Aerosol and Air Quality Research, 18: 2014–2028, 2018
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ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2018.03.0099

Tire Abrasion as a Major Source of Microplastics in the Environment

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ABSTRACT

Traffic-related non-exhaust particulate matter mainly consists of tire wear, brake wear, and road wear. For this study, passive-samplers were placed near highly frequented roads in industrial, agricultural, and urban environments with the aim of collecting and characterizing super-coarse (> 10 µm) airborne particles. Single-particle analysis using SEM-EDX was conducted on more than 500 particles with nearly 1500 spectra to determine their size, shape, volume, and chemical composition. The ambient aerosol near all studied roads is dominated by traffic-related abrasion particles, amounting to approximately 90 vol%. The majority of the particles were composites of tire-, road-, and brake-abrasion material. The particle assemblages differed in size distribution, composition, and structure depending on driving speed, traffic flow, and traffic fleet. Our study documents that tire wear significantly contributes to the flux of microplastics into the environment. A decrease in the release of this abrasion material, however, is unlikely in the near future.

Keywords: Microplastics; Tire wear; Road wear; Brake wear; SEM-EDX analysis; Chemical composition.

INTRODUCTION

Traffic-related non-exhaust particulate matter (PM) in ambient air is still a phenomenon that grows in scale worldwide. These emissions are dispersed in an uncontrolled fashion and may have considerable health and environmental impacts on a local (e.g., vegetation, soil) to global (e.g., oceans) scale (WHO, 2005; Miklos *et al.*, 2016; Nizzetto *et al.*, 2016). For example, 30 vol% of the microplastic particles that pollute rivers, lakes and oceans consist of tire wear, thus affecting aquatic wildlife (Ott *et al.*, 2015; Kooi *et al.*, 2016; Boucher and Friot, 2017; Zeit-online, 2017; Machado *et al.*, 2018; Peeken *et al.*, 2018). Microplastics are small plastic particles less than five millimeters in size consisting of synthetic organic compounds. The wide range of plastic products is made of just six major polymer types: polyethylene terephthalate (PET), polyethylene, polypropylene, polyvinyl chloride, polyamide (nylon), and polystyrene (GESAMP, 2015). Tire treads consist of styrene butadiene rubber, which is based on styrene, a precursor of polystyrene, in a mix with natural rubber and many other additives (Sundt *et al.*, 2014).

Along with the debate about greenhouse-gas emissions, the exhaust emissions produced by combustion engines came into the focus of policy makers, leading to a series of measures that succeeded in reducing this part of the traffic-related emissions. Moreover, the anticipated transition to electric-motor cars will further reduce the PM exhaust emissions. However, this is not the case for brake-, tire-, and road-wear particles. The interaction between tire and road surface as well as brake pad and brake disk necessarily yields a frictional connection and thus, a reduction of this abrasion material is not to be expected in the near future (Amato *et al.*, 2012; Grigoratos and Martini, 2015). Since several components of tires and brakes are proven toxic (Wik and Dave, 2006; Marwood *et al.*, 2011; Bejgarn *et al.*, 2015; Malachova *et al.*, 2016), reducing the amounts of this material emitted into the environment is highly desirable (Fig. 1).

With the rapidly increasing traffic volume during the 1980ies, a consciousness for the possible environmental impact developed. Starting with the publication of Golwer (1991), the relation between increasing traffic and pollution of soil and groundwater, as well as health effects, was examined. In the following years, Stechmann, (1993), Krömer *et al.* (1999), Tegethof (1998), Hillenbrand *et al.* (2005), Seling and Fischer (2003a, b, c), Becker (2006),

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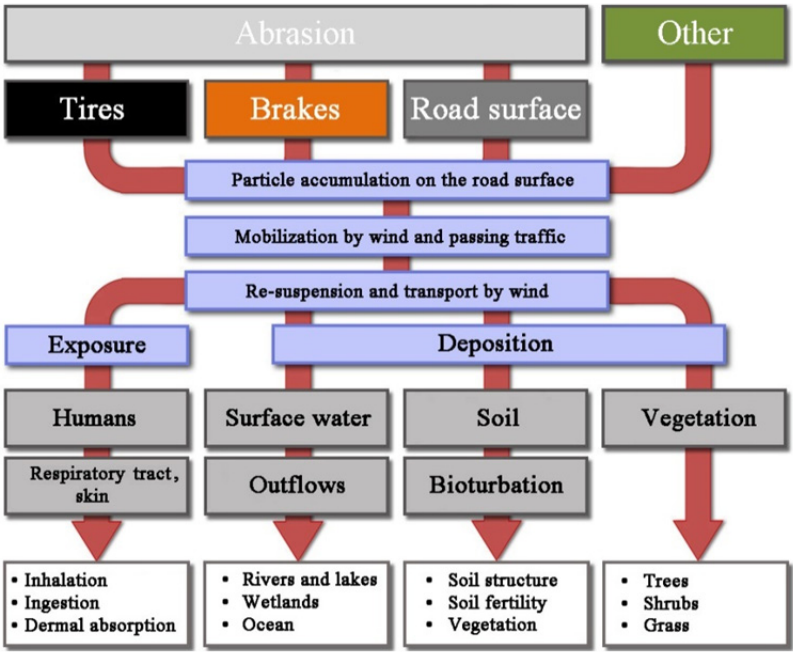

Fig. 1. Traffic-related non-exhaust and other particulate matter (PM) from emission source to possible impact range.

Herngren *et al.* (2006), Kocher *et al*. (2010), and the U.S. Environmental Protection Agency (2014) documented the increasing amount of traffic-related pollutants deposited in water, air, and soil.

The literature focuses on the emission factors of traffic-related non-exhaust particles (abrasion from tires, brakes, wearing course of roads), and on the deposition and contamination close to the road. Most of the PM literature concentrates on the impact on human health and thus, on the breathable PM_{10} fraction. The present study, however, focusses on particles with sizes > 10 µm, i.e., super-coarse particles (Lipfert *et al.*, 2000) and, moreover, we do not examine material directly emitted and deposited on the road surface, but rather investigate the airborne particles after mobilization (suspension) and re-suspension by wind and passing traffic.

Our main focus is on the chemical analysis and mineralogical single-particle characterization of traffic-related abrasion materials. The particles we found and examined are not simply pure tire, brake, or road particles, but rather composites of various types of materials. In the literature, a distinct and detailed individual-particle characterization for tire-wear particles of the PM_{10-80} fraction is difficult to find. Furthermore, we propose an improved, more specific nomenclature based on individual particle shape, structure, and chemical composition of these particles: in the following text, we use *tire-core particles* for the original emissions of pure tire treads, whereas the terms *tire-wear particles* or *tire-abrasion particles* are used for the contaminated and encrusted tire-core particles. Road-wear particles, or road-abrasion particles, are the materials abraded from the wearing course, i.e., the uppermost part of the road. Brake-wear particles, or brake-abrasion particles, originate from brake disks, brake pads, and other brake parts.

SAMPLING AND EXAMINATION METHODS

Sampling: Ambient aerosol particles were collected by using the cost-effective and easy-to-handle passive-sampler device Sigma-2 at ground-based sampling sites. This technology ensures a wind-sheltered, low-turbulence air volume inside the sampler. The design of the Sigma-2 device allows for protection of the particles from direct radiation, wind, and precipitation (Dietze *et al.*, 2006; VDI 2119, 2013; Tian *et al*., 2017). Two passive-sampler stations were set up at about 1.5 m height and at a horizontal distance of 4.6 m from the roadway. Particles were collected on a transparent adhesive acceptor surface, which was exposed for seven consecutive days. This collection plate is specifically designed for subsequent optical single-particle analysis by Transmitted Light Microscopy (TLM) as well as for single-particle analysis via Scanning Electron Microscopy (SEM) combined with Energy-Dispersive X-ray (EDX) spectroscopy (see Sommer *et al.*, 2016).

Sampling sites: In this study, we selected three highly frequented roads in Germany: motorways A 555 and A 4 (both in North Rhine Westphalia), and federal highway B 31 in Baden-Württemberg. The A 4 is located close to the motorway interchange Köln-Gremberg, about 6 km east of Cologne between intersections with exit ramps. It has a total traffic count of approximately 86,000 vehicles per day, including 11,000 heavy-duty vehicles (HDV). During weekdays, this motorway is characterized by slow-moving traffic, with rush hours that regularly cause "stop-and-go" traffic conditions (Tian *et al*., 2017). The A 555 is located approximately 17 km south of Cologne, and average total traffic counts are about 70,000 vehicles per day, including about 4,000 HDVs. The samples studied here, displaying a high PM_{10-80} particle load, were selected from a sample set collected over a period of four years, starting in calendar week 22 of 2013 (CW 22/2013). The sampling site at the federal highway B 31 is located inside the city of Freiburg in southwestern Germany. This road displays a total traffic count of about 35,400 vehicles per day, including 3,000 HDVs, and is characterized by constant stop-and-go traffic in a densely built-up area (Table 1).

The sampling sites exhibited average weekly maximum temperatures ranging from 5°C (CW 05/2015) to 11°C (CW 10/2014) at the two motorways, and 22°C at the B 31 (CW 27/2017). All sampling sites display weather conditions with low precipitation and predominant easterly winds.

Transmitted light microscopy (TLM): The single-particle analysis via TLM was carried out using a computer-controlled light microscope equipped with a high-resolution CCD digital camera for imaging (for details, see Tian *et al.*, 2017).

Scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDX): An 18 × 18 mm square was cut from each of the 67 × 67 mm acceptor surfaces and subsequently coated with 20 nm of carbon. The SEM used for analysis was a LEO 1525 equipped with an Oxford/Link EDX analysis system. The visual inspection was conducted with secondary electron (SE) and backscattered electron (BSE) detectors (acceleration potential: 15 kV). An area of 10 mm × 6 mm was mapped by determining 10 squares of 1 mm × 1 mm size placed in a meandering pattern, which ensures randomness of particle selection for analysis. For each area, about 100 particles (> 10 µm) were selected and analyzed by EDX spectroscopy. For each particle, an image was taken for size determination, and depending on the particle's physical appearance in SE mode and chemical composition, between one and twenty EDX spectra have been collected.

Single-particle analysis: For carbonaceous materials (e.g., rubber), the difference between the highest signals from the sample substrate (acceptor surface) and the signals from particles under the SEM is low because the substrate is coated with an adhesive that also consists of light elements, such as hydrogen, carbon, and oxygen. Hence, the carbonaceous particles are very difficult to spot and in some cases nearly invisible. To facilitate our analysis, TLM and BSE images were overlain to determine size, edge, and outline of all particles. According to the results of the chemical composition and its optical features, each particle was assigned to one of the following categories: tire-wear particles, road-wear particles, brake-wear particles, and other materials (see Table 2).

Image processing: Each of the SEM images was segmented from the original 256 grey-value image to a black-and-white binary image by applying the public-domain image-processing and analysis software package *ImageJ* (National Institutes of Health, USA). The binary transformation by *ImageJ* is based on the ISODATA cluster algorithm (Ball and Hall, 1965). The threshold was manually adjusted until the outlines of the resulting binary picture best matched the particle outlines of the grey-scale image. The binary images were used to measure the projected area of the particles. Subsequently, the geometric equivalent diameters (d_{eq}) of the particles were calculated by using the circle equivalent of the projected area of the particle $d_{\mathrm{eq}} = 2\,(A/\pi)^{0.5}$ to obtain the particle-size distribution.

Volume calculation: The volume of each particle was calculated to reflect its three-dimensional geometric characteristics. Compared to the particle number, the particle volume is more useful to express the input of pollutants into the environment and their possible contamination. For example, a particle with a diameter of 10 µm has a volume 1000 times smaller than a particle with a diameter of 100 µm (see e.g., Verschoor, 2016). The calculation of the approximate volume for each particle is based on d_{eq}, and the first approximation uses the formula for spherical volumes. Since most ambient aerosol particles are not spherical, however, a correction factor was implemented. Empirical examinations conducted by the German Meteorological Service suggest a volume correction factor α_V of 0.75 (VDI 2119, 2013), resulting in the formula:

$$V = 4/3\ \pi \times r^3 \times 0.75 \tag{1}$$

with $r = \mathrm{d_{eq}}/2$. For elongated particles, this result is bound to be too high. Since tire-wear material is observed to be mostly cylindrical (see below), the formula for cylindrical volumes will yield improved results:

$$V = \pi \times r^2 \times h \tag{2}$$

where h is obtained by measuring the longest axis of the particle, and r from dividing the measured particle area, A_{particle}, by the main axis according to:

$$h \times 2r = A_{particle}. \tag{3}$$

Table 1. Traffic characteristics at the sampling stations.

	A 4[*]	A 555[**]	B 31[***]
Vehicles per day (total)	85,662	70,506	35,400
HDV per day (total)	11,477	3,915	3,000
HDV proportion	13.4%	5.6%	8.5%
Traffic mode	flowing/stop-and-go	flowing	stop-and-go
Street type	motorway	motorway	federal highway
Lanes	2 × 3	2 × 3	2 × 2
Orientation	West-East	North-South	West-East
Specification	Aligned by embankments (↕ 5 m)	Open area	Street canyon
Surrounding	industrial/residential	agricultural	urban/residential

[*] AD Heumar (BASt, 2014); [**] Godorf (BASt, 2014); [***] B31 Freiburg Ost Tunnel (BASt, 2016).

Table 2. SEM-EDX identification of traffic-related and other PM.

Type		Diagnostic features	Elements	Origin
Tire wear	Rubber, roundish or kidney-shaped, elongated:	Partly covered with road- and brake wear.	C, S ± Zn; Si, Al, Na, Ca, K, Mg; Fe, Cu	Tire abrasion.
		Completely covered with road and brake wear.	Si, Al, Ca, Na, K, Mg; Fe, Cu, Zn, Ti, Mo, Mn, Ba, Sn, W	
Road wear	Variable shapes, one or more minerals joined by bitumen (crushed grains), colorless or colored, in some cases pleochroic (e.g., biotite). Individual minerals (quartz, feldspar, pyroxene, amphibole, mica) and rock fragments (e.g., granite).		Si, Al, Ca, Na, K, Mg; Fe, S	Abrasion of road surface.
Brake wear	Irregularly shaped fragments with sharp edges and points.		Fe, Cu, Zn, Ti, Mo, Mn, Ba, Sn, W	Abrasion of brake pads, brake discs, and calipers.
Concrete	Irregularly shaped fragments consisting of calcium carbonate, gypsum, quartz and calcium-aluminum-silicate hydrate.		Ca, Mg, Cl, S, Si, Fe, Al	Weathering of bridges, curbs, and buildings.
Soil (mostly loess)	Irregularly shaped fragments consisting of silt-sized carbonate, clay, and quartz with organic material and fertilizer.		Si, Al, Ca, Na, K, Mg, P, S	Farm fields and curb sides.

RESULTS

Characterization of Super-coarse Particles via SEM-EDX

Tire-wear Particles

Of the 508 super-coarse particles examined, 171 were identified and classified as produced by abrasion of tires. By volume, the tire-wear particles represent more than half of all particles studied in all samples (see below), and they also represent consistently the largest particles found. Our observations show that tire-wear particles consist of a central rubber core (tire-core particle), which was abraded from a tire tread and now is partly (Figs. 2(a) and 2(b)) or totally (Fig. 2(c)) encrusted by smaller particles derived from brake wear, road wear, and other road dust (e.g., soil, concrete). The shape of tire-wear particles is elongated and cylindrical, resembling a cigar (length [x-axis] = 10–200 µm, width [y-axis] < 20 µm).

The composition of tire treads varies considerable according to type (e.g., summer vs. winter; passenger car vs. HDV) and brand. To determine tire wear we rely on generalized specifications from the literature. The treads of tire consist of five components to yield a combination of durability, flexibility, and grip (Camatini *et al.*, 2001; Gieré *et al.*, 2004; Kocher *et al.*, 2010; Apeagyei *et al.*, 2011; Gunawardana *et al.*, 2012; Wu, 2016). Since the production of tires is a well-kept secret of the manufacturers, especially as far as the composition of the additives is concerned, the following figures are approximate values for these components:

1. Basic material (40–50 mass%): made of natural rubber (Polyisopren [C_5H_8]), with synthetic rubber.
2. Filler (30–35 mass%): typically soot/carbon black (C), silica (SiO_2), and chalk ($CaCO_3$).
3. Softener (15 mass%): consists of oil and resin.
4. Vulcanization agents (2–5 mass%): sulfur (S) and zinc oxide (ZnO).
5. Additives (5 to 10 mass%): unknown.

Silica (SiO_2) is common in road wear, brake wear, concrete, and soil (e.g., as quartz) and thus is not an indicator for tire-core particles. On the other hand, zinc may be a reliable chemical indicator for tire-core particles. Tire-wear particles, however, are best identified by their shape, surface, and structure.

As tire-wear particles are typically elongated (see e.g., Rauterberg-Wulff *et al.*, 1995; Kreider *et al.*, 2010), we compared their axial ratio and volume and observed that the particle volume is characteristic for the different roads (Fig. 3). We found that more than 90% of the tire-wear particles have an axial ratio, d_y/d_x, of ≤ 0.6 (red horizontal line in Fig. 3), with an average of 0.36. All of the B 31 particles display volumes ≥ 10^4 µm^3, whereas more than two-thirds of the A 555 particles have volumes < 10^4 µm^3. The A 4 particles show a more even distribution (Fig. 3).

Both the structure and the volume of the encrustment of tire-core particles show considerable differences between the studied roads. Tire-wear particles from A 555, for example, appear as clusters of particles under the SEM. The superposition of the BSE and the TLM images was needed to find the true edges of the particle (Figs. 2(a) and 2(b)). The examination of the tire-core particles of the A 555 (a representative example is shown in Fig. 4(a)) reveals that the particles attached to the rubber core are the same minerals as those found in the wearing course: quartz, plagioclase, orthoclase, ferromagnesian silicates, and calcite. In addition, materials typical of brakes and brake pads were observed, including: metals (Fe, Cu, Zn, Al), alloys (Fe ± Cu, Mo, Mn), and barite. Other particle types identified were road salt (NaCl).

To determine the structure of airborne tire-wear particles, the volume for the tire-core particles and the additional encrustment with particles was calculated. For detailed structural analysis, five tire-wear particles > 40 µm from

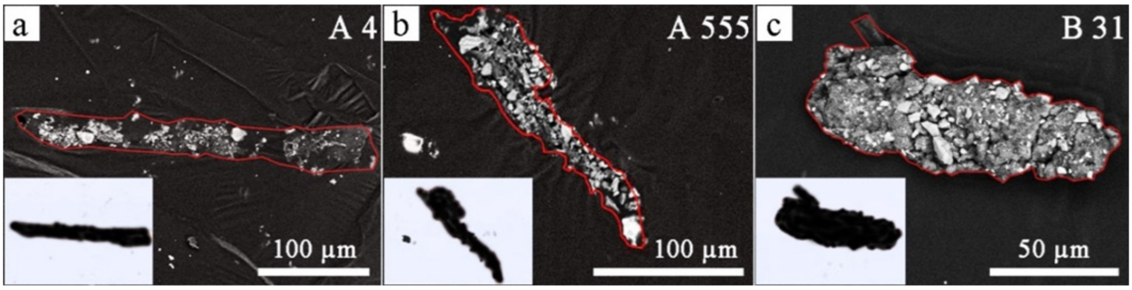

Fig. 2. Typical super-coarse tire-wear particles from motorways A 4 and A 555 and the federal highway B 31, exhibiting different extents and volumes of encrustment. The red line shows the outline of the particles as reconstructed from their appearance in TLM images (lower left insets). (a) The particle from motorway A 4 displays the typical long cylindrical form of a tire-core particle (darkest part within the red particle outline), partly contaminated and covered with smaller particles (encrustment < 50 vol%), (b) Tire-core particle from motorway A 555, partly covered with coarse particles (encrustment < 50 vol%), and (c) Tire-core particle from the B 31 highway, totally covered with particles (encrustment > 50 vol%) that range in d_{eq} from 0.5 μm to 10 μm.

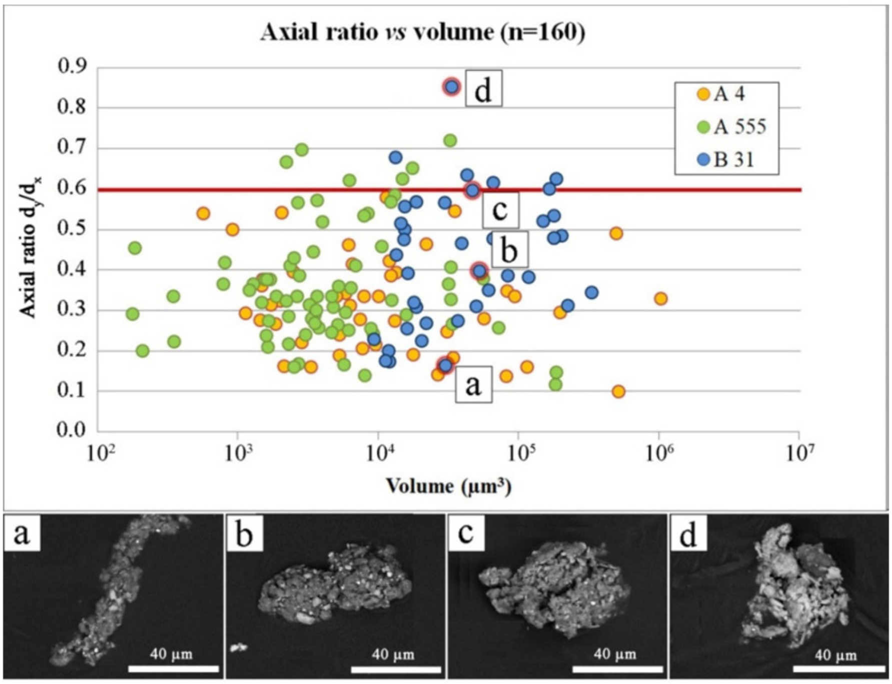

Fig. 3. Shape vs. volume scatterplot of tire-wear particles (n = 160) for motorways (A 4, A 555) and federal highway (B 31). SEM images below (a)–(d) display a series of tire-wear particles (identified by red circles in the diagram) with increasing axial ratio as well as a range of shape, structure and volume from the B 31 highway.

the A 555 motorway were selected. The particles of the encrustment were mapped and characterized, with one example shown in Fig. 4. The particle size distribution (d_{eq}) of the encrustment particles (n = 873 for five tire-wear particles) ranged from 0.5 to 12 μm, with an average d_{eq} of 1.5 μm and a standard deviation of ± 0.9 μm. The total volume of these particles ranged from 6 to 10 vol% of an entire tire-wear particle. The volume ratio for minerals (mainly from abrasion of the wearing course) to iron particles (from brake materials) is about 5:1. Given a density of 1 g cm^{-3} for rubber, 2.6 g cm^{-3} for minerals, and 8 g cm^{-3} for iron, the resulting density of the whole tire-wear particle (rubber core plus encrustment) can be calculated at 1.26 g cm^{-3}.

Tire-core particles of the federal highway B 31 (urban area) are completely encrusted by relatively large (d_{eq} = 1–10 μm) particles from the road surface (wearing course), which are embedded in a matrix of smaller dust particles (e.g., Fig. 5). The larger particles were identified as minerals (quartz, plagioclase, orthoclase, ferromagnesian silicates, calcite, gypsum, and barite) and metals (Fe, Fe alloy, and Cu). The smaller dust particles of the matrix cannot be examined by EDX because of their small size (< 1 μm) and tight packing. However, the resulting mixed EDX spectra, without larger particles, point to a matrix that consists of the same minerals and metals as those identified as larger particles from the wearing course. Additionally, the elements (Zn, Ti, Mg, Mo, W, S, and Cl) were detected in the matrix (Fig. 5).

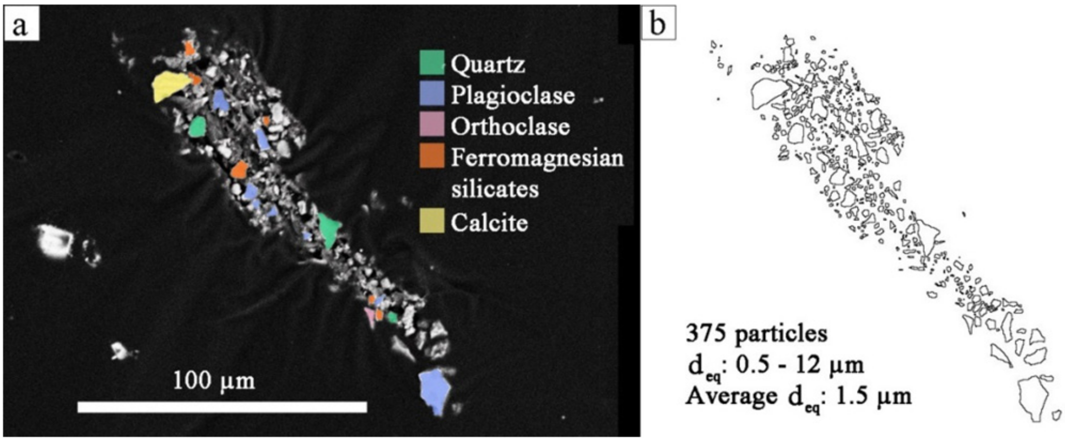

Fig. 4. Typical tire-wear particle (< 50 vol% encrustment) from motorway A 555. (a) Particle types, identified on the basis of elemental analysis, occurring in the crust surrounding the rubber core and (b) Mapped binary outline of the particles located on the surface of the tire-core particle. Note that, coincidentally, both the range in d_{eq} and the average d_{eq} are identical to the range and average size obtained from all five tire-wear particles studied in such detail.

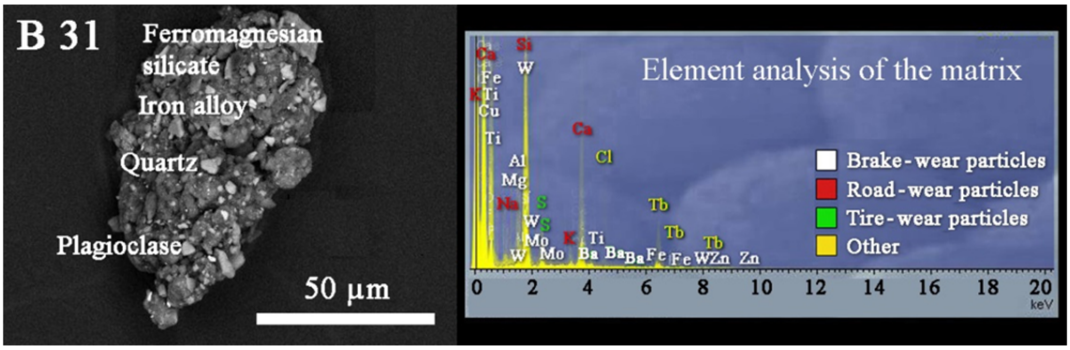

Fig. 5. SEM image of a representative tire-wear particle with an encrustment > 50 vol%, typical for the federal highway B 31. The EDX diagram on the right displays the superposition of 25 spectra from the imaged tire-wear particle with subsequent particle classification.

Without exact geometric data for the shape of the original tire-core particle an estimation of the volume ratio between rubber core and encrustation is difficult. We assume that the original tire-core particles from B 31 and A 555 are comparable in shape and size as indicated by their axial ratios (Fig. 3). The calculated volumes of tire-wear particles from the B 31 highway are approximately ten times higher than the particles from the A 555. Therefore, we conclude that the volume ratio of encrustment to rubber core is at least 1:1. To distinguish and finally classify the two different particle types we use the term *tire-wear particle type 1* (TWP-1) for rubber particles with less than 50 vol% encrustation, and *tire-wear particle type 2* (TWP-2) for tire-core particles with more extensive encrustation.

Using this classification, all tire-abrasion particles on the A 555 were classified as TWP-1 (n = 77), whereas on the federal highway B 31 they are exclusively TWP-2 (n = 44). For the A 4 motorway both types, TWP-1 (n = 43) and TWP-2 (n = 7), can be found.

Road-wear Particles

Of the 508 particles examined, 194 were identified as road-wear particles. The source of the road-wear particles is the wearing course of the motorway or highway at or near the sampling point. The material is defined as a mineral aggregate bound together with bitumen. Detailed analysis of the road-wear material in five of our samples revealed a quartz-rich mixture, pointing to granite and quartzite as likely source materials (Figs. 6(a), 6(b), and 6(c); Table 3).

Two samples from the A 4 motorway were investigated: the first sample (CW10/2014) consisted of 42 vol% feldspar (23 vol% plagioclase, 19 vol% orthoclase), 9 vol% ferromagnesian silicates (pyroxene/augite, amphibole, mica), and 49 vol% quartz particles (Table 3). The results of the second sample (CW05/2015) are very similar, except that the feldspar class is now enriched orthoclase (Table 3). Similarly, two samples from the A 555 motorway were investigated: in the first sample (CW10/2014), the feldspar class contained 9 vol% plagioclase and 27 vol% orthoclase, the ferromagnesian silicates (pyroxene/augite, amphibole, mica) amounted to 18 vol%, and 46 vol% of the particles were quartz, with the results of the second sample (CW05/2015) in relatively good agreement (Table 3). Both motorways display a mineral mix typical for quartz-rich granite or granodiorite. This finding is consistent with the information given about the asphalt top coat used as

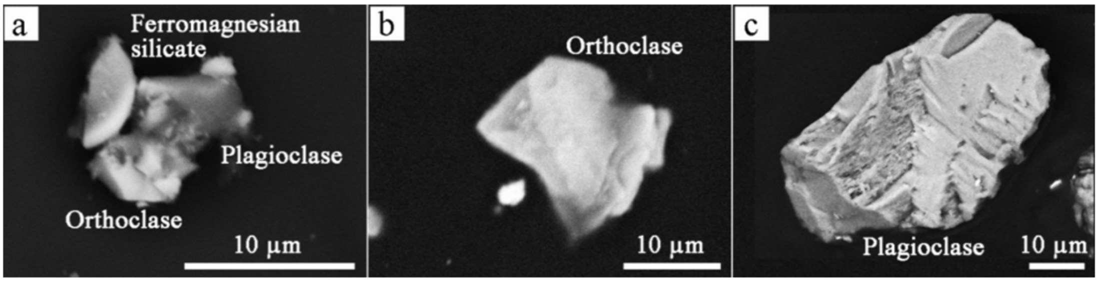

Fig. 6. BSE images of crushed granite and its mineral components from the wearing course: (a) Composite of minerals typical of granite, held together with bitumen; size fraction 10–20 µm d_{eq}, (b) Single mineral, size fraction 20–40 µm d_{eq}, and (c) Single mineral, size fraction 40–80 µm d_{eq}.

Table 3. Mineral composition of the road-wear particles (in vol%).

Minerals	A 4		A 555		B31
	CW10/2014	CW05/2015	CW10/2014	CW05/2015	CW27/2017
	(n = 50)	(n = 42)	(n = 44)	(n = 34)	(n = 24)
Plagioclase	23	8	9	10	4
Orthoclase	19	32	27	28	21
Ferromagnesian Silicates	9	4	18	7	36
Quartz	49	49	46	49	37
Calcite	0	7	0	6	2

wearing course for these motorways (BASt, unpublished information), which consists of crushed granite, granodiorite, or quartzite, with grain sizes ≤ 5 mm (see also Ntziachristos and Boulter, 2009). As expected, the composition of the B 31 (CW27/2017) wearing course deviates from that of the A 4 and A 555 motorways since the material used in southwestern Germany originates from a different quarry (BASt, unpublished information). Of note is the high amount of ferromagnesian silicates, most likely augite (a pyroxene) or amphibole, in the B 31 sample (Table 3). Three of the five samples investigated in more detail also contain calcite.

Even though bitumen is not easily detected by SEM-EDX, it can be identified on the basis of its sulfur content when occurring in agglomerates of different minerals glued together (according to the manufacturer's information, asphalt contains 2–8 mass% bitumen with 2–6 mass% S) (Fig. 6(a)). It must be stated, however, that sulfur is not an unequivocal marker element for bitumen because it also appears in tire wear in similar concentrations (see Gieré *et al.*, 2004).

Brake-wear Particles

During our analysis, 86 particles were identified as derived from brake abrasion, and a total of 94 EDX spectra were collected from these particles. The sources of brake-wear particles are mainly brake pads and brake discs but also other brake parts (e.g., brake caliper). Fig. 7 displays typical examples of three different types of brake-wear particles as well as EDX spectra of both individual points (left side) and superpositions of all available point analyses (right side) from the two motorways and the B 31 federal highway.

According to Stechmann (1993), Chan and Stachowiak (2004), Adachino and Tainosho (2004), Hillenbrand *et al.* (2005), Grigoratos and Martini (2015), and Wahid (2018) typical brake discs (Fig. 7(b)) consist of cast iron (Fe ± Cr, Cu, Mo, Ti) or sometimes ceramics, whereas brake pads (Figs. 7(a) and 7(c)) are made of five components:

1. Fibers (6–35 vol%), for mechanical stability; made of metals (Fe, Cu, Ti, Zn), carbon (C), glass fibers, or Kevlar (Fig. 7(a)).
2. Abrasives (up to 10 vol%), for the friction; made of alumina (Al_2O_3), iron (Fe), iron oxide (e.g., Fe_2O_3), copper (Cu), brass ($CuZn_x$), quartz (SiO_2), zirconium (Zr), and zircon ($ZrSiO_4$) (Figs. 7(a), 7(b), and 7(c)).
3. Lubricants (5–29 vol%), for the frictional properties; made of graphite (C), metals, metalloids, and sulfides (e.g., Sb_2S_3).
4. Filler (15–70 vol%), for processing and quality; made of barite ($BaSO_4$), calcite ($CaCO_3$), $Sb_2(SO_4)_3$, MgO, Cr_2O_3, or silicates (Fig. 7(c)).
5. Binder (20–40 vol%), for durability; made of resins, COPNA (condensed polynuclear aromatic compounds), phenol-based, cyanate-, epoxy-, silicon-modified, thermoplastic polyamides.

Since iron is the main component of the brake disc and an important component of the brake pad, the metal also dominates the particles. Copper, Al, Ti, and Zn are also found frequently and so are filler materials, such as calcite and barite, abrasive materials (e.g., quartz), and sulfide for the lubricants. It is striking that the urban sample (Fig. 7(c)) contains a greater variety of elements (e.g., Sb, Mo, Sn). Antimony, however, was found only in four brake-wear particles and in the encrustment of two tire-wear particles. The element, therefore, is a useful indicator of brake wear but it is not an explicit tracer.

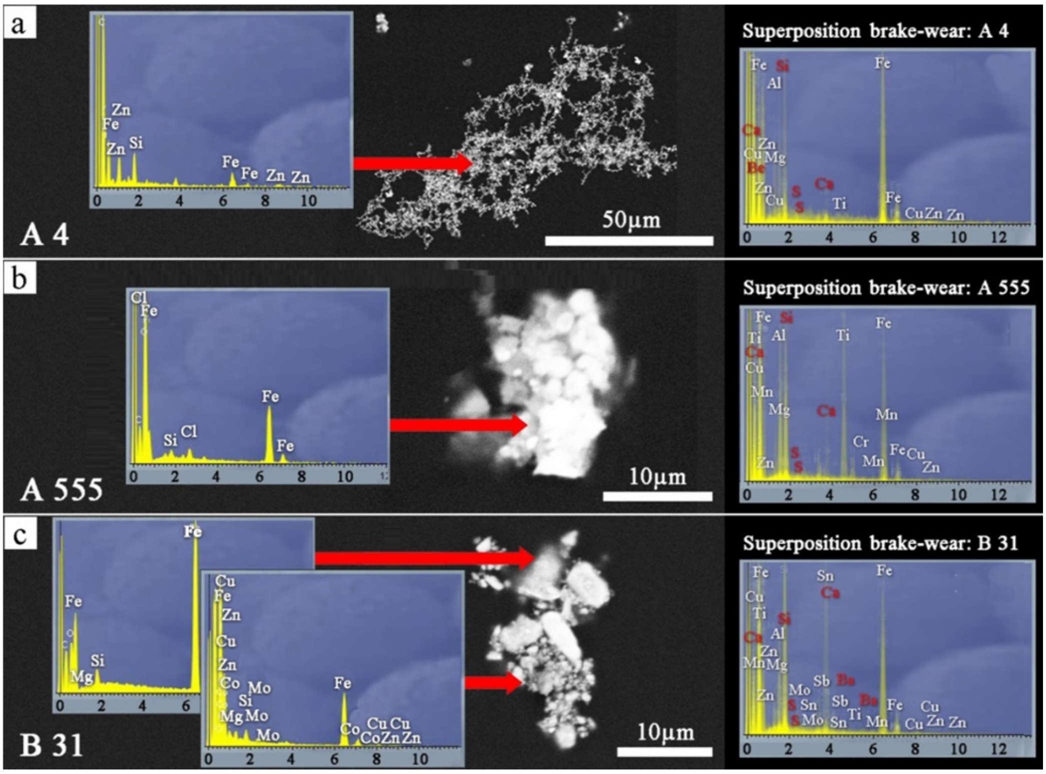

Fig. 7. Examples of BSE images of brake-wear particles with EDX element analyses of individual points (left side) and element overview (right side, superposition of the spectra from all samples and all brake-wear particles for the A 4 and A 555 motorways and the B 31 federal highway (Elements of metallic or metalloid components in white, of minerals in red). BSE images from (a) A 4: Brake pad, network of fibers and abrasives where the filler and lubrication is partially decomposed, (b) A 555: Iron-abrasion particle typical for brake disc, and (c) B 31: Brake-pad particle with iron (abrasive), copper (thermal dissipation), and silica (filler).

Other Particles

About 10 vol% of the particles (n = 57) found in the samples are not directly traffic-related, including road salt (1 vol%), concrete (3 vol%), soil (1 vol%), and plant debris (2 vol%). Road salt (NaCl) is applied for deicing in winter (Fig. 8(a)). Concrete, in general a composite material of calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), quartz (SiO_2), and gypsum ($Ca[SO_4]\cdot 2H_2O$), can be derived from abrasion of road components, such as medial strip barriers and bridges, or it can be introduced by the vehicles (Fig. 8(b)). The source of soil particles, a variable mix of clay minerals (hydrous aluminum silicates), calcite, quartz, and fertilizer (Ca, Si, Al, Mg ± Na, K, Cl, Fe, Ti, P), can be the agricultural area around the motorways or the green strip along the roads (Fig. 8(c)).

In addition, we observed occasionally particles with elements normally used in electronic devices (e.g., Tb, Se, Hf).

Particle Overview

During our study, we characterized 508 particles with 1450 EDX spectra in samples from the A 4 (CW10/2014 and 05/2015) and the A 555 (CW10/2014 and 05/2015) motorways and from federal highway B 31 (CW27/2017). This investigation led to three important results:

i) The single-particle analysis revealed that for all five samples combined, 89% of all analyzed particles were derived from traffic-related sources: road wear (39%), tire wear (33%), and brake wear (17%) (Fig. 9(a)). The remaining 11% originated from various sources in the surrounding area (e.g., concrete construction, farm fields, plants). In terms of volume, 93% were traffic-related, and 7% were derived from non-traffic sources (Fig. 9(b)). The differences between the particle number and particle volume calculations for the traffic-related and non-traffic particle sources are marginal, as the volume of all traffic-related particles is only 4% higher than their particle number. On the other hand, the volume of the tire-wear particles is 21% higher than their proportion based on particle number. For the road- and brake-wear particles, the volume is 11% and 6% lower, respectively (Figs. 9(a) and 9(b)).

ii) A comparison of the samples from the different roads documents that they are all dominated by traffic-related particles but that both volume and source of the particles differ considerably. Motorways A 4 and A 555 display a similar distribution of $PM_{10\text{-}80}$, with tire-wear particle percentages of 40 and 44 vol%, respectively, which is much lower than at B 31 (70 vol%; Fig. 10(a)). It is noticeable that the percentage of tire-wear particles in the B 31 sample is highest in the fraction > 40 µm (Fig. 10(d)).

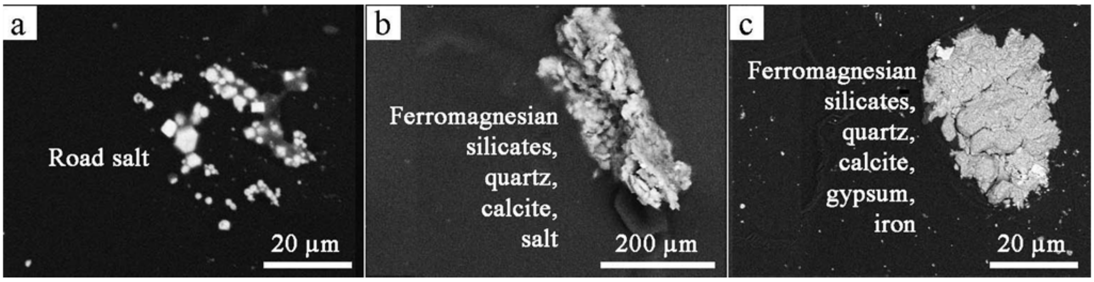

Fig. 8. Examples for the most common particles not directly related to traffic. (a) Road salt was found on both motorways, (b) Concrete was found near all roads, and (c) Soil was found most commonly on the A 555 (surrounded by agricultural area). Note: For the discrimination between concrete and soil, additional optical morphological properties were applied.

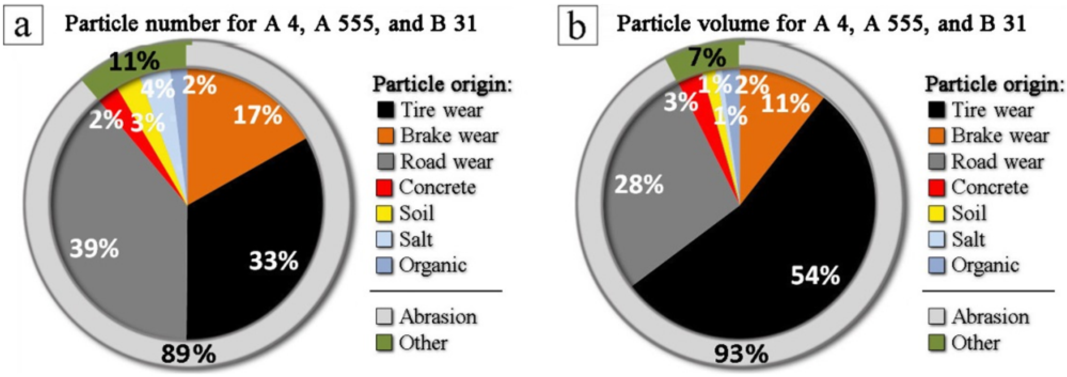

Fig. 9. Particle distribution according to their emission source based on (a) particle number and (b) particle volume.

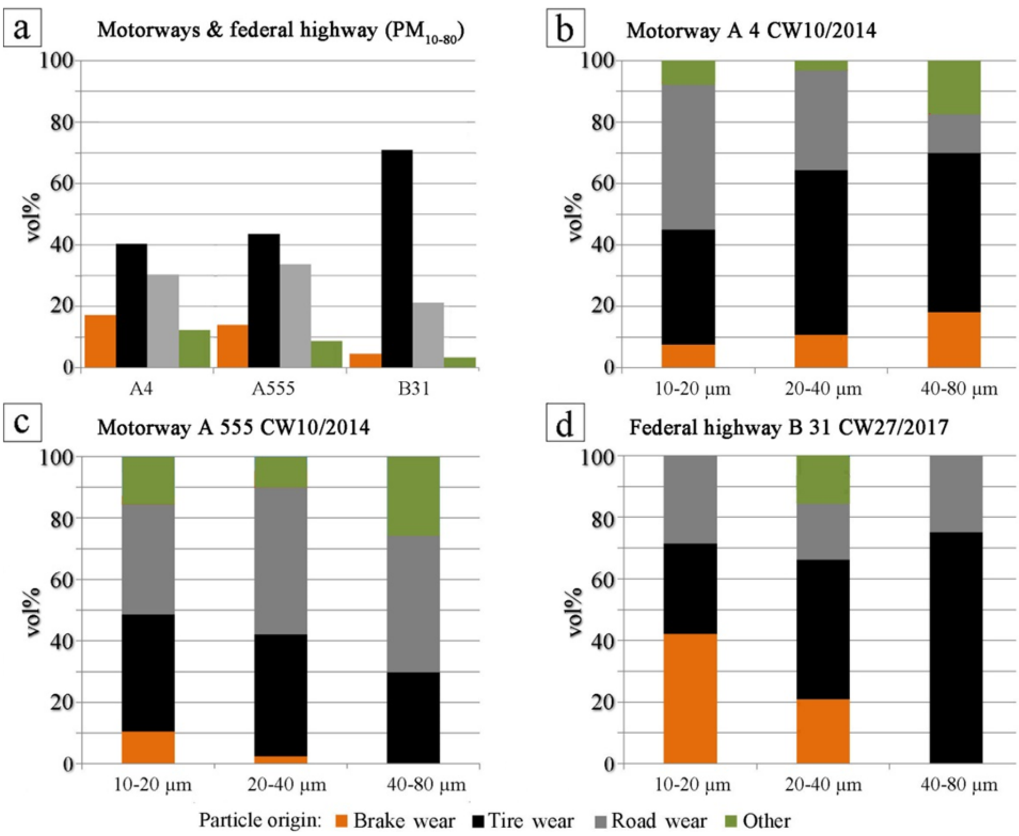

Fig. 10. Relative frequency of traffic-related particle types (in vol%). (a) Overall comparison for motorway A 4, motorway A 555, and federal highway B 31 for PM_{10-80}. The particle types in three size classes for (b) motorway A 4, (c) motorway A 555, and (d) federal highway B 31.

Overall, brake-wear particles contribute 11 vol% to the PM_{10-80} collected along the three investigated roads (Fig. 9(b)). The highest volume percentage of brake-wear particles in PM_{10-80} was found on the A 4 (18 vol%, Fig. 10(a)) and, unlike on the other roads, we find most of the brake-wear particles in the 40–80 µm partition (Fig. 10(b)). In contrast, the B 31 displays the smallest amount of $PM_{10–80}$ brake-wear particles (5 vol%; Fig. 10(a)), and these particles are mainly found in the size fraction 10–20 µm (Fig. 10(d)). Neither on the B 31 nor on the A 555 did we observe brake-wear particles > 40 µm (Figs. 10(c) and 10(d)).

iii) Our EDX data did not indicate the presence of the highly toxic metal Cd in any of the 508 examined particles. Lead was detected only in one particle (Table 4). Chromium and Mo were found as part of iron alloys in 31 and 24 particles, respectively, Sb in 9, and Ba in 30. The most common metal besides Fe was Cu. Zinc was found in 37 particles. The Zr detected in one particle probably results from remains of a technical device or from brake wear.

DISCUSSION

About 93 vol% of the PM_{10-80} at all our sampling sites is exclusively traffic-related. Our analysis reveals an extremely low input of particles from the adjoining areas (7 vol%). The 35,000 to 80,000 vehicles passing the sampling stations per day continuously generate abrasion particles, especially through the wear of tires. The average loss of tire material through abrasion was estimated at 20 mg km^{-1} for light-duty vehicles (LDV) and at 200 mg km^{-1} for HDV (Baumann and Ismeier, 1998; Krömer *et al.*, 1999; Camatini *et al.*, 2001; Hillenbrand *et al.*, 2005). In the past, it was postulated for tire-wear particles that equilibrium exists between their total emission into the environment and their chemical and biological degradation, and therefore, pollutant entry was classified as low (Krömer *et al.*, 1999). However, these assumptions are overruled by a continuously increasing traffic volume (Councell *et al.*, 2004). The amount of PM abrasion from the road surface has similar ranges as the average loss of tire material (Muschack, 1988). All abraded particles, which are deposited on the road surface, can be mobilized, e.g., suspended and re-suspended by wind and turbulence effects of the passing traffic. However, PM_{10-80} has a generally high sedimentation velocity and therefore a short residence time in the atmosphere. The PM_{10-80} load from areas surrounding the roads (e.g., farm fields) is extremely low due to the longer transport path. Consequently, the roads with their moving traffic can be considered as the nearly sole PM source at all our sampling sites (see also Kupiainen, 2007). Our data document that tire-wear particles are volumetrically the most important component of the PM_{10-80} load at highly frequented motorways and highways and thus represent a substantial fraction of microplastics released into the environment. This illustrates that traffic can distribute any kind of material that can reach the driving lanes (e.g., remains from accidents, lost cargo, and broken items, including electronic devices).

As described by Smith and Veith (1982) and Rogge *et al.* (1993), tire-wear particles are generated through abrasion due to the interaction between the tire tread and the road surface. A frictional connection between tire tread and road surface is inevitable, even required, for propulsion and directional stability of the vehicles. When overcoming the rolling resistance, the tire tread undergoes a continuous stress, and the rubber is pressed into a bulge in the driving direction, which creates a prolonged stretching and generates material fatigue, known as the Mullins effect (Schramm, 2002; Klempau, 2003). When the damaged rubber slides against surface asperities, abrasive wear is the dominant abrasion mechanism: stress concentrations generated by the sharp points of contact damage the rubber, which can then reach the limiting strength of the material, resulting in micro-cutting or scratching of the tire tread. This creates elongated particles of rubber (Wu, 2016), which develop the typical cylindrical shape when repeatedly overrun and rolled by vehicles. Consequently, the observed tire-abrasion particles are described as elongated, cylindrical or "cigar-shaped" (Rauterberg-Wulff *et al.*, 1995; Smolders and Degryse, 2002; Tian *et al.*, 2017). Our determination of the geometric parameters is in accordance with the specifications given above: more than 90% of the particles display an axial ratio ≤ 0.6 (see also Kreider *et al.*, 2010).

Once deposited on the road surface, tire-abrasion particles attract road dust. This is due to the consistency of the rubber itself. Made for close contact with the road surface, rubber is flexible and exhibits good adhesion to the underground materials (Schramm, 2002). Moreover, the surface of rubber particles is rough and offers a large contact zone (Figs. 2 and 3; see also Gunawardana *et al.*, 2012). In addition, the particles display a rounded cross section, which allows them to roll over the road surface easily, thereby collecting other road-dust particles like a rolling snowball (Figs. 3 and 5; see also Rauterberg-Wulff *et al.*, 1995; Kreider *et al.*, 2010; Gunawardana *et al.*, 2012). In regard to this snowball effect, a distinct difference is observed between the tire-abrasion particles from B 31 and A 555: the tire-abrasion particles from A 555 show a partial encrustment by larger particles, whereas those from B 31 are completely encrusted with a mix of larger particles embedded in a matrix of sub-micrometer road dust.

Table 4. Particles with heavy metals.

	Total particles (n)	Ba	Cd	Cr	Cu	Mo	Pb	Sb	Zn	Zr
A 4	201	2	0	3	6	8	0	1	3	1
A 555	202	17	0	19	23	9	1	2	14	0
B 31	105	11	0	9	42	7	0	6	20	0
Sum	508	30	0	31	71	24	1	9	37	1

In our investigation of $PM_{10–80}$, we have not found any tire-core particles at any of the sites. The extent of encrustment (coating) observed for all tire-abrasion particles ranges from of about 10 vol% (A 555) to more than 50 vol% (B 31). We conclude that the decisive factors for the development of such large differences in the extent of encrustment are traffic flow and traffic velocity, or driving speed: on roads with low velocities (e.g., urban thoroughfares), the tire-core particles are exposed to repetitive cycles of slow roll-over processes with long-term contact between the rubber and road dust, which results in a high degree of encrustment. On roads with high velocities (e.g., motorways), however, a more efficient removal of material from the road surface due to vehicle-induced turbulence is observed (Kupiainen *et al.*, 2007), and therefore, less road dust can be accumulated on the tire-core particles. The urban B 31 highway is characterized by continuous stop-and-go traffic and slow driving speeds that, in addition, are capped by speed limits of 50 km h^{-1} (day) and 30 km h^{-1} (night), leading to high encrustment levels. On the other hand, the A 555 motorway is characterized by fluid traffic and high driving velocities, leading to lower extents of encrustation. The A 4 motorway combines characteristics of both slow (morning and evening rush hours during the week) and fast (weekends and non-rush hour periods) traffic, and therefore, the level of encrustment is widely variable. For this motorway, the cumulative duration of stop-and-go traffic is approximately 25 hours per week (five hours per day, Monday–Friday), which corresponds to about 15% of the 168 hours in a week and is in good accordance with the 15% of particles exhibiting a high encrustation level.

A substantial influence of weather parameters on the level of encrustment could not be observed.

i) In calendar weeks 10/2014 and 05/2015, the average humidity at the A 4 and A 555 sites was 59% and 88%, respectively, and no difference in the extent of encrustment of tire-wear particles could be detected.
ii) An influence of air temperature on the encrustment is unlikely. More probable is that the tire temperature might have an influence, as it depends predominantly on tire pressure and driving speed and affects the abrasion, whereby abradability increases with increasing temperature (Thavamani and Bhowmick, 1993; Wintergerst, 2013; Wu, 2016). However, we could not find data on a possible effect of tire temperature on the encrustment process.
iii) An influence of wind parameters on the encrustment process is highly unlikely because the mobilization of abrasion particles and road dust is dominated by the vehicle-induced turbulence (Macciacchera and Ruck, 2001; Ruck and Lichtneger, 2014).

In terms of chemical composition, our study confirms the statement of Camatini *et al*. (2001) that the application of SEM-EDX alone is not sufficient to identify tire-abrasion particles. The element analysis shows that the particle coatings for all roads are chemically very similar but unspecific. This result means that the encrustation mainly consists of road-abrasion particles (from the wearing course), with lesser amounts of brake-wear particles and only minor amounts of material from other sources (e.g., concrete, soil). Our study did not confirm the frequently described importance of zinc oxide as a tracer for tire-abrasion particles (Smolders and Degryse, 2002; Councell *et al.*, 2004; Kocher *et al.*, 2010; Apeagyei *et al.*, 2011; Gunawardana *et al.*, 2012). Zinc oxide is used as an activator and accelerator during the vulcanization step of tire production, but the applied quantity can vary considerably (Councell *et al.*, 2004; Wu, 2016), and substitutes (e.g., magnesium oxide) can be used. In our study, it was not possible to determine tire-related zinc by single-particle analysis in the tire-wear particles with complete encrustment. Among the partly encrusted tire-wear particles, only very few measurements of zinc could be definitely assigned to tire material. This result supports the observation of Adachino and Tainosho (2004) that *the presence or absence of particulate ZnO may depend on the tire type and on the manufacturing process of the tire treads*.

Modern tires consist of natural rubber and synthetic rubbers, such as styrene-butadiene rubber (SBR) and butadiene rubber (BR), i.e., plastic. Only the natural rubber is susceptible to degradation (Berekaa, 2006). More than 50% of car tires are made from various types of artificial rubber (Wu, 2016). Thus, our results document a continuous emission of microplastics produced by traffic into the direct vicinity of the motorways. Since the traffic infrastructure of developed countries is very extensive, emission of microplastics through tire abrasion is a far-reaching problem. Tire-wear particles are thus disseminated on a large scale, which can lead to substantial changes in marine and continental environments, even in particle-rich habitats, such as soils and freshwater ecosystems (Lechner *et al.*, 2014; Wagner *et al.*, 2014; Machado *et al.*, 2018). In addition, it has to be taken into account that microplastics are both possible sources and possible sinks for hazardous contaminants (Klein, 2015).

The analysis of brake-wear particles revealed that besides the driving speed and traffic mode, the traffic fleet is an additional important factor determining the size distribution for the PM_{10-80} composition. We observe that the motorways A 4 and A 555 display an opposite trend regarding the brake-wear in their vol% size distribution. Moreover, brake-abrasion particles > 40 µm can be found only on the A 4, where there is a wide range of driving speeds and thus, of speed changes and braking actions. These conditions lead to increased stress on brake parts, especially for HDV brakes. Consequently, it can be assumed that the high proportion of brake-wear particles > 40 µm is the result of the high proportion of HDVs. In contrast, on the A 555 we have fluid traffic and high velocities. HDVs can drive an even speed (~80 km h^{-1}), brake actions of HDVs are rare, and thus, tire-wear particles > 40 µm are not found. The trend for the size distribution observed at the B 31 is similar to that observed for the A 555 but the volume% of all super-coarse brake-wear particles is distinctly higher on the motorway. On the B 31, traffic is characterized continuously by stop-and-go conditions. Therefore, braking maneuvers are frequent for both LDVs and HDVs, generating high numbers of brake-wear particles (see also

Grigoratos and Martini, 2015; Wakeling *et al.*, 2017). However, with low driving speeds (< 50 km h^{-1}) on the B 31, the stress for the brakes is low, thus generating a high volume% of small brake-wear particles (< 20 µm).

In the literature, a range of heavy metals is associated with non-exhaust traffic particles (Camatini *et al.*, 2001; Smolders and Degryse, 2002; Adachino and Tainosho, 2004; Hillenbrand *et al.*, 2005; Kocher *et al.*, 2010; Apeagyei *et al.*, 2011; Adamiec *et al.*, 2016). In general, a reduction of toxic substances can be observed compared with observations in the past (Kocher *et al.*, 2010). Zinc and Cu are regularly found in brake-abrasion particles and consequently, as part of the encrustment of tire-wear particles, mainly of the TWP-2 type. In regard to clutch wear, it should be noted that current vehicles are produced with encapsulated clutch systems to avoid contamination by road dust and therefore do not emit abrasion particles. No indication of airborne clutch-wear particles was found in our study.

SUMMARY AND CONCLUSION

In this study, single-particle analysis via SEM-EDX was conducted on coarse-sized ambient aerosols from two highly frequented motorways and one federal highway passing an urban area. The selected roads differ in traffic mode, traffic speed, and traffic fleet.

The importance of these findings is that on both motorways and on the urban highway, > 90 vol% of the super-coarse particles are derived from the abrasion of tires, the road surface, and brake systems; no clutch-wear particles were detected. Our findings further show that the usual focus on traffic density as the only criterion for characterizing the emission conditions at a specific roadside is not sufficient. Clearly, traffic speed, traffic mode, and traffic fleet, generally described as level of service (LOS), are important parameters as well. In particular, brake-wear particles are sensitive to changing traffic parameters: their proportion in the PM_{10-80} increases with the number of braking maneuvers according to traffic mode, and the particle size increases with a growing proportion of HDVs.

This is the first study to show that tire abrasion contributes considerably to the pollution of the environment by microplastics. The possible environmental and ecological impacts of these tire-derived microplastics in PM_{10-80} are probably restricted to the immediate vicinity of roads. Our study further shows that super-coarse tire-wear particles are encrusted by road dust, ranging from a partial encrustment under fluent traffic conditions to complete encrustment under stop-and-go conditions. Therefore, the tire-derived microplastics consist not only of the original rubber core with its various additives (e.g., Al, Ti, Fe, Zn, Cd, Sb, or Pb) but also of potentially hazardous metals and metalloids contained in the attached brake-abrasion particles (e.g., Al, Fe, Cu, Sb, or Ba). These additional materials present in the encrustment thus increase the potential of environmental damage resulting from tire-wear particles. In our study, however, Zn was not a reliable tire tracer, and Cd could not be found at all.

Targeted traffic management that controls the velocity and unbundling of traffic flow in urban areas or provides automated traffic control on motorways will significantly reduce the proportion of tire wear in the larger fraction of super-coarse particles, i.e., sized 40–80 µm.

In light of our findings, further studies are necessary to examine the deposition and mobilization of traffic-related abrasion particles directly on the road surface. Such studies should be expanded to include road-simulator measurements and on-site sampling of representative dust from the road surface (e.g., with cyclone vacuum cleaners). As a result of the continuous dispersion into the environment of natural and artificial rubber contaminated with brake-abrasion particles emitted from the roads, the impacts on ecosystems and the food chain should also be investigated. Another important topic will be a detailed individual particle analysis of the $PM_{2.5-10}$ breathable particle fraction.

ACKNOWLEDGEMENTS

This work was supported by the Federal Highway Research Institute (BASt), in cooperation with the German Meteorological Service (DWD). We also thank Dr. Andreas Danilewski from the Institute for Crystallography and Material Science–Albert Ludwigs University of Freiburg for his support while using the SEM. We also thank Sergej Metzger for the sampling and for maintenance of the sampling equipment. Travel funds from the University of Pennsylvania have helped us in making this study possible. We are grateful to the reviewers and the editor who helped us greatly in improving the manuscript.

REFERENCES

Adachino, K. and Tainosho, Y. (2004). Characterization of heavy metal particles embedded in tire dust. *Environ. Int.* 30: 1009–1017.

Adamiec, E., Jarosz-Krzemińska, E. and Wieszała R. (2016). Heavy metals from non-exhaust vehicle emissions in urban and motorway road dusts. *Environ. Monit. Assess*. 188: 369.

Amato, F., Karanasiou, A., Moreno, T., Alastuey, A., Orza, J.A.G., Lumbreras, J., Borged, R., Boldoe, E., Linares, C. and Querol, X. (2012). Emission factors from road dust resuspension in a Mediterranean freeway. *Atmos. Environ*. 61: 580–587.

Apeagyei, E., Bank, M.S. and Spengler, J.D. (2011). Distribution of heavy metals in road dust along an urban-rural gradient in Massachusetts. *Atmos. Environ.* 45: 2310–2323.

Ball, G.H. and Hall, D.J. (1965). Isodata: A method of data analysis and pattern classification. Stanford Research Institute, Menlo Park (NTIS No. AD 699616).

BASt (Bundesanstalt für Straßenwesen) (2014, 2016). Verkehrszählung 2014, 2016: www.bast.de/BASt_2017/DE/Verkehrstechnik/Fachthemen/v2verkehrszaehlung/zaehl_node.html.

Baumann, W. and Ismeier, M. (1998). *Kautschuk und Gummi – Daten und Fakten zum Umweltschutz*. Springer-Verlag, Berlin.

Becker, R. (2006). *Einflussfaktoren auf die Mobilisierbarkeit von PCB und PAK in Rieselfeld-Bodenproben.* Dissertation TU Berlin.

Bejgarn, S., MacLeod, M., Bogdal, C. and Breitholtz, M. (2015). Toxicity of leachate from weathering plastics: An exploratory screening study with Nitocra spinipes. *Chemosphere* 132: 114–119.

Berekaa, M. (2006). Colonization and microbial degradation of polyisoprene rubber by nocardioform actinomycete nocardia sp. strain-MBR. *Biotechnology* 5: 234–239.

Boucher, J. and Friot, D. (2017). *Primary microplastics in the oceans: A global evaluation of sources*. IUCN, Gland, Switzerland.

Camatini, M., Crosta, G.F., Dolukhanyan, T., Sung, C., Giuliani, G., Corbetta, G.M., Cencetti, S. and Regazzoni, C. (2001). Microcharacterization and identification of tire debris in heterogeneous laboratory and environmental specimens. *Mater. Charact.* 46: 271–283.

Chan, D. and Stachowiak, G. (2004). Review of automotive brake friction materials. *Proc. Inst. Mech. Eng. D* 218: 953–966.

Councell, T.B., Duckenfield, K.U., Landa, E.R. and Callender, R. (2004). Tire-wear particles as a source of zinc to the environment. *Environ. Sci. Technol*. 38: 4206–4214.

Degryse, I.L., van der Meulen, M.D., Maes, T., Bekaert, K., Paul-Pont, I., Frère, L., Robbens, R. and Vethaak, A.D. (2015). Microplastic contamination in brown shrimp (Crangon crangon, Linnaeus 1758) from coastal waters of the Southern North Sea and Channel area. *Mar. Pollut. Bull.* 98: 179–187.

Dietze, V., Fricker, M., Goltzsche, M. and Schultz, E. (2006). Air quality measurement in German health resorts Part 1: Methodology and verification. *Gefahrstoffe - Reinhalt. Luft* 66: 45–53.

GESAMP (2015). Sources, fate and effects of microplastics in the marine environment: A global assessment. Kershaw, P.J. (Ed.), (IMO/FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). Reports and studie GESAMP No. 90, 96 p.

Gieré, R., LaFree S.T., Carleton, L.E. and Tishmack, J.K. (2004). Environmental impact of energy recovery from waste tyres. In *Energy, waste, and the environment: a geochemical perspective*. Gieré R. and Stille P. (Eds.), Special Publications, Vol. 236, Geological Society, London, UK, pp. 475–98.

Golwer, A. (1991). Belastung von Böden und Grundwasser durch Verkehrswege. *Forum Städte-Hygiene* 42: 266–275.

Grigoratos, T. and Martini, G. (2015). Brake wear particle emissions: A review. Environ. *Sci. Pollut. Res. Int.* 22:2491–2504.

Gunawardana, C., Goonetilleke, A., Egodawatta, P., Dawes, L. and Kokot, S. (2012). Source characterization of road dust based on chemical and mineralogical composition. *Chemosphere* 87: 163–170.

Herngren, L., Goonetilleke, A. and Ayoko, G.A. (2006). Analysis of heavy metals in road-deposited sediments. *Anal. Chim. Acta.* 571: 270–278.

Hillenbrand, T. Toussaint, D., Böhm, E., Fuchs, S., Scherer, U., Rudolphi, A., Hoffmann, M., Kreißig, J. and Kotz, C. (2005). *Einträge von Kupfer, Zink und Blei in Gewässer und Böden – Analyse der Emissionspfade und möglicher Emissionsminderungsmaßnahmen*. UBA-Texte 19/05, Umweltbundesamt, Germany.

Klein, S. (2015). *Microplastics in freshwater systems: Analysis, occurrence, and sorption of organic contaminants*. Ph.D. Thesis, TU Dresden, Germany.

Klempau, F. (2003). *Untersuchungen zum Aufbau eines Reibwertvorhersagesystems im fahrenden Fahrzeug*. Ph.D. thesis, Technischen Universitat Darmstadt, Germany.

Kocher, B., Brose, S., Feix, J., Görg, C., Peters, A. and Schenker, K. (2010). *Stoffeinträge in den Straßenseitenraum – Reifenabrieb*. Berichte der Bundesanstalt für Straßenwesen (BASt), Verkehrstechnik Heft V 188.

Kooi, M., Besseling, E., Kroeze, C., van Wenzel, A.P. and Koelmans, A.A. (2016). Modeling the fate and transport of plastic debris in freshwaters: Review and guidance. In *Freshwater microplastics - emerging environmental contaminants? The handbook of environmental chemistry*, Wagner, M. and Lambert, S. (eds.), Vol. 58, pp. 125–141.

Kreider, M.Z., Panko, J.M., McAtee, B.Z., Sweet, L.I. and Finley, B.L. (2010). Physical and chemical characterization of tire-related particles: Comparison of particles generated using different methodologies. *Sci. Total Environ*. 408: 652–659.

Krömer, S., Kreipe, E., Reichenbach, D. and Stark, R. (1999). *Produkt-Ökobilanz eines Pkw-Reifens*. Continental AG (Hrsg.), Schrift der Continental AG, Hannover.

Kupiainen, K. (2007). *Road dust from pavement wear and traction sanding*. Monographs of the Boreal Environment Research 26. Finnish environment institute, Helsinki.

Lechner, A., Keckeis, H., Lumesberger-Loisl, F., Zens, B., Krusch, R., Tritthart, M., Glas, M. and Schludermann, E. (2014). The Danube so colourful: A potpourri of plastic litter outnumbers fish larvae in Europe's second largest river. *Environ. Pollut*. 188: 177–181.

Lipfert, W.F., Morris, C.S. and Wyzga, E.R. (2000). Daily mortality in the Philadelphia Metropolitan area. *J. Air Waste Manage. Assoc.* 50: 1501–1513.

Macciacchera, I., Ruck, B. (2001). Pressure fluctuations induced by road vehicles in ambient air –A model study. Proceedings of the Workshops on physical modelling of environmental flow and dispersion, University of Hamburg, Germany.

Machado, A., Kloas, W., Zarfl, C., Hempel, S. and Rillig, M. (2018). Microplastics as an emerging threat to terrestrial ecosystems. *Global Change Biol.* 24: 1405–1416.

Malachova, K., Kukutschova, J., Rybkova, Z., Sezimova, H., Placha, D., Cabanova, K. and Filip, P. (2016). Toxicity and mutagenicity of low-metallic automotive brake pad materials. *Ecotoxicol. Environ. Saf.* 131: 37–

44.

Marwood, C., McAtee, B., Kreider, M., Ogle, R.S., Finley, B., Sweet, L. and Panko, J. (2011). Acute aquatic toxicity of tire and road wear particles to alga, daphnid, and fish. *Ecotoxicology* 20: 2079–89.

Miklos, D., Obermaier, N. and Jekel, M. (2016). Mikroplastik: Entwicklung eines Umweltbewertungskonzepts. Publisher: Umweltbundesamt Dessau. https://www.umweltbundesamt.de/publikationen/mikroplastik-entwicklung-eines.

Muschack, W. (1988). Belastung des Gewässers durch Straßenoberflächenwasser. Roads and Traffic 2000 – Traffic ecology. Proceedings of the International Road and Traffic Conference, 5: 35.

Nizzetto, L., Futter, M. and Langaas, S. (2016). Are agricultural soils dumps for microplastics of urban origin? *Environ. Sci. Technol*. 50: 10777–10779.

Ntziachristos, L. and Boulter, P. (2009). *Road vehicle tire and brake wear*. EMEP/EEA emission inventory guidebook.

Ott, G., Wurster, U. and Zipperle, J. (2015). M*ikro-Kunststoffe: Grundlagen und sachstand*. LUBW Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg, Germany.

Peeken, I, Primpke, S., Beyer, B., Gütermann, J., Katlein, C., Krumpen, T., Bergmann, M., Hehemann, L. and Gerdts, G. (2018). Arctic sea ice is an important temporal sink and means of transport for microplastic. *Nat. Commun.* 9: 1505.

Rauterberg-Wulff, A., Israel, G.W., Pesch, M. and Schlums, C. (1995). *Bestimmung des Beitrags von Reifenabrieb zur Russimmission an stark befahrenen Straßen*, VDI-Berichte Nr. 1228: 81–92, VDI-Verlag, Düsseldorf.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A. and Cass, G.R. (1993). Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks. *Environ. Sci. Technol.* 27: 1892–1904.

Ruck, B. and Lichtneger, P. (2014). Wind loads on flat boards and walls induced by passing vehicles. Proceedings of the Conference "Lasermethoden in der Strömungsmesstechnik", Karlsruhe 2014.

Schramm, E.J. (2002). *Reibung von elastomeren auf rauen oberflächen und beschreibung von nassbremseigenschaften von PKW-Reifen*. Thesis, University of Regensburg, Germany.

Seling, S. and Fischer, P. (2003a). Schadstoffbelastung von Straßenbegleitgrün. Teil I. Gehalte des Mähgutes an Schwermetallen (Cd, Cr, Cu, Hg, Ni, Pb, Pt, Zn). *Müll und Abfall* 35: 289–293.

Seling, S. and Fischer, P. (2003b). Schadstoffbelastung von Straßenbegleitgrün. Teil II. Gehalte des Falllaubs an Schwermetallen (Cd, Cr, Cu, Hg, Ni, Pb, Pt, Zn). *Müll und Abfall* 35: 410–413.

Seling, S. and Fischer, P. (2003c). Schadstoffbelastung von Straßenbegleitgrün. Teil III. Gehalte des Böschungsmähgutes und Falllaubs an organischen Schadstoffen (PAK, PCB, PCDD/F). *Müll und Abfall* 35: 542–546.

Smith, R.W. and Veith, A.G. (1982). Electron microscopical examination of worn tire treads and tread debris. *Rubber Chem. Technol.* 55: 469–482.

Smolders, E. and Degryse, F. (2002). Fate and effect of zinc from tire debris in soil. *Environ. Sci. Technol.* 36: 3706–3710.

Sommer, F., Maschowski, C., Dietze, V., Grobety, B. and Gieré, R. (2016). Comparing single-particle analysis data obtained from scanning electron and light microscope images. *Eur. J. Mineral.* 28: 855–868.

Stechmann, H. (1993). *Charakterisierung kraftfahrzeugspezifischer partikelförmiger emissionen und quantifizierung ihrer beiträge zu aerosolen und gewässerverunreinigungen*. Thesis, University Hamburg, Germany.

Sundt, P., Syversen, F., Skogesal, O. and Schulze, P.E. (2016). Primary microplastic-pollution: Measures and reduction potentials in Norway (MEPEX): www.miljodirektoratet.no/Documents/publikasjoner/M545/M545.pdf.

Tegethof, U. (1998). *Straßenseitige belastung des grundwassers*. Berichte der Bundesanstalt für Straßenwesen (BASt), Verkehrstechnik Heft V 60.

Thavamani, P. and Bhowmick, A.K. (1993). Influence of compositional variables and testing temperature on the wear of hydrogenated nitrile rubber. *J. Mater. Sci.* 28: 1351–1359.

Tian, Z., Dietze, V., Sommer, F., Baum, A., Kaminski, U., Sauer, J., Maschowski, C., Stille, P., Kuang, C. and Gieré, R. (2017). Coarse-particle passive-sampler measurements and single-particle analysis by transmitted light microscopy at highly frequented motorways. *Aerosol Air Qual. Res.* 17: 1939–1953.

U. S. Environmental Protection Agency – EPA (2014). *Brake and Tire Wear Emissions from On-road Vehicles in MOVES2014.* EPA-420-R-14-013.

VDI 2119 (2013). Ambient air measurements sampling of atmospheric particles > 2.5 µm on an acceptor surface using the Sigma-2 passive sampler. Characterization by optical microscopy and calculation of number settling rate and mass concentration. ICS: 13.040.01. Beuth Verlag, Berlin.

Verschoor, A.J. (2016). *Towards a definition of microplastics. Considerations for the specification of physico-chemical properties*. RIVM Letter report 2015-0116, National Institute for Public Health and the Environment, The Netherlands.

Wagner, M., Scherer, C., Alvarez-Muñoz, D., Brennholt, N., Bourrain, X., Buchinger, S., Fries, E., Grosbois, C., Klasmeier, J., Marti, M.T., Rodriguez-Mozaz, S., Urbatzka, R., Vethaak, A.D., Winther-Nielsen, M. and Reifferscheid, R. (2014). Microplastics in freshwater ecosystems: What we know and what we need to know. *Environ. Sci. Eur.* 26: 12.

Wahid, S.M. (2018). Automotive brake wear: A review. *Environ. Sci. Pollut. Res.* 25: 174–180.

Wakeling, D., Murrells, T., Carslaw, D., Norris, J. and Jones, L. (2017). *The contribution of brake wear emissions to particulate matter in ambient air*. FAT Forschungsvereinigung Automobiltechnik e.V.

WHO (2005). WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide. World Health Organization, Switzerland.

Wik, A. and Dave, G. (2006). Acute toxicity of leachates of tire wear material to Daphnia magna—Variability and toxic components. *Chemosphere* 64: 1777–1784.

Wintergerst, E. (2013). *Die technische physik des kraftwagens*. Springer (in German).

Wu, G. (2016). *The mechanisms of rubber abrasion.* Theses, Queen Mary University of London, UK.

Zeit-online (2017). Plastikpartikel aus Kleidung und Reifen müllen die Meere zu (dpa-message: 22. Februar 2017. www.zeit.de.

Received for review, March 17, 2018
Revised, June 22, 2018
Accepted, June 24, 2018