentrations above 8 g/kg (Table 1). Concentrations of As, Bi, Cd, Co, Cr, Cu, Ni, Pb and Sb are three orders of magnitude lower (< 15 mg/kg) (Table 1). Zn is also the element with the most uniform concentration between different TP samples (RSD 23%). Concentrations of further elements, which are ubiquitous and therefore not suitable as markers, are listed in the appendix (Table A2).

The determined mean concentrations agree well with literature data for Cr, Cu, Ni, Pb, S and Zn, but are notably lower for As, Bi, Cd and Sb (Kocher et al., 2010; Kreider et al., 2010). Harsher conditions of digestion have been used in previous studies such as a mix of nitric acid, sulfuric acid and perchloric acid (Kocher et al., 2010), or thermal decomposition followed by analysis of ash residues (Kreider et al., 2010). This may account for some of the differences, e g. of Sb and As. Lower concentration of some heavy metals in this study, e.g. of Cd, may also be due to the use of less contaminated raw materials nowadays as compared to the tires analyzed by Kocher et al. (2010), which were obtained from an archive with tire samples from 1980 to 2003.

Table 1. Mean elemental contents and standard deviation of 20 tread samples and one composite sample (TP_{mix}) (n=21) and literature data. Cu is based on analyses of 9 tires and the composite sample.

Element	Unit	TP Mean (n=21)	TP Median (n=21)	Kocher et al. (2010) Mean (n=65)	Kocher et al (2010) Median (n=65)	Kreider et al. (2010) (composite of 3 tires)
As	mg/kg	0.28 ± 0.21	0.20	2 ± 0	2	<64.5
Bi	mg/kg	1.1 ± 1.9	0.44	not reported	not reported	86.8
Cd	mg/kg	0.35 ± 0.30	0.21	1.66 ± 1.16	1.36	<4.99
Co	mg/kg	4.2 ± 15	0.20	not reported	not reported	<164
Cr	mg/kg	2.2 ± 1.1	2.1	4.60 ± 1.75	4.16	<245
Cu	mg/kg	4.8 ± 5.5	3.1	7.09 ± 3.96	6.35	21.5
Ni	mg/kg	3.7 ± 5.6	1.7	8.70 ± 6.43	6.79	not reported
Pb	mg/kg	14 ± 11	9.4	18.2 ± 17.2	13.2	<13.9
Sb	mg/kg	0.039 ± 0.047	0.016	3.76 ± 12.4	1	76.5
S	g/kg	16 ± 7.1	14	not reported	not reported	12
Zn	g/kg	8.7 ± 2.0	8.1	11.3 ± 3.92	10.3	9

3.2. Density separation of TP

The particulate matter into which TRWP are embedded in the environment may contain the same elements found in TRWP also from other sources (Table A1). Therefore, prior to analysis, a separation of TRWP from the particulate matrix is required, which may be achieved by density separation. TRWP are expected to enrich in the top (light fraction) whereas denser particulate materials remain at the bottom (heavy fraction). Soluble Zn species dissolve in the separation solution and are washed out.

The enrichment of TRWP in the light fraction was first tested by spiking a sediment sample with TP_{mix} (at 60 mg/g dry weight), because this is the only material linked to TRWP which is well available. Separation was performed using a separation solution with a density of 1.9 g/cm³. For the spiked sediment, the Zn determination in the light fraction perfectly represented the amount added as TP_{mix} (100 ± 4%), while calculations according to other elements overestimate the TP mass (160 – 21’000%). These overestimations by all elements except Zn are due to their relatively low concentrations in TP_{mix} (Table 1, Table A1) but relatively higher concentration in the sediment material (Table A5). Leaching of elements from TP_{mix} in SPT solution over a period of 192 h was found to be negligible (see also appendix). Consequently, Zn was selected as the marker element for further method development.

3.3. Density separation of TRWP

Since TRWP reference material is not available for method optimization, the sedimentation or flotation rates of various potential sample constituents, including TP and TRWP, and the time required for their separation was calculated using Stokes’ law, assuming spherical particles (Figure 1).

A spherical TRWP with a density of 1.8 g/cm³ and a diameter of 10 µm rises at a speed of 0.86 cm/h; after 23 h separation duration this particle can be expected in the light fraction (Figure 1). For larger particles of the same density or particles of the same size but of lower density, the rising speed is higher and they are also enriched in the light fraction (Figure 1). For example pure TP (density 1.2 g/cm³) rise faster (6.1 cm/h for a particle size of 10 µm) than TRWP.

Smaller particles, such as fine particulate matter (<2.5 µm), remain suspended in the separation solution.

Particle size distributions of real-world TRWP are not well known especially for larger particles (> 10 µm; Wagner et al., 2018). Coarse particles, however, appear more relevant in terms of absolute particle mass: For TRWP generated in a road simulator for example, only a minor fraction (by mass) was reported to be below 10 µm (Kreider et al., 2010). Furthermore, Aatmeeyata et al. (2009) found that PM10 and PM2.5 comprised less than 0.1% of the mass of larger particle non-exhaust emissions. Nonetheless, TRWP in the nano- and lower µm-range have been reported (Dahl et al., 2006; Mathissen et al., 2011). Based on the current knowledge, small particles are considered negligible for the total mass compared to larger particles and particle size therefore should not limit TRWP determination in the light fraction under the described conditions.

A further increase in fluid density also increases the risk for non-TRWP particles with Zn content to enrich in the buoyant fraction. This could lead to a decrease in selectivity and a potential overestimation of TRWP. Such particles could be for example clay minerals (density 1.8 – 2.6 g/cm^3) (Lide, 2008), for some of which Zn^{2+} adsorption has been described (Harter, 1991). Soil particles could also be enriched in the light fraction. In soils, Zn retention by hydrous iron oxides was reported, while organic matter only adsorbs a small fraction of Zn in soil solutions (Harter, 1991). The results therefore support the selection of a separation solution density of 1.9 g/cm^3 for TRWP separation.

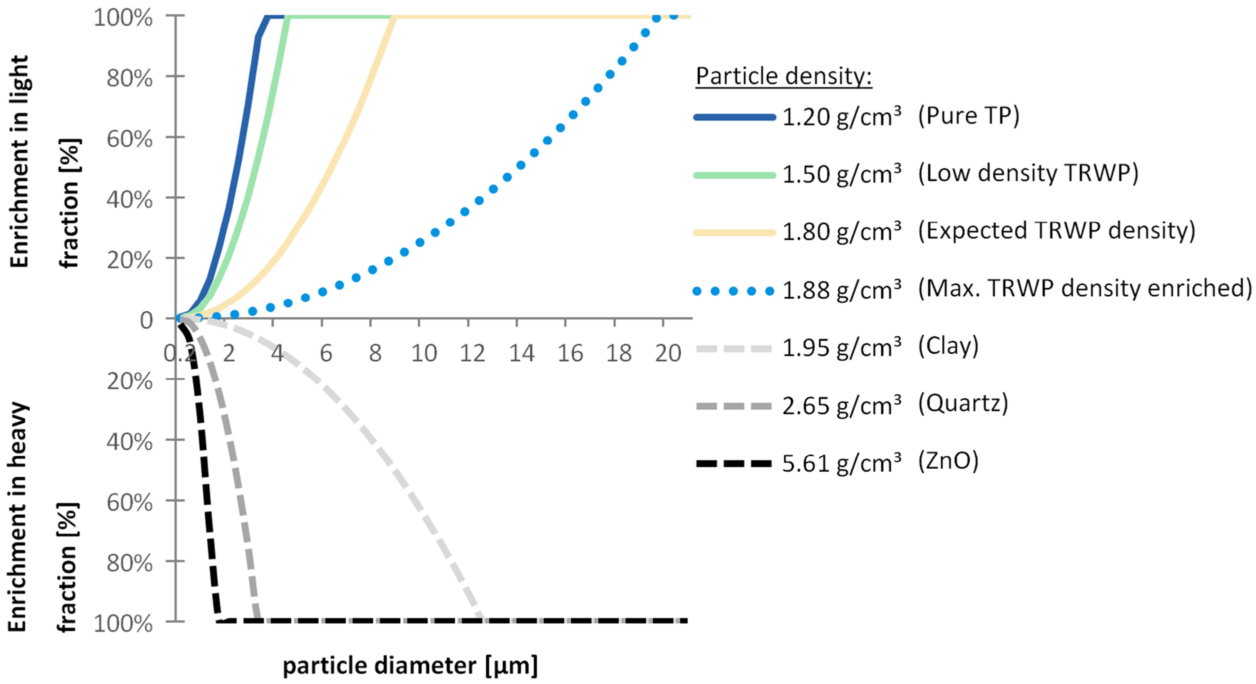

Figure 1. Enrichment of particles after 23 h density separation in the light or heavy fraction for a separation solution with a density of 1.9 g/cm^3. Enrichment [%] describes the fraction of particles that travelled the maximum distance (16 cm) within 23 h.

3.4. Fractionation of interfering Zn species in density separation

As mentioned above, other Zn species besides TRWP occur in road runoff in dissolved or particulate form. The density fractionation should separate TRWP from them. ZnO is an insoluble Zn species of high density (5.6 g/cm³) (Lide, 2008) that can be formed from galvanized steel by corrosion (Del Angel et al., 2015). ZnS may precipitate under reducing conditions in the presence of dissolved Zn(II) and sulfide (Cleven et al., 1993); it has a high density (4.1 g/cm³) and is soluble in diluted acids (Lide, 2008). $ZnCl_2$ is highly soluble (4,080 g/L), as well as Zn complexed as $ZnSO_4$ (577 g/L) (Lide, 2008). Correspondingly, ZnS, $ZnCl_2$ and $ZnSO_4$, if present in a sample, are expected to dissolve completely in the separation solution (density 1.9 g/cm³, pH = 4.2), while ZnO is expected to remain in the heavy fraction. This was verified by spiking known amounts of ZnO, $ZnCl_2$, ZnS and $ZnSO_4$ into a sediment sample, with and without adding TP, and subjecting the samples to density separation. In the sediment sample spiked with TP and Zn-salts, Zn enriching in the light fraction was 86 ± 4% of the Zn spiked as TP_{mix} (TP-Zn; Figure A2). In the sediment sample with only Zn-salts added, 1.2 ± 0.3% of the Zn spiked as Zn-salts were determined in the light fraction. Zn determined in the heavy fractions was 119 – 125% of the Zn added as insoluble ZnO. In the separation solution, 110 ± 45% of the Zn added as soluble Zn-salts were determined. The density separation therefore effectively keeps inorganic Zn species out of the TRWP fraction (light fraction).

3.5. Optimizing density fractionation with a real sample

The effect of varying density of the separation solution (from 1.2 to 2.2 g/cm^3) was tested using a real sample of road runoff sediment (HAL_SED) with unknown TRWP concentration. TRWP concentrations in a sample were calculated from the mass of Zn determined in the light fraction, the mean Zn concentration found for pure TP (8.7 mg Zn/g TP; Table 1) and an assumed TP contribution to TRWP heteroaggregate mass of 50% (Kreider et al., 2010; Panko et al., 2013; Unice et al., 2019, 2013). The variation of the Zn concentration in pure TP of approximately ± 20%, (Table 1) can be neglected, as environmental samples contain TRWP from countless tires. The fraction of mineral particles in TRWP heteroaggregates is presumably more variable, but no data exist on this (Wagner et al., 2018).

At densities below 1.5 g/cm³, the determined TRWP concentrations were low with 6.6 – 11 mg TRWP/g (Figure 2a). The quantified TRWP concentrations increased with increasing densities of the separation solutions to 158 ± 9 mg TRWP/g at a density of 1.9 g/cm^3 (Figure 2a), accounting for 33 ± 11% of the total Zn of the sample (Figure 2b). With further increasing the density to 2.1 g/cm^3 also the TRWP concentration increased further, to 198 ± 24 mg TRWP/g (42 ± 5% of total Zn). This increase, however, was no more statistically significant ($p = 0.058$; $\alpha = 0.05$; paired t-test, two-tailed). As was described above (see also 3.3), the use of separation solution with higher density increases the risk of enriching non-TRWP-Zn.

Repeated fractionations were not found to increase the yield of TRWP from the sediment material: of the mass obtained by three consecutive fractionations, 95% were gathered during the first fractionation, already (Figure A4).

While the Zn concentration in the light fraction increased with increasing density of the separation solution, the Zn concentration in the heavy fraction decreased. The sum of Zn in both fractions was, however, not constant and was accounted for by dissolved Zn (40 – 50 % of total Zn of the sample; Figure 2b). Dissolved Zn was not analyzed instrumentally but calculated via a mass balance of Zn in the unseparated sample and in the respective fractions. The density of 1.9 g/cm^3 is considered ideal for the separation of TRWP from environmental media.

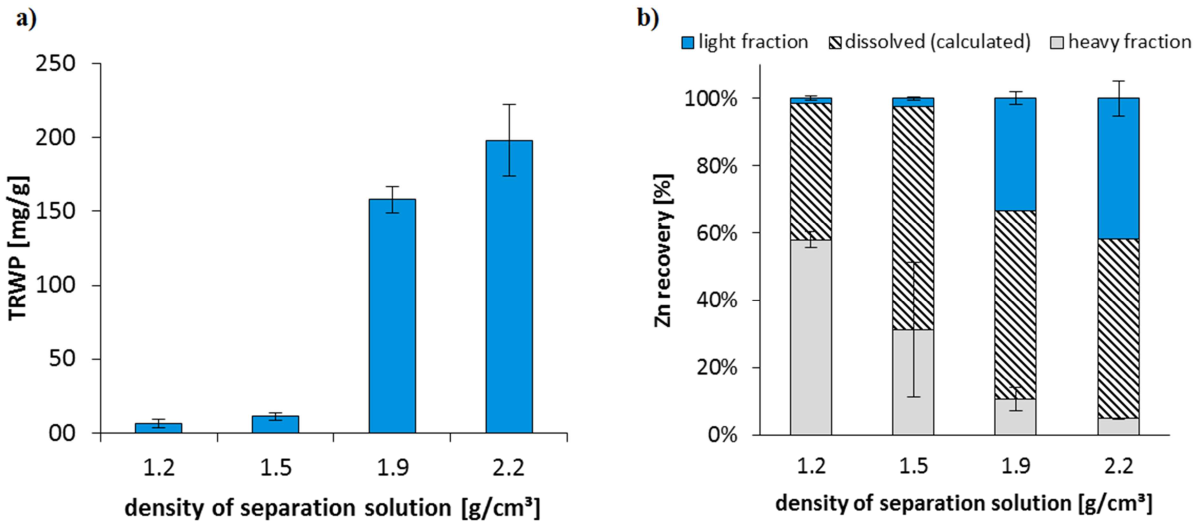

Figure 2. Calculated TRWP concentrations (mg/g) after density separation at varying densities (a) and Zn partitioning in light and heavy fractions [%] at varying densities compared to total Zn of the sample before fractionation (n= 3) (b). Error bars indicate standard deviation. The dissolved fraction was determined with the help of a mass balance.

3.6. Validation of TRWP separation by an independent method

To further validate the separation of TRWP with the SPT solution of a density of 1.9 g/cm^3, the light and heavy fractions of the road runoff sediment presented before were analyzed for TRWP using a recently developed method based on TED-GC-MS, assuming an average SBR-content of 11.3 % in the tire material (Eisentraut et al., 2018) and a TP contribution in TRWP heteroaggregates of 50% (Kreider et al., 2010; Panko et al., 2013; Unice et al., 2019, 2013). According to this method, 336 ± 17 mg TRWP were found in the light fractions and 34 ± 4.6 mg TRWP remained in the heavy fractions (n=3). Thus, the density separation enriched 91 ± 0.7% of the samples' TRWP in the light fraction, showing an adequate density of the separation solution. As mentioned before, density data on TRWP generated on streets are scarce and yet only calculated. The results of these density fractions prove that more than 90% of TRWP found in the sample has a density below 1.9 g/cm^3; this finding supports the density estimate of 1.8 g/cm^3 for TRWP (Unice et al., 2019).

3.7. Working range of the method

The working range of the method was determined by spiking an environmental background sample from an urban lake sediment (Lake Tegel) with TP_{mix} in the concentration range from 2 to 200 mg/g, corresponding to 4 – 400 mg/g TRWP (Table 2). Such concentrations are expected for samples with a strong traffic influence since TP concentrations of up to 80 mg TP/g (160 mg TRWP/g) were reported for road surfaces and road side soils (Wagner et al., 2018).

Table 2: Recovery [%] for TP_{mix} in the light fractions at varying densities (working range) ± standard deviation. Sediment was spiked with TP_{mix}. Recovery values and Zn values were background corrected. Light fraction Zn in the background sample was 0.083 ± 0.014 mg/g. Zn content in TP_{mix} was 14.02 mg/g.

Spiking level [mg TP_{mix}/g]	Recovery [%]	Light fraction Zn (background corrected) [mg/g]
2 (n=3)	123 ± 3.0	0.039 ± 0.0035
5 (n=3)	102 ± 31	0.073 ± 0.012
10 (n=3)	110 ± 23	0.15 ± 0.022
20 (n=1)	86	0.24
40 (n=1)	78	0.42
100 (n=1)	84	1.1
200 (n=1)	85	2.0
mean ± std.dev	95 ± 17	

The recovery ranged from 123% for the 2 mg/g concentration to 85% at 200 mg/g, with an average of 95 ± 17%. In the lower concentration range (2 – 10 mg TP_{mix}/g) the mean recovery was 112 ± 21%.

The recoveries were achieved using TP_{mix}, as TRWP was not available. Since the density separation was optimized for TRWP, the recovery results are expected to be transferable.

The TRWP determination in environmental samples is expected not to be limited by the sensitivity of Zn determination after digestion, as the instrumental sensitivity (ICP-MS) would allow a TRWP determination down to 0.002 mg/g with this method. Rather, the sensitivity of

TRWP detection is expected to depend upon the portion and the quality of non-TRWP-Zn of a sample and on the extent to which this is separated from the TRWP (light) fraction. Zn in the light fraction of the non-spiked sediment sample was 0.083 mg Zn/g. However, this Zn may also derive from other sources and cannot be clearly assigned to TRWP. TED-GC-MS analyses of the sediment did not identify TRWP marker substances (LOQ = 0.73 mg TRWP/g). This suggests incomplete separation of TRWP-Zn from background Zn.

A combination of three factors may have hampered complete separation: i) the sediment used for the spiking was rich in organic carbon (16.5% dry weight) and Zn adsorbed to organic matter may have interfered with TRWP determination. ii) The total Zn content of the sediment was high (0.86 mg/g) compared to natural background concentrations (0.070 – 0.175 mg/g in European sediments (European Commission, 2010). iii) The sediment was taken far-off street environment, so that the fraction of TRWP-Zn was expected to be negligible compared to non-TRWP-Zn.

This outlines, that a general limit of quantification cannot be provided for this method consisting of density separation and Zn determination, because the completeness of TRWP separation will dependent upon a sample’s matrix and background concentration of Zn. However, the selectivity and, thus, the sensitivity of this method may be further increased by applying a 2-step density separation. In a first step, particles with a density of e.g. < 1.2 g/cm³ (light organic material) could be removed before fractionating the TRWP in a density range of 1.2 – 1.9 g/cm³.

The present sensitivity should be adequate for samples with a relatively high TRWP load, such as road surface samples or roadside soils (Wagner et al., 2018). The presented method may also be used for lower concentration ranges if not all three of the above hampering factors (high organic carbon content, high Zn content, low traffic impact) apply. The method is less sensitive than Pyr-GC-MS or TED-GC-MS, for which detection limits for TRWP in the medium to low µg/g-range are reported (Eisentraut et al., 2018; Unice et al., 2013); those methods appear more suitable for samples with low traffic influence such as river sediments or remote environments. The accuracy of Pyr-GC-MS and TED-GC-MS could be increased by a broader data base for the yield of marker compounds in a larger number of tires.

3.8. Application to samples from road environment

The presented method was applied to samples from two treatment systems for road runoff. In the first system, TRWP concentrations of 16 – 150 mg/g were determined, with total particulate Zn in the range from 0.3 to 1.1 mg/g (Table 3). Thus, TRWP-Zn comprised 22 – 83% of total particulate Zn (Figure 3). Highest TRWP concentrations were found in the sedimentation basin (130 mg/g, HAL_SED) as well as in the upper layer of the subsequent soil retention filter close to its inlet (150 mg/g, HAL_SRF1), while the concentration markedly decreased towards the opposite side of the soil retention filter, with an approximate distance of 35 m to the point of discharge. Even though the TRWP concentration decreased in the SRF, the relative mass contribution of TRWP to the light fraction remained constant (34 – 36%; Table 3). While the portion of the light fraction (density < 1.9 g/cm3) decreased along the treatment train, its composition hardly changed. These three samples indicate that the initial sedimentation basin is insufficient to retain all TRWP and that concentrations in the SRF area are not equally distributed but further sedimentation takes place while the runoff water flows along the top SRF. Correspondingly, the relative contribution of non-TRWP-Zn to total Zn increased from 17 to 78 % (Figure 3). This outlines that in urban settings other Zn sources than TRWP contribute substantially to the particulate Zn in road runoff. Thus, total Zn of whole samples would be a poor marker of TRWP even in samples from roadside environment.

TRWP concentrations in the particulate matter collected at the second treatment system were remarkably lower, with 2 mg/g in the first (LE_S1) and 0.4 mg/g in the second settling basin (LE_S2; Table 3); also the contribution of TRWP to total particulate Zn was low (2 – 3 %)

(Figure 3), as well as the TRWP contribution to the light fraction mass (Table 3). These findings were astonishing, because this system treats pure highway runoff for which a high TRWP content was expected in the particulate matter.

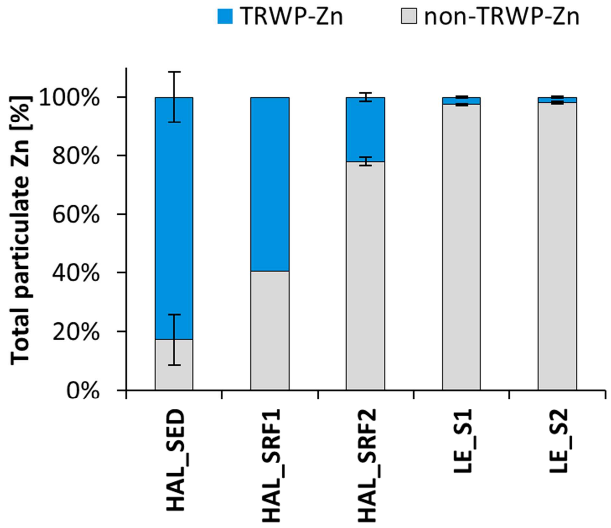

Figure 3: Relative contributions of TRWP-Zn (light fraction) and non-TRWP-Zn (heavy fraction) to total particulate Zn. Error bars indicate standard deviations. HAL_SRF1 is based on two samples only and no standard deviation can be given.

These differences in TRWP concentration at the two treatment sites may be explained by differences in the surrounding environment, by traffic density and driving behavior. While the highway next to the HAL system has an average daily traffic of about 160’000 cars and 8’000 trucks, traffic density at the LE site was much lower (40’000 cars and 7’000 trucks per day (BASt, 2018a, 2018b)). Due to frequent congestions, vehicles brake and accelerate more often on the HAL highway compared to the LE highway; higher abrasion rates and higher total emissions may therefore be expected. Furthermore, the rural environment surrounding the LE sampling site, where agriculture dominates the landscape, may lead to higher deposition of soil particles on the highway, which in turn might dilute the TRWP. The influence of surrounding environments on road dust composition was shown before (Gunawardana et al., 2012).

The TRWP concentrations found in the HAL system are within previous findings for road surface concentrations (see also 3.7). Concentrations in the LE system are within the range of TP data previously reported for highway settling ponds and road runoff detention systems of 0.3 to 11 mg TP/g (equivalent to 0.6 – 22 mg TRWP/g; Reddy and Quinn, 1997; Wik et al., 2008).

Comparing the results for HAL_SED with the TED-GC-MS analysis (see also 3.6), determined TRWP concentrations differed by a factor of two. Given the analyzed sample mass (5-25 mg for TED-GC-MS and 157 ± 43 mg in acid digestion) and the potential heterogeneity of environmental samples, this can be rated as good agreement between the methods.

The compositional differences of the particulate matter in the two systems (HAL vs. LE) as visible in Table 3 may also be explained by changes in TRWP dynamics due to ageing, such as aggregation and degradation processes. The runoff treatment system HAL is maintained and the sediment removed regularly, while this was not the case for the LE system. Rather, the latter system was operated for 12 years without removal of any particulate material. During this long period TRWP collected together with other particulate matter may have aged and increased in density, e.g. by heteroaggregation with further mineral material, which would explain the lower mass percentages of light fractions (Table 3). Ageing processes leading to the incorporation of TRWP into larger (and denser) heteroaggregates would strongly reduce the distance along which TRWP are transported before they settle. They would also preclude the material from being detected as TRWP by the applied method.

Zn leaching from TP was reported earlier and may hamper TRWP quantification. For example, particles of up to 2.8 mm diameter were shown to leach 5% of total Zn within 28 days at pH 3 (Selbes et al., 2015). Experiments conducted in filtered river water led to leaching of up to 8% Zn from TP after 5 days (pH 6.7, median particle size 420 µm; Degaffe and Turner, 2011). However, information on Zn leaching from TRWP is missing.

Since the percentages of the light fractions relative to the total sample mass were low (1.3 – 2.5%; Table 3), a potential Zn leaching from TRWP and binding to the soil matrix (Smolders and Degryse, 2002) is not the reason for the low TRWP concentrations determined at this site: even without Zn the TRWP would contribute to the mass of the light fraction. Furthermore, components preventing microbial decomposition may have leached from the TRWP over time, making them available to biodegradation processes. Tire particles were shown to be available for microbial degradation under aerobic and anaerobic conditions if toxic constituents are removed from the tire rubber (Stevenson et al., 2008). While the explanations of TRWP dynamics remain speculative at this stage, the data clearly show that the developed method has a high precision (RSD in the range of 9 – 20 %, Table 3) and that total (particulate) Zn is not suited as indicator of TRWP in road-runoff (Figure 3). The results underline that present knowledge on TRWP generation, properties and ageing is insufficient.

Table 3: TRWP concentrations in samples from road environment, total particulate Zn (sum of TRWP-Zn and non-TRWP-Zn), TRWP-Zn of the total sample, relative mass of the light fraction and TRWP mass in the light fraction. No standard deviation can be provided for particulate Zn of HAL_SRF1 due to sample loss of the heavy fraction of one sample. For all other values, n=3.

Sample	TRWP [mg TRWP/g]	Total particulate Zn [mg Zn/g]	TRWP-Zn [mg Zn/g]	Mass of light fraction [%]	TRWP mass in light fraction [%]
HAL_SED	130 ± 15	0.68 ± 0.06	0.57 ± 0.07	52 ± 1.2	24 ± 3%
HAL_SRF1	150 ± 30	1.1	0.65 ± 0.13	40 ± 3.5	36 ± 1%
HAL_SRF2	16 ± 1.4	0.32 ± 0.008	0.07 ± 0.01	4.4 ± 0.23	34 ± 3%
LE_S1	2.0 ± 0.3	0.35 ± 0.006	0.01 ± 0.001	2.5 ± 1.0	8.9 ± 2%
LE_S2	0.38 ± 0.04	0.09 ± 0.005	0.002 ± 0.0002	1.3 ± 0.43	3.1 ± 1%

4. Conclusions

The developed method for TRWP quantification from particulate environmental samples based on Zn determination after density separation is suitable for samples from highly traffic-influenced environments. The selectivity and, thus, sensitivity of the method is expected to increase further by the application of a 2-step density separation.

TRWP contents of materials from road-runoff treatment systems were found to be highly variable in the range from 0.38 to 150 mg/g. However, these concentrations are in line with previous estimates for highway runoff.

The separation of TRWP from other particulate matrix components using density fractionation can help in TRWP characterization or examination of particle dynamics (ageing, aggregation, transport) and associated changes in density. Another application would be the detection of TRWP on a single particle level. Knowledge on TRWP composition and physical properties may be deepened in this way, providing valuable information for the assessment of TRWP fate in the environment. TRWP density in particular is of high relevance for their environmental fate. Factors contributing to or determining TRWP concentrations in runoff are still poorly understood.

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Highlights:

- Density separation is able to enrich TRWP
- Density separation can be a powerful tool for TRWP characterization
- TRWP density was determined and may change upon ageing
- Zn is the best suited elemental marker for TRWP quantification
- Samples from road environment were analysed for TRWP