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Tire wear particles in the aquatic environment - a review on generation, analysis, occurrence, fate and effects

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Abstract

Tire wear particles (TWP), generated from tire material during use on roads have gained increasing attention as part of organic particulate contaminants, such as microplastic, in aquatic environments. The available information on properties and generation of TWP, analytical techniques to determine TWP, emissions, occurrence and behavior and ecotoxicological effects of TWP are reviewed with a focus on surface water as a potential receptor. TWP emissions are traffic related and contribute 5 – 30 % to non-exhaust emissions from traffic. The mass of TWP generated is estimated at 1,327,000 t/a for the European Union, 1,120,000 t/a for the United States and 133,000 t/a for Germany. For Germany, this is equivalent to four times the amount of pesticides used. The mass of TWP ultimately entering the aquatic environment strongly depends on the extent of collection and treatment of road runoff, which is highly variable. For the German highways it is estimated that up to 11,000 t/a of TWP reach surface waters. Data on TWP concentrations in the environment, including surface waters are fragmentary, which is also due to the lack of suitable analytical methods for their determination. Information on TWP properties such as density and size distribution are missing; this hampers assessing the fate of TWP in the aquatic environment. Effects in the aquatic environment may stem from TWP itself or from compounds released from TWP. It is concluded that reliable knowledge on transport mechanism to surface waters, concentrations in surface waters and sediments, effects of aging, environmental half-lives of TWP as well as effects on aquatic organisms are missing. These aspects need to be addressed to allow for the assessment of risk of TWP in an aquatic environment.

Keywords

benzothiazoles, cities, elastomers, leaching, markers, removal

Abbreviations

24MoBT	2-(4-morpholinyl)benzothiazole
6-PPD	N-(1,3-dimethylbutyl)-N’-phenyl-1,4-phenylenediamine
AAS	Atomic absorption spectroscopy
Al	Aluminum
Ba	Barium
Ca	Calcium
Cd	Cadmium
Cr	Chromium
Cu	Copper
CBS	N-Cyclohexyl-2-benzothiazole sulfenamide
DHA	Dehydroabietic acid
DPG	1,3-diphenylguanidine
EC50	Half maximal effective concentration
EDXS	Energy dispersive X-ray spectroscopy
EU	European Union
Fe	Iron
GC	Gas chromatography
GC-FID	Gas chromatography flame ionization detection
GC-FPD	Gas chromatography flame photometric detection
GC-MS	Gas chromatography mass spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
ISO	International standard organization

LC50	Median lethal concentration
LC-MS	Liquid chromatography mass spectrometry
LOEC	Lowest observed effect concentration
MBT	2-Mercapto-benzothiazole
MBTS	Mercapto-benzothiazole disulfide
MTBT	2-methylthiobenzothiazole
Na	Sodium
NCBA	N-Cyclohexylbenzothiazole-2-amine
NR	Natural rubber
OBS	N-Oxydiethylene benzothiazole-2-sulfenamide
PAHs	Polycyclic aromatic hydrocarbons
Pb	Lead
PM0.1	Ultrafine particle size fraction
PM10	Coarse particle size fraction
PM2.5	Fine particle size fraction
Py-GC	Pyrolysis gas chromatography
Py-GC-MS	Pyrolysis gas chromatography mass spectrometry
S	Sulfur
Sb	Antimony
SBR	Styrene-butadiene rubber
Se	Selenium
SEM	Scanning electron microscopy
Si	Silicon
SiO_2	Silicon dioxide
SPE	Solid phase extraction
TWP	Tire wear particle
Te	Tellurium
Ti	Titanium
TMBZ	3,3′,5,5′-tetramethylbenzidine
U.S.A.	United States of America

Zn	Zinc
$ZnCl_2$	Zinc chloride
ZnO	Zinc oxide

1 Introduction

The ongoing debate on effects of plastic debris and microplastics in the aquatic environment has raised the awareness that organic contaminants reach the aquatic environment not only in dissolved, but also in particulate form. It has been recognized that both the plastic particle as a physical entity and the plastic particle constituents, as chemicals may cause adverse effects to the ecosystems. Research on microplastic has only focused on thermoplastic material like polyethylene or polystyrene and did not consider elastomers such as rubber. According to ISO, rubber is not covered by the definition for plastic (ISO, 2013), while others suggest to use a more general definition for microplastic that covers all man made macromolecular materials and would, thus, include rubber (Verschoor, 2015).

One of the most relevant sources for rubber emissions is automobile traffic (Kole et al., 2017). While total traffic related non-exhaust particulate emissions have been estimated and recognized as potential environmental contaminants, less data is available specifically on tire wear particles (TWP), which is formed from tires undergoing friction on the road. This is astonishing as TWP were suggested as a major contributor of metals (e.g. Zn) released into the environment (Councell et al., 2004; Goonetilleke et al., 2017).

TWP emissions split up into airborne and non-airborne emissions. Non-airborne emissions make up 90%-99.% of the total TWP emissions and can be found deposited on the road or at the road side (Panko et al., 2013a). While the fate and effects of airborne TWP have been investigated intensively (Amato et al., 2014; Grigoratos and Martini, 2015; Thorpe and Harrison, 2008; van der Gon et al., 2013), the non-airborne TWP are far less studied. It is expected that surface runoff transports TWP from the road or road side towards wastewater treatment plants or the receiving water body (Huber et al., 2016). This may lead to pollution of surface waters and the pedosphere.

Data on TWP pollution of surface waters as well as on their concentration and fate in surface waters are rare. It is known that particle properties and local conditions, such as rain intensity and infrastructure, control TWP accumulation and transport (Goonetilleke et al., 2017). For instance, in highway runoff total suspended solid concentration is efficiently reduced by more than 80% in sedimentation ponds (Vollertsen et al., 2007) or wetlands (Gill et al., 2017). In many cases, surface runoff from rural roads is not collected and TWP may accumulate at the road side and distribute further (Kole et al., 2017). However, quantitative data on TWP accumulation and distribution are not available.

Environmental concentrations of TWP have been assessed based on TWP marker concentrations (Kumata et al., 1996; Pant and Harrison, 2013; Wik and Dave, 2009). TWP markers are tire constituents which occur in specific concentrations in tire material. This approach is limited due to multiple sources of most available marker substances and variations of the marker content in the tires. Therefore, source apportionment of non-exhaust emission has been largely hampered (Thorpe and Harrison, 2008) by the lack of reliable data due to missing analytical methods. Typically, TWP are composed of rubber, filling agents, oils, vulcanization agents and further additives (Kreider et al., 2010). Due to interactions with other particulate matter, TWP are subjected to changes in morphology and composition, which makes it difficult to track and quantify them in the environment. TWP are often examined in conjunction with the pavement material as it is not easy to distinguish between these two sources (Amato et al., 2014; Boulter et al., 2006; Harrison et al., 2012; Kreider et al., 2010). Therefore this review uses the term TWP for all particles originating from tire abrasion.

This review assesses information and data on properties and generation of TWP, analytical techniques to determine TWP emission, occurrence and behavior, and ecotoxicological effects focusing on the surface waters as potential receptor. We thereby aim i) to address the relevance of TWP for the aquatic environment and ii) to identify data and information gaps which have to be closed in order to be able to conclude on risks related to the occurrence of TWP in surface waters.

2 Characteristics of tire wear particles and their emission into the environment

2.1 Tire materials

Tire materials are complex mixtures, as various chemicals are used during the manufacture of tires. Besides the rubber itself, fillers, reinforcement agents, processing aids, accelerators and retarders, adhesives, and activators may be added (Tab. 1). Despite consistent usage of the general ingredients, the composition of a specific tire depends on its application. For example, a common-sized all season passenger commercial tire contains approximately 30 types of synthetic and 8 natural rubbers, 8 kinds of carbon black, steel cord for belts, polyester and nylon fiber, steel bead wire and 40 different chemicals, waxes, oils, pigments, silica and clays (Baumann and Ismeier, 1998).

Natural rubber (NR) is a linear polymer of isoprene (2-methyl butadiene). Due to its high structural regularity, natural rubber tends to crystallize spontaneously at low temperatures or when it is stretched. The polymer network of NR allows the elasticity and flexibility to be combined with crystallization-induced strength and toughness through the vulcanization of raw NR with sulfur or hardening with carbon black as filler (Baumann and Ismeier, 1998). Given the superior performance in terms of tear strength and heat resistance, NR is the preferred material for high-performance tires used on aircraft, trucks and buses (Thaptong et al., 2014). For example, typical truck tires contain 80% NR, whereas passenger car tires contain only 15% NR (Camatini et al., 2001). In many cases, synthetic rubber is used as a substitute for NR. Synthetic petroleum-based rubbers are, among others, polyisoprene, chloroprene or styrene-butadiene rubber (SBR). Depending on the chemicals added and the properties associated with them, the synthetic rubber may have versatile properties such as being very hard, resilient or soft. SBR is characterized as more difficult to mill, mix, or calender than NR, as well as being deficient in building tack, and having relatively poor inherent physical properties.

The potential hazard of oils with high contents of polycyclic aromatic hydrocarbons (PAHs) has led to the regulation of their use in rubber manufacturing by EU Directive 2005/69/EC and replacement with low-PAH alternatives. New tires, or tire tread used for retreading, manufactured after the first of January 2010 may not contain any extender oil with PAH concentrations exceeding certain threshold limits. Tires that were manufactured prior to this date are not covered by these threshold limits and may still be sold on the market (Sadiktsis et al., 2012).

2.2 Tire Wear Particles (TWP)

Generation

TWP have been defined as particles generated mechanically by the rolling shear of tread against a surface (Rogge et al., 1993), or by volatilization, which results in the generation of much smaller particles, usually in the fine mode (< 2.5 µm). For the emission of TWP, the tread and shoulder of the tire are of major importance, as both components may be in contact with the pavement (Lee et al., 2013). The interaction of tires with the pavement alters both, the chemical composition and the characteristics of the particles generated in this interaction, compared to the original tire tread. This is due to heat and friction, as well as to the incorporation of material from the road surface (Panko et al., 2013a) and of other particulate traffic-related emissions such as brake dust (Adachi and Tainosho, 2004).

Investigations on properties of TWP have used material generated in one of the following ways: i) by "real" on-road driving conditions using mobile units (Hussein et al., 2008; Kwak et al., 2013; Mathissen et al., 2011) under controlled conditions, where the contribution from existing road dust and minerals from the road surface present under ambient conditions is considered (Kumar et al., 2013; Q. Wang et al., 2017). ii) by sampling and analysis of particles from ambient air, followed by application either of source apportionment methods (Bukowiecki et al., 2009; Luhana et al., 2004) or specific tire wear tracers (Harrison et al., 2012; Panko et al., 2013a). iii) by a road simulator in the laboratory (Dahl et al., 2006; Gustafsson et al., 2008; Kreider et al., 2010; Kupiainen et al., 2005; Panko et al., 2009). iv) Alternatively, TWP may be generated in the laboratory using a steel brush, grit paper, or other abrasive media, which are, however, not able to replicate driving conditions (Kreider et al., 2010). The shape of TWP generated on road was therefore found to be very different from that of cryogenically ground tire material, which has sharper, more defined edges (Fig.s 1 and 2).

Thus, TWP at the road surface and in the environment are mostly not present as pristine material and it is likely that these multicomponent TWP will differ in physical and chemical properties from the original tire material (Tab. 2). It appears that knowledge on how particle generation and particle properties are connected is insufficient. For example, no information is available on the densities of TWP. These knowledge gaps obviously hamper a comprehensive prediction of the fate of these particle entities in aquatic environment.

Physical properties

The size distribution and density of particles are important parameters that determine their fate in the environment. Abrasion of tire tread leads to the emission of TWP that can be classified into coarse (PM10), fine (PM2.5), and ultrafine (PM0.1) particles (Fig. 1). While TWP are mainly found in the coarse size fraction, only 0.1 - 10% are estimated to become airborne (PM10 and below) (Barlow et al., 2007; Boulter et al., 2006; Panko et al., 2013a; Wik and Dave, 2006). Ultrafine particles are generated by a thermo-mechanical process; spots on the tire surface reach temperatures high enough for the evaporation of volatile tire constituents which rapidly condense and form microparticles (Mathissen et al., 2011). Despite the fact that the majority of particles emitted during wear are in the coarse fraction, the research with regard to the characterization of TWP size distribution has focused on airborne PM10 and PM2.5.

The size distribution of TWP ranges from a few nanometers to several hundred micrometers (Fig. 1). Kreider et al. (2010) tested different types of tires on asphalt based pavements in a road simulator and found that the size distribution of collected TWP ranged between 5.0 µm and 220 µm with a maximum abundance at 70-80 µm (Kreider et al., 2010). There was no PM0.1 found under controlled driving conditions. Similar observations were made by Smolders and Degryse (2002), who found roadside TWP with a mean diameter of 65 µm for passenger vehicles and 80 µm for trucks.

However, a number of studies report bimodal mass size distributions with one peak in the coarse fraction and another one in the fine fraction (Fukahori and Yamazaki, 1994; Gustafsson et al., 2008; Q. Wang et al., 2017). These discrepancies in the obtained particle size distributions can result from different conditions of particle formation, in sampling and in analytical instrumentation used (Kreider et al., 2010), which hampers the comparisons of available data. For a bimodal size distribution of TWP, small particles (<PM10) originated from microvibration and larger particles in the range of a few hundred micrometers were attributed to stick-slip motion (Fukahori and Yamazaki, 1994). The speed of driving and the pavement material were reported to influence the amount of particles emitted rather than their size distribution (Gustafsson et al., 2008; Kwak et al., 2013).

Ultrafine TWP have very heterogenic forms such as droplets, fibers and granules. These particles form agglomerates (Dahl et al., 2006). Contrary to coarser particles, the ultrafine TWP seem to originate from organic constituents of tires (softening filler and specifically mineral oils) (Gustafsson et al., 2008). Most of the particles within the fine fraction are composed mainly of carbon (Panko et al., 2009). Further studies indicated (Fig. 2) that fine TWP are elongated in shape and contain incrustations of minerals from the road surface. The morphology of TWP was reported as an elongated “sausage-like” shape with a mode of circularity of 0.83 and an aspect ratio of 0.64 (Adachi and Tainosho, 2004; Cadle and Williams, 1978; Kreider et al., 2010; Williams and Cadle, 1978).

Other factors influencing the generation of TWP are the pavement properties, its composition and texture. For example, the PM10 concentration has been shown to increase when anti-skid aggregates were used in the asphalt pavements (Tervahattu et al., 2006) and also the PM2.5 and PM0.1 concentrations were influenced by differences in the asphalt mixtures (Fullova and Ďurcasnka, 2016). In addition, TWP size distribution and concentration are influenced by the adhesion mechanism of friction, for which surface energy and wear pattern of the tire are of major importance (Vieira et al., 2015; D. Wang et al., 2017).

Chemical composition

Depending on their formation processes, TWP exhibit a chemical composition that differs from the composition of the initial tire material. Similar to the size characterization, there is more data on the chemical composition of airborne fine TWP than on coarse ones (> PM10). The chemical composition of TWP seems to differ depending on the size range considered. For example, in the coarse fraction of particles, the concentrations of Fe, Ca, and Zn were found to be high compared to concentrations of Ti and Sb (Kwak et al., 2013). In the fine fraction of particles, the concentrations of Fe, Ca, Ti, Ba, and Sb dominated, but Zn was not found (Kwak et al., 2013) and Al and Si dominated in the smaller sized airborne wear particles (Gustafsson et al., 2008; Kupiainen et al., 2005; Panko et al., 2009). Sulfur was reported to be enriched in the sub-micrometer fraction, particularly when friction tires were tested (Gustafsson et al., 2008; Panko et al., 2009). The Zn contribution to the total particle mass was similar (0.3 – 0.4%) for road-collected and laboratory generated wear particles (Kreider et al., 2010) but different between passenger vehicles (1.1%) and trucks (2.4%) (Smolders and Degryse, 2002).

The carbonaceous fraction of TWP is dominated by organic substances (88%), with trace amounts of elemental carbon (4%) and carbonate carbon (8%). The PAH composition of coarse TWP and the concentrations of individual PAHs varied from the mg/kg-range for pyrene, phenanthrene and fluoranthene to not detectable concentrations of these PAHs in road wear particles (Aatmeeyata and

Sharma, 2010; Rogge et al., 1993). Other sources, such as asphalt, automobile exhaust and fuel combustion products, are often more dominant PAH contributors (Kreider et al., 2010; Kumar et al., 2013). The PAH content of TWP increased with increasing mileage of the tire (Aatmeeyata and Sharma, 2010) due to thermal degradation of tires (Kwon and Castaldi, 2012). Benzothiazoles are another substance class commonly found in TWP. A large variety of other organic compounds have been identified in TWP, such as n-alkanes, n-alkanoic acids, and natural resins (Rogge et al., 1993).

3 Emission of TWP from automobile traffic

The quantity of TWP emissions is often related to the mileage: the so-called “emission factor” defines the amount of TWP generated per kilometer driving distance (mg/km). This emission factor is controlled by: i) tire characteristics (e.g. size/width, chemical composition, accumulated mileage), ii) vehicle characteristics (e.g. weight, engine power, state of maintenance), iii) road surface characteristics (e.g. material (bitumen/concrete), texture pattern, wetness, temperature) (van der Gon et al., 2013), and iv) vehicle operation and operation conditions (e.g. speed, linear acceleration, radial acceleration, extent of braking and cornering) (Boulter et al., 2006). Accordingly, the reported abrasion rates cover a wide range. Heavy duty vehicles such as trailer trucks have been reported to emit approximately ten times more TWP than light duty vehicles and passenger cars. For instance median TWP emission factors have been reported for passenger cars with 90 mg/km (53 - 200 mg/km), for trucks with 700 mg/km (105 - 1,700 mg/km) and for trailer trucks with 1,200 mg/km (1000 - 1,500 mg/km) (Hillenbrand et al., 2005). For passenger cars this agrees well to the average of data collected by Councell et al. (2004) with 112 mg/km (16 data points and a standard deviation of 174 mg/km). The scatter in the experimental data may reflect the different experimental conditions (laboratory or field) and methods of determination (tire mass loss or direct measurement).

Absolute TWP emissions at the regional scale have been calculated either based on emission factors and annual travel distances of various vehicle categories or from average weight loss of tires and the number of tires in use. For Germany, TWP emissions for 2005 were estimated based on emission factors to be 111.42 x 10^3 t/a (Hillenbrand et al., 2005). A recent review calculated population specific TWP emissions for various countries including China, India, Japan, Norway, Sweden, Denmark and the United States of America (USA) (Kole et al., 2017). Data ranged between 0.23 and 1.9 kg/(a capita) in the investigated countries. In the USA, however, significantly higher emission of 4.7 kg/(a capita) were found because of longer travel distances per capita (Kole et al., 2017).

A new estimation of the quantity of TWP emissions was performed here for Germany, the European Union (EU) and the USA for different vehicles categories and for urban and rural roads (Tab. 3). These considerations are important for the identification and localization of most relevant sources, for example trucks on highways. TWP emissions in Germany and the USA were calculated based on average emission factors provided by Hillenbrand et al., (2005) and recent data on total travel distance on highways and urban roads for various vehicle categories including passenger cars, trucks, busses and trailer trucks (Bäumer et al., 2017). Our estimation of TWP emissions in the EU is based on car registration data and average travelled distances for each vehicle category.

Based on this data we estimate that 133 x 10^3 t/a TWP were released in 2014 in Germany (Tab. 3). This exceeds the amount estimated for 2005 by 20% (see above). Emissions were dominated by trucks and busses (60%). Largest distances in Germany are traveled on highways and rural roads with 550 x 10^9 km followed by urban areas with 190 x 10^9 km (Tab. 3). Accordingly, 70% of the TWP emissions are likely generated on highways and rural roads and 30% in cities (Tab. 3).

According to our estimation using data from 2010 in the USA, TWP emissions from passenger cars and trucks are of equal importance and sum up to 1,120 x 10^3 t/a (Tab. 3). A portion of 66% of these emissions occurs in urban environments, compared to less than 30% in Germany. This difference is primarily due to the much higher urban travel distances in the USA (Tab. 3) which have been reported earlier (Councell et al., 2004).

This estimate of TWP emissions for the USA are higher than earlier ones, due to an increase in automobile traffic. . Pierson and Brachaczek (1974) estimated 600 x 10^3 t/a of tire wear for the USA in 1974. A more recent publication by Councell et al. (2004) estimated Zn emissions in the USA originating from TWP in 1999. From this data, TWP emissions were deduced to be between 900 x 10^3 t/a and 1,000 x 10^3 t/a assuming tire wear contains 1.1wt.% Zn (Smolders and Degryse, 2002).

In the EU, the total number of registered passenger cars and trucks was 210 x 10^6 and 36 x 10^6, respectively (EU, 2016; Eurostat, 2017) in 2014. The average distance travelled in the EU was approximated from average distances traveled in Germany for passenger cars, trucks and busses. It is noted that average travel distance of trucks in Germany might be higher compared to the EU average because of the high proportion of transit traffic in Germany. In total, 260 x 10^3 t/a TWP are estimated to be emitted by passenger cars and 1,100 x 10^3 t/a TWP by trucks including busses. These emissions could not be further attributed to highway, rural, and urban roads due to the lack of data on the respective travel distances.

While engine exhaust emissions have decreased continuously during the last decades as a result of technical improvements, the non-exhaust emission remained constant or increased with rising traffic (van der Gon et al., 2013). This global development is expected to continue due to a growth of automobile traffic (Goonetilleke et al., 2017) leading to an increase in TWP emissions. The differentiation between vehicle categories makes clear that passenger cars and trucks emit almost equal percentage of TWP in Germany and the USA. In Germany, TWP emissions occur predominantly on highways, whereas in the USA urban roads are more important (Tab. 3).

In order to assess the environmental importance of TWP emissions, one may compare them with other non-exhaust traffic emissions comprising of brake wear, road wear and tire wear. Total traffic related emissions are composed of approximately 5-30% tire wear (Harrison et al., 2012). Due to complex generation processes, the individual share of non-exhaust emission components varies. For instance, studded tires exhibit much higher road surface erosion rates than non-studded tires (Gültlinger et al., 2014; Lindbom et al., 2007). The vehicle category plays another important role. For medium sized cars for example, road wear dominates non-exhaust emissions and TWP mass fraction equals approximately 30% of the total non-exhaust emissions (Simons, 2016) (Fig. 3).

TWP emissions may also be compared with the emission of other classes of xenobiotic compounds. For Germany, the TWP emission of 133 x 10^3 t/a (Tab. 3) is four times the amount of active substances of pesticides used and released into the environment per year (approx. 33 x 10^3 t/a in 2016 (BVL, 2017)) and 16 times the amount of environmentally relevant human pharmaceuticals (8.1 x 10^3 t/a in 2012) (Ebert et al., 2014). However, pesticides and pharmaceuticals are emitted in dissolved form while TWP are released as particles.

With respect to the aquatic environment, however, it would be important to know which portion of the emitted TWP ultimately ends up in surface waters. This is controlled by the environmental fate of TWP.

4 Analytical methods to determine the amount of TWP in the environment

This section focuses on methods suitable for the determination of the amount of TWP in environmental samples such as dust, sediments, soil or water. Neither does it consider methods for the analysis of tire constituents directly from tires, nor methods for the determination of tire-born dissolved compounds in the aqueous phase, after their release from tires.

The determination of the amount of TWP in environmental samples requires an increase in sensitivity and selectivity with increasing distance between the source of TWP emission and the sampling site. The concentration of TWP is expected to decrease with this distance, while the complexity of the matrix and the importance of other sources increase. For these reasons, analytical methods developed for tire analysis are usually not suitable for the determination of TWP from environmental samples. Also, methods to determine tire particles in road dust with higher TWP contributions may not work for roadside soils with a lower portion of TWP.

Analytical strategies to determine the amount of TWP in environmental samples involve the determination of either the rubber (SBR or NR) as the major constituent of tires, or of additives from the tire material that serve as markers for tires. A marker should ideally fulfill the following criteria:

- be present in all tire materials in comparable portion, largely independent from manufacturer or manufacturing process,
- not leach easily from tire particles into the surrounding environment
- not be easily transformed while the tire particles reside in the environment (air, water, soil)
- be sufficiently specific for tires, namely not present in relevant concentration in other traffic-related particulate matter, such as brake dust, roadway particles or surface runoff.
- have a concentration in tire material significantly higher than in the particles forming the sample matrix (soil, sediment, road dust, suspended matter, aerosol)
- be analytically accessible by methods of high precision, accuracy, and sensitivity at reasonable analytical effort.

Markers may either be metals or organic compounds. The major elements considered as markers for TWP are Zn (used as activator in the vulcanization process) and S, originating from various reduced organic sulfur species that are used as vulcanization accelerators (Rogge et al., 1993). A variety of organic marker constituents have also been tested as discussed in more detail below.

Detection of TWP particles from dust and water

The detection of individual TWP is of interest when particulate matter has been collected on filters, e.g. by aerosol sampling with impactors. For the detection of TWP on filters spatially resolved analytical methods have been employed. Spectroscopic methods like Raman spectroscopy, however, cannot be used as the black TWP do not deliver a specific spectrum. Instead, the determination of marker elements may help. For example energy dispersive X-ray spectroscopy (EDXS) has been used to detect TWP in dust collected in the laboratory environment using its S and Zn signature (Adachi and Tainosho, 2004; Camatini et al., 2001) (Fig. 4). The authors noted, however, that this approach was not selective enough to identify tire particles in road dust collected from the environment, as there are many other sources for Zn, like brake dust and paint used for road marking. Obviously, these approaches are limited to situations where the contribution of TWP to the particulate fraction of samples is comparatively large. Moreover, the suitability of these methods for quantitative analyses remains questionable.

In principle, TWP detection by spatially resolved analysis of filters should also be suitable for the detection of TWP in water samples after filtration. However, this application has not been reported yet.

Sediments and Soils

For more complex particulate samples or more diluted conditions, the detection of (each) single TWP is not feasible any longer. Then, elemental analysis may be used to determine the total quantity of TWP mass from sample digests.

Complete digestion of tire material is, however, challenging. Often, particulate matter remains in the digest. This is not critical, provided that only the SiO_2 (filler) remains; otherwise it may lead to an underestimation of the true value. Strong acids (nitric acid, sulfuric acid, perchloric acid), elevated temperature (> 100 °C) and digestion times of several hours are, therefore, used (Kocher et al., 2010; Smolders and Degryse, 2002). Metal determination in the diluted digest may involve AAS, ICP-OES (Kocher et al., 2010; Smolders and Degryse, 2002) or ICP-MS, depending on the sensitivity required and the number of elements to be detected.

Although some elements, namely Al, Na and Fe, exhibit higher concentrations than Zn in tires, they are not suited as elemental markers for TWP as their environmental concentrations (e.g. in soil) are typically even higher (Kocher et al., 2010). Rhodes et al. (2012) studied the loss of Zn from tire particles: some leaching of Zn occurred, but the Zn content of the tire particles was not significantly reduced. Thus, leaching did not limit the use of Zn as marker of TWP.

As mentioned above, there are other traffic related sources that emit particulate Zn. Moreover, particulate Zn may be formed in the aqueous phase in urban environments by adsorption or precipitation of dissolved Zn^{2+}-ions that are discharged with surface runoff and originate from gutterings, facades, road signs and other surfaces plated with Zn (Councell et al., 2004). This further limits the specificity of particulate Zn as tire marker in samples that are influenced by surface runoff, such as from sewers, urban creeks and receiving waters.

To increase selectivity, Fauser et al. (1999) proposed not to determine the total Zn content of particulate samples, but more specifically the zinc-accelerator complexes (organic zinc) as marker of TWP. The analytical approach first involves the extraction of the organo-Zn-complexes from particulate matter by dichloromethane, followed by digestion of the organic extract with nitric acid and determination of total Zn in the digest (Fauser et al., 1999). Unfortunately, there may be other traffic-related sources of organo-zinc such as engine oil (Fauser et al., 1999). Additionally, Unice et al. (2013) pointed out that the solvent dichloromethane does not reliably exclude inorganic ZnO from extraction. Both aspects would lead to an overestimation of the content of TWP in environmental samples and question the suitability of organo-zinc as tire marker.

Rubber is the major component and the backbone of tires. Therefore, it seems straightforward to determine the amount of rubber if one is interested in the amount of TWP in a sample. However, rubber is a polymer of high molecular weight, which is not amenable as such to chemical analysis. Therefore, rubber determination involves destructive measures that generate rubber-specific volatile breakdown-products, typically by pyrolysis, where the sample is heated to temperatures of 600 – 800°C for a few seconds. The volatile products are transferred to and analyzed by gas chromatography, either by GC-FID or by GC-MS (Unice et al., 2012). The markers generated by rubber pyrolysis and determined by GC are styrene for SBR (Lee et al., 1989; Saito, 1989; Unice et al., 2012) and isoprene or dipentene (1-methyl-4-isopropylcyclohexene) for NR (Lee et al., 1989; Saito, 1989; Unice et al., 2012) (Fig. 5). Some authors also included vinylcyclohexene and butadiene as SBR markers (Cadle and Williams, 1980; Unice et al., 2012).

Usually, py-GC is applied to the entire particulate sample. To increase sensitivity, the rubber of a sample can first be extracted and then only the extract is subjected to py-GC. Rubber is, however, not easily brought into solution, so that comparatively harsh extraction conditions have to be used (Cadle and Williams, 1980).

Py-GC-MS suffers from limited precision. To improve this, Unice et al., (2012) have added defined amounts of an internal standard material to the sample, that generates a deuterated volatile monomer (deuterated (poly)butadiene or (poly)isoprene) which can be analyzed together with the rubber markers (Unice et al., 2012).

Py-GC-MS methods were typically applied to road dust (Lee et al., 1989; Panko et al., 2013a; Saito, 1989) and to soils (Unice et al., 2012). The most recent studies reached method detection limits of 2 – 30 µg/g in soil depending on the kind of rubber (Unice et al., 2012) and 300 – 800 µg/g from 1 mg of dust collected on a filter (Panko et al., 2013a).

Many organic compounds are added during rubber and tire manufacturing (see section 2). Most of them are, however, not suited as markers, because they are not specific for tires but have also other traffic related sources. For example PAHs and aliphatic hydrocarbons are present in tires but they are also found in asphalt, automobile exhausts, and fuel combustion products (Kreider et al., 2010).

One class of chemicals that have been used as markers of TWP are benzothiazoles (Fig. 6): 2-(4-morpholinyl)benzothiazole (24MoBT) from the vulcanization accelerator OBS and N-cyclohexyl-2-benzothiazolamine (NCBA) from the accelerator CBS, which contains mainly N-cyclohexyl-2-benzothiazolesulfenamide (Kumata et al., 2002; Spies et al., 1987). CBS is the more frequently used vulcanization accelerator (Kumata et al., 2002) and was claimed to be also the more environmentally friendly one (Pan et al., 2012). During the vulcanization process, however, these vulcanization accelerators are transformed to a large extent: less than 1 % of CBS was found to survive the curing of rubber (Unice et al., 2015).

Owing to the tight structure of rubber, the extraction of organic constituents from tire material requires comparatively harsh conditions. Obviously, such harsh conditions are also required to extract tire markers from environmental samples, provided that they are still fixed in the rubber matrix as they should be. Most extraction methods involve Soxhlet extraction using solvent mixtures such as benzene/methanol (6:4 v/v) (Kumata et al., 1996), toluene/methanol (1:1 v/v) (Kumata et al., 2000), or dichloromethane/acetone (1:1 v/v) (Ni et al., 2008). To date, accelerated solvent extraction (ASE) may be applicable instead, but this would need to be validated.

While a clean-up may not be required for extracts of tire material itself, this becomes increasingly important with increasing distance from the emission source, as the concentration of tire particles decreases while the portion of sample matrix increases. Moreover, the harsh extraction conditions further increase the matrix content in an extract.

Clean-up procedures for benzothiazole analysis involved partitioning between an organic and an aqueous phase, making use of the acid/base properties of NCBA and MoBT (Kumata et al., 2000) and column clean-up with deactivated silica (Kumata et al., 1996) or alumina:silica mixes (1:2 in volume) (Ni et al., 2008).

The instrumentation that has been used for the determination of the benzothiazole marker compounds in sample extracts reflects the general development in analytical instrumentation, with GC- based methods used initially, first with GC-FPD (selective for sulfur) (Kumata et al., 2002, 1996), then with GC-MS (Ni et al., 2008), and from the 2000s onwards complemented by LC-MS (Avagyan et al., 2013; Kloepfer et al., 2004; Reemtsma, 2000).

The benzothiazole marker compounds 24MoBT and NCBA clearly show the challenges related to the use of organic markers for tires in a heterogeneous environment. Only a low portion of the CBS accelerator added to rubber before curing is found afterwards as NCBA, while other benzothiazoles, namely mercapto-benzothiazole (MBT) and also cyclohexylamine were more relevant (Unice et al., 2015). Indeed, many other benzothiazoles are present in tire rubber, like benzothiazole itself, the MBT, and its methylation product methylthiobenzothiazole (MTBT) as well as the oxidation product mercaptobenzothiazole disulfide (MBTS) (Avagyan et al., 2013). Due to their lower molecular weight and a higher polarity, these transformation products are preferentially leached from tire particles which makes them unsuited as alternate markers for tire particles (Unice et al., 2015). Benzothiazoles found in the aqueous phase may also have other sources (Kloepfer et al., 2005) and are subjected to transformation processes (Reemtsma et al., 1995). Thus, it is not fully clear yet to which extent the two benzothiazoles NCBA and MoBT are reliable tire markers.

Two other compounds were therefore tested for their suitability as tire markers, the vulcanization agent 1,3-diphenylguanidine (DPG) and the antioxidant (N-(1,3-dimethylbutyl)-N′-phenyl-1,4-phenylenediamine (6-PPD) (Fig. 6). Both were more stable than the benzothiazoles during curing with approximately 50% loss. DPG is partially transformed into the water-soluble and easily leachable aniline (Unice et al., 2015). 4-Aminodiphenylamine was found as degradation product of the antioxidant 6-PPD, but the number of possible transformation products was much larger (Unice et al., 2015). 6-PPD is also less prone to leaching, as it is comparatively hydrophobic (logK_{ow} > 4) (Unice et al., 2015). While the antioxidant 6-PPD is also reported to be used in lubricants and dyes (Prosser et al., 2017) its major application is in elastomers (Krüger et al., 2005). On this basis one may consider 6-PPD an interesting candidate as marker for TWP that deserves more scientific scrutiny.Resin acids, namely dehydroabietic acid (DHA), are added during rubber manufacturing as emulsifiers (Rogge et al., 1993) and have recently been proposed as an alternative marker for TWP (Kumata et al., 2011). Resin acids such as DHA do have, however, many natural sources. In biogeochemistry for example, resin acids are considered biomarkers for the input from conifers (Medeiros and Simoneit, 2008). Elevated levels of DHA in the environment have also been related to discharges from pulp and paper production (Leppänen and Oikari, 1999), questioning the specificity of DHA as marker.

It appears that satisfactory analytical approaches to determine the amount of TWP in environmental samples are not readily available. The analytical challenges increase with increasing distance from a source of emission. While benzothiazoles have been proposed as markers, they cannot fulfill many of the criteria needed. 6-PPD appears an interesting but yet poorly studied alternative. Another option is to improve methods for the determination of rubber as such, rather than searching for novel markers.

5 Occurrence and behavior of TWP in the aquatic environment

Role of particulate TWP mass flow

The concentration of TWP in soil or water is determined by transport into these environmental compartments, translocation, transformation and degradation within these compartments as well as by transport out of these compartments.

The predominant portion of TWP is coarse (> 10 µm) and is assumed to remain at the road side (Cadle and Williams, 1979; Dannis, 1974). Once generated and deposited, TWP are subjected to interaction with other traffic-related particles from brakes, tire, pavement, street furniture, as well as with atmospheric deposition, which results in the formation of aggregates (Charters et al., 2015). This makes it difficult to distinguish between individual particle types/sources (Adachi and Tainosho, 2004). Hence, most of the studies on traffic related particles were based on the so-called “total non-exhaust traffic related particle emission” or “road-deposited sediments”. Consequently, there is insufficient information specifically on the occurrence and behavior of TWP.

Depending on their size, TWP and their aggregates are eventually transported off the street by surface runoff, by street cleaning or transferred into the atmosphere by resuspension (Huber et al., 2016; Wicke et al., 2012). Mobilization of TWP by road runoff may lead to a translocation especially during stormwater events (Aryal et al., 2010). The translocation of TWP by rainfall strongly depends on the infrastructure installed for the collection and treatment of road runoff water. In case there is no runoff sewer installed, TWP are likely quantitatively transferred to the roadside soil and to some extent to the nearest waterway. If road runoff is collected in separate sewer systems, a runoff treatment is usually foreseen before the water is discharged into receiving waters or percolated into groundwater (Barbosa et al., 2012). In the centers of urban areas of industrialized countries, surface runoff is often collected in sewers combined with municipal wastewater, and treated in municipal wastewater treatment plants. Although no data on TWP removal in wastewater treatment plants are available, data on microplastics removal may allow a rough estimate; removals exceeding 96% have been reported for microplastic in municipal wastewater treatment plants (Magnusson and Norén, 2014; Mintenig et al., 2017; Murphy et al., 2016) but small particles are less efficiently removed compared to larger ones (> 300 µm) (Kole et al., 2017). On this basis one may expect removal efficiencies above 90% for TWP > 300 µm and lower removal for TWP < 300 µm in municipal wastewater treatment plants. In the case of strong rainfall events, however, combined sewer overflow may occur and the wastewater be discharged into surface waters without any treatment (Reemtsma et al., 2000).

The majority of treatment of road runoff collected in separate sewer systems are based on filtration or sedimentation (Aryal et al., 2010). Their efficiency is strongly depending on the treatment process and on the properties of the particulate material (Hallberg et al., 2007; Jotte et al., 2017). The runoff waters are typically characterized by high total suspended solid and high metal concentration as well as a bimodal particle size distribution with maxima between 6-10 µm and 70-100 µm (Brombach et al., 2005; Charters et al., 2016; Huber et al., 2016). The mass percentage of particle sizes < 63 µm, so-called fine sediments, varies between 17 wt% and 100 wt% (Charters et al., 2015).

A survey on treatment systems revealed that removal efficiencies increase with increasing particle size and increasing hydraulic retention time. For metals partitioned in the fine sediment fraction (< 63 µm), retention in settling ponds is unlikely (Charters et al., 2015; Hilliges et al., 2017) and removal efficiency is typically below 50 % (Boogaard et al., 2017) leading to metal emissions of Zn and Ni. For instance, Gill et al. (2017) reported average removal efficiencies of 86% for Zn in a wetland with long hydraulic retention times (Gill et al., 2017) whereas Fettig et al. (2017) showed that lamella sedimentation systems removed only 21 % of particulate Zn (Fettig et al., 2017). Therefore, TWP might not be efficiently removed in runoff treatment systems that are based on sedimentation with only short hydraulic retention times. Under high hydraulic loads, removal rates of TWP are expected to decline in sedimentation ponds and TWP can be flushed out (Gill et al., 2017). It has been observed that during stormwater events, TWP concentrations increased in the receiving water body (Kumata et al., 2000).

Rural roads are mostly not equipped with a sewer and road runoff is treated only passively by percolation. Data on coverage of runoff treatment systems is not available. Therefore, it is not possible to estimate the global amounts of TWP that reach aquatic environments. Such estimation can be performed only on the local scale, if adequate information is available.

For example, TWP concentrations were determined locally in road runoff (Ni et al., 2008; Unice et al., 2013; Wik and Dave, 2009). Environmental TWP concentrations were estimated based on marker concentrations because analytical methods for the reliable determination of TWP concentrations in the environment are not available (see section 4) Such estimated data are available for road dust, road surfaces, soils in the close vicinity of the road, road runoff, settling ponds, wastewater effluent, river sediments and air (Fig. 7). As one may expect, TWP concentrations appear to decrease with increased distance from the road. Highest concentrations were detected in tunnels and soils next to the road (Fig. 7). Towards the receiving water body, TWP concentration decreases because particles are being retained already at the road side and due to dilution. Contamination of groundwater by TWP transported through the unsaturated soil zone is unlikely. However, groundwater contamination may occur by dissolved TWP constituents that were leached from TWP at the soil surface (Padoan et al., 2017).

TWP concentrations in sediment are higher than those in surface water (Fig. 7), because particles settle down and accumulate in the sediments. Correspondingly, not only sediments in runoff treatment ponds, but also sediments in the receiving water body act as a sink for TWP (Fig. 7). Thus, the question arises under which conditions TWP accumulate in the sediment. In principle, the finer fraction of TWP is expected to be easily transported during runoff, while the coarser particles are more effectively retained because they settle in drainage channels, canals, and gully pots (Loganathan et al., 2013). Occurrence and characterization (i.e. particle size distributions and chemical composition) of road-deposited sediments and other sum parameters, for example total suspended solids, have been studied in a number of case studies throughout the world (Sutherland et al., 2012; Q. Wang et al., 2017; Zhou et al., 2017). Research focusing explicitly on TWP-specific properties and the processes affecting the fate of TWP, such as aggregation, sedimentation, or aging are still lacking. In order to link TWP emission, environmental concentration and effects in various compartments, it is crucial to understand the processes controlling the mass flow of TWP from their source to surface waters and to determine the mass flows from sources to surface water.

In this review the yearly mass of TWP entering water bodies is estimated for German highways. TWP emission from highways is estimated with 48,000 t/a (Tab. 3). A portion of 10% of this is emitted into the atmosphere while the remaining mass is deposited on the road or at the road side. The amount being retained and the amount reaching the receiving water body depends on the collection and treatment infrastructure. Two scenarios are calculated, assuming that A) 50% of the deposited TWP are mobilized via surface runoff (Kaufmann et al., 2007) and B) that only 15% are mobilized (Hillenbrand et al., 2005). The remaining TWP accumulate at the road side. In both scenarios, it is assumed that all surface runoff is treated prior to full discharge into the receiving water body with no infiltration into the soil and that the average treatment efficiency is 50% TWP removal.

Fig. 8 illustrates the mass flows of TWP for both scenarios. The mass of TWP estimated to reach the receiving German water body ranges from 3,000 t/a (scenario B) to 11,000 t/a (scenario A), corresponding to 6% and 23% of the total TWP emission, respectively. Kole et al. (2017) estimated TWP release in the aquatic environment with approximately 7% of the total TWP emission in The Netherlands, which is similar to the estimation in scenario A. In case no treatment systems are in place, TWP outflow into the aquatic environment increases to 13% and 45% of the total emitted TWP for scenarios A and B, respectively. These estimations are solely based on assumptions and need to be verified by field data. However, the results underline the importance of road and roadside management as well as the possible efficiency of runoff treatment systems regarding the prevention of TWP release into the aquatic environment.

Once emitted into surface waters, TWP will distribute further. Literature data on TWP concentrations in rivers and sediments (Fig. 7) suggest that sedimentation is an important process that removes TWP from the surface waters. Correspondingly, TWP concentrations of 400 – 2,200 µg/g in river sediments have been determined (Ni et al., 2008; Unice et al., 2013; Wik and Dave, 2009).

TWP relevant fate processes

At their point of emission on road surfaces, TWP may aggregate with other TWP (homoaggregation) or other particles (heteroaggregation). With increasing distance from the road homoaggregation is likely to be negligible due to the decreasing TWP concentration (Fig. 7) compared to the concentrations of other particles. Heteroaggregation with (suspended) particulate matter is strongly influenced by particle sizes and densities (Therezien et al., 2014). While particle size distributions of TWP and their aggregates have been reported (see section 2.2), other important physical properties such as TWP density or surface charge have not been reported yet. One may assume that TWP density depends upon their composition; while carbon black has a density of 1.8 g/cm^3 the density of SBR ranges from 0.94 - 1.04 g/cm^3 depending on its styrene portion (Sigma-Aldrich, 2013, 2012a, 2012b). The density of shredded tire materials has been reported to range between 1.13 and 1.16 g/cm^3 (Rhodes et al., 2012). The lower densities of TWP compared to other road derived particles (e.g. asphalt: 2.36 g/cm^3 (Rumble, 2017)) or suspended particulate matter (e.g. quartz: 2.65 or limestone 2.0 g/cm^3 (Rumble, 2017)) lead to the assumption that pure TWP have a high potential to remain in suspension and be transported over longer distances, while TWP heteroaggregates with a higher density would be subjected to sedimentation. This illustrates the need to investigate aggregation processes of TWP in more detail.

As found for other particulate matter such as nanoparticles and microplastics one may assume that heteroaggregation is dependent on the surface characteristics of the TWP and, thus, also affected by the characteristics of the surrounding water, e.g. its ionic strength and the presence of natural organic matter (Besseling et al., 2017; Praetorius et al., 2014; Smith et al., 2015).

Furthermore, aging processes may change the properties of TWP in the aquatic environment. These processes may involve mechanical stress, oxidation (as long as TWP are not deposited in sediments) as well as microbial colonization and degradation. Considering the major components of TWP (rubber and carbon black), it can be expected that TWP in the aquatic environment are persistent and degrade only slowly.

The available data do not allow to conclude e on TWP mass flows in the aquatic environment beyond those shown in Fig. 8. Reliable information and data on infrastructure to collect and treat road-runoff, on the dynamics of TWP transport (e.g. mobilization) during stormwater events as well as treatment efficiency for particles < 50 µm would be required to estimate environmental concentrations of TWP more precisely. Furthermore, experimental or model based studies on the fate processes of TWP are needed. The latter could be achieved similar to the development of nanoparticle models. First simple mass flow models evolved into validated spatiotemporal explicit models (Gottschalk et al., 2013). For other particulate contaminants, such as engineered nanomaterials or microplastics, complex transport models were developed (Besseling et al., 2017; Domercq et al., 2018; Praetorius et al., 2014). These models simulate explicit spatial and temporal hydrodynamic particle behavior and account for advective transport, particle aggregation, sedimentation and resuspension. Such modeling approaches could be adapted for TWP in smaller and larger size ranges. This would be necessary to allow the identification of relevant fate processes and potential mitigation strategies.

Compounds released from TWP

The quality of the aquatic environment may be affected by the introduction of TWP as particulate entities. However, also compounds released from TWP and transferred into the aqueous phase may also affect water quality. The leaching from TWP exposed to water has been investigated for a wide spectrum of substances including heavy metals, such as Zn (Smolders and Degryse, 2002), Cu, Cd, Cr and Pb, (Malmstrom, 1956) and organics such as PAHs and benzothiazoles (Reddy and Quinn, 1997; Wik and Dave, 2009).

Leaching from tire materials has been investigated in laboratory leaching studies (e.g., tire crumb or tire wear). The experimental conditions strongly affect the outcome of the experiment. For example, the removal of the metal wires from crumb rubbers minimized leaching of iron and manganese (Selbes et al., 2015). The influence of the particle size on leaching from TWP is inconclusive, as organic carbon and Zn were found to be leached more effectively from smaller particle sizes, whereas the leaching of some elements were found to be independent from particles sizes of tire crumb rubber (Rhodes et al., 2012).

For Zn it has been shown that leaching was reduced with both, increasing salinity and pH of the leaching solution (Degaffe and Turner, 2011). On the contrary, no effect of pH was observed for leaching of Na and S from tire materials (Selbes et al., 2015). For other compounds, however systematic studies on the effect of the composition of the leaching solution, its ionic strength (e.g.

mono-/divalent cations) or natural organic matter on the extent of leaching are missing and should be included in future research.

A mechanistic interpretation of leaching results would require knowledge on the chemical speciation in the TWP matrix as well as on the factors and constraints governing their dissolution. This information is missing in many cases, as the organic and inorganic species present in tire material vary among tire models and may be altered in the production process as well as during tire use (for example Zn accelerators). Inconsistent results have been obtained regarding the influence of physico-chemical properties, methodological parameters (sampling, analytics), hydrochemical conditions (pH, ionic strength) on leaching (Degaffe and Turner, 2011; Rhodes et al., 2012; Selbes et al., 2015)). Thus, experimental parameters should be described in detail for each study to allow a comparison of the results obtained. The leaching of PAHs from tires was either investigated using samples obtained by artificial abrasion of the tire (using files or knifes, etc.) (Aatmeeyata and Sharma, 2010; Sadiktsis et al., 2012) or by sampling traffic related particles (Boonyatumanond et al., 2007; Rogge et al., 1993; Takada et al., 1990), with highly variable results. Therefore, the use of shredded tires is not recommended

It should be taken into account that most substances leaching from TWP may also have other sources. Such other sources are other traffic-related particles or traffic area runoff, including wear of brakes, vehicle components, pavement materials, road equipment and road maintenance activities (Dongarra et al., 2007; Hjortenkrans et al., 2007; Johansson et al., 2009; Moreno et al., 2006; Querol et al., 2007; Shah et al., 2006). Other contributions may stem from point sources such as steel plants and other industrial activities in cities (Espinosa et al., 2004; Querol et al., 2007; Shah et al., 2006) and corrosion of metallic material alongside streets. It has been estimated that e.g. the largest portion of Zn in stormwater runoff originates from building materials (70 %) rather than from TWP and that most PAH stem from atmospheric deposition (40%) (Petrucci et al., 2014). A detailed apportionment of the contribution of dissolved compounds from TWP is necessary to assess whether aside from potential risks connected to the particulate TWP themselves, TWP act as a significant source of dissolved compounds for receiving waters.

6 Effects on biota in the aquatic environment

Effects on biota can be caused by physical interactions between particle and organism often related to particle size and shape, and/or by toxic compounds released from the particles (Skjolding et al., 2016). The majority of studies examined effects of TWP leachates independent from the environmental compartment. Only a few studies considered different environmental compartments e.g. surface water, sediments and soil (Tab. 4). Most investigations focused on airborne TWP, which is reflected by the high number of available publications (Gustafsson et al., 2008; Mantecca et al., 2010, 2009).

In order to study toxicity of TWP in the aquatic environment, leaching tests in aquatic media in the absence of soil and sediment were conducted. After leaching, the TWP were removed and only the leachate was used for toxicity testing. Toxicity of TWP leachates was related to the presence of Zn, other toxic metals like Pb and Cd as well as organic compounds like benzothiazole derivatives, phthalates, phenolic derivatives, hydrocarbons, aromatic amines and resin acids (Wik and Dave, 2009). In fact, several studies found Zn and organic compounds to be among the most important leachable tire constituents (Turner and Rice, 2010; Wik et al., 2009). Treatment of leachates with ion-exchange columns or SPE columns led to significantly reduced toxicity, indicating that not only metals are responsible for toxicity, but also lipophilic organic compounds (Wik et al., 2009).

PAHs bound to tires are not easily extracted even under harsh extraction conditions. The bioavailability of PAHs from TWP to organisms in the environment is expected to be low (Kreider et al., 2010). The acute effect concentrations of TWP in aquatic media including marine environments were found to cover a range of 25 to 100,000 mg TWP/L, while chronic effect concentrations vary from 10 to 3,600 mg TWP/L. Varying test designs, tire materials and species sensitivity might be responsible for a high variability of leachate toxicity data (Turner and Rice, 2010; Wik and Dave, 2009). It was shown that TWP leachates have sublethal effects, i.e. teratogenic, mutagenic and estrogenic effects. The TWP concentrations, at which these sublethal effects were shown, ranged between an equivalent of 500 mg TWP/L and 500,000 mg TWP/L (Menz and Seip, 2004; Wik and Dave, 2009).

These TWP concentrations in water do not represent realistic environmental conditions. Even a dilution to 1% would represent extremely contaminated water (equivalent to 500 mg TWP/L). Reported environmental concentrations in river water and settling ponds do not exceed 10 mg TWP/L (Fig. 7). Only in surface runoff, TWP concentrations > 100 mg/L have been reported. As reported earlier, TWP from road simulators are not appropriate to study ecotoxicological effects because they behave differently compared to real TWP (Kreider et al., 2010).

TWP toxicity in soils and sediments is most probably linked to leaching of toxic constituents (Panko et al., 2013b). TWP from a road simulator were mixed with sediment and the leachate was not acutely toxic under environmental relevant conditions (temperature and TWP concentration) (Marwood et al., 2011; Panko et al., 2013b). Conclusively, the risk of leachate toxicity resulting from TWP in sediments is low, since observed effects were low or absent at TWP concentrations of up to 10,000 mg TWP/kg sediment (Panko et al., 2013b).

In order to study chronic toxicity of TWP in sediments, the accumulation of leached Zn from weathered TWP by amphibians (*Rana sylvatica*) during larval development was analyzed and compared to $ZnCl_2$ spike soils. Zn was shown to be bioavailable from TWP and $ZnCl_2$. There were no significant differences in effects between both. Sublethal effects were observed. However, increased mortality of larvae could not be observed at a statistically significant level and an impact on amphibian survival in traffic influenced environments cannot be expected from the presence of TWP (Camponelli et al., 2009).

To assess the risk of TWP in the aquatic environment, two requirements have to be fulfilled. Environmental exposure conditions (e.g. TWP concentration) have to be known and test conditions have to be selected keeping environmental conditions in mind. From the reviewed studies, however, it can be concluded that effects vary due to inconsistent experimental conditions and the heterogeneous nature of TWP composition. Further, the applied test conditions differed strongly from environmental conditions as either TWP concentrations were well above expected environmental concentrations or the leaching conditions were harsher than in the environment. These test results are therefore hardly suitable for an environmental risk assessment of TWP.

7 Conclusions

Based on this review the following conclusions can be drawn:

- TWP are a mixture of tire wear and particulate matter from the pavement or road dust. The share of TWP of non-exhaust emissions from traffic was estimated to 5 to 30%. The amount of TWP generated in Germany (2014), the European Union (2014) and the USA (2010) were re-estimated as 1.3 x 10^5 t/a, 1.3 x 10^6 t/a and 1.1 x 10^6 t/a.
- The infrastructure for collection of surface runoff and the conditions of its treatment determine how much of the released TWP eventually reaches surface water. Estimates are highly uncertain and vary between 0.1 and 10% of TWP emissions. For Germany between 3,000 to 10,000 t/a were estimated to reach surface waters.
- Concentrations of TWP are estimated to range from micrograms per litre in surface water to milligrams per kilogram in sediments, suggesting that sediments act as a sink for TWP.
- Ecotoxicity studies mostly used unrealistically high concentrations and leachates of laboratory produced tire particles rather than real TWP. Direct effects of TWP have rarely been studied.

The following research needs are seen:

- Novel TWP markers should be found and analytical methods be developed for the determination of TWP concentration in various environmental compartments.
- Knowledge on physico-chemical properties of TWP (e.g. particle density, particle size distribution in water, surface charge) should be improved to assess transport and fate of TWP in surface waters.
- Novel analytical methods should be used to determine the flux of TWP and their environmental concentrations.
- An assessment should be made on the mass flows of elements and chemicals related to the TWP fluxes in comparison to inputs from other sources.
- Ecotoxicity studies should be performed involving real TWP and should consider possible direct effects of particles.
- On the basis of improved exposure and effect data the risks related to TWP in the aquatic environment should be assessed.

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9 Competing interests

We declare no conflict of interest.

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Figure Captions

Figure 1

Particle size ranges and obtained TWP size distributions.

[1] (Kwak et al., 2013); [2] (Dahl et al., 2006); [3] (Gustafsson et al., 2008); [4] (Kreider et al., 2010); [5] (Q. Wang et al., 2017)

Figure 2

Particle morphologies of tire materials obtained under varying sampling conditions

[1] (Specht et al., 2007) SEM image adopted from Specht et al. (2007) is licensed under CC BY 4.0;

[2] (Kreider et al., 2010), Reprinted from Science of The Total Environment, 408/3, M. L. Kreider, J. M. Panko, B. L. McAtee, L. I. Sweet, B. L. Finley, Physical and chemical characterization of tire-related particles: Comparison of particles generated using different methodologies, 652-659, Copyright 2010, with permission from Elsevier;

[3] (Camatini et al., 2001) Reprinted from Materials Characterization, 46/4, M. Camatini, G. F. Crosta, T. Dolukhanyan, C. Sung, G. P. Giuliani, G. M. Corbetta, S. Cencetti, C. Regazzoni, Microcharacterization and identification of tire debris in heterogeneous laboratory and environmental specimens, 271-283, Copyright 2001, with permission from Elsevier,

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Figure 3

Mass distribution of non-exhaust traffic emissions, adapted from Simons (2016) Reprinted from The International Journal of Life Cycle Assessment, 21/9, A. Simons, Road transport: new life cycle inventories for fossil-fueled passenger cars and non-exhaust emissions in ecoinvent v3, Copyright 2013, with permission from Elsevier

Figure 4

Cross-section of tire tread, (a) SEM image of ZnO particle in tire tread and b) EDX spectra of the ZnO particle (Adachi and Tainosho, 2004), Reprinted from Environment International, 30/8, K. Adachi, Y. Tainosho, Characterization of heavy metal particles embedded in tire dust, 1009-1017, Copyright 2004, with permission from Elsevier)

Figure 5

Pyrograms of tire tread rubbers and atmospheric dusts. Peaks: 1=1,3-butadiene; 2= isoprene; 3= C6H10; 4= benzene; 5= toluene; 6=vinylcyclohexene; 7=ethylbenzene; 8=xylene; 9=styrene; 10=C10H16; 11=dipentene, (Lee et al. 1989), Reprinted from Journal of Analytical and Applied Pyrolysis , 16/7, Y-K. Lee, M.G. Kim, K-J. Whang, Simultaneous determination of natural and styrene-butadiene rubber tire tread particles in atmospheric dusts by pyrolysis-gas chromatography, 49-55, Copyright 1989, with permission from Elsevier

Figure 6 Molecular structures of organic compounds used or proposed as markers for TWP: a) 24 MoBT (CAS 4225-26-7); b) NCBA (CAS 028291-75-0; c) 6-PPD, N-(1,3-dimethylbutyl)-N’-phenyl-1,4-phenylenediamine (CAS 793-24-8); d) DPG, 1,3-diphenylguanidine (CAS 102-06-7)

Figure 7 TWP concentrations in different environmental media (Ni et al. (2008); Unice et al. (2013); Wik and Dave (2009) and citations therein); (black dots (mean); colored boxes (one standard deviation); dotted line (media))

Figure 8

Estimation of mass flow of TWP emission on German highways based on TWP generation in 2014 for a) scenario A and b) scenario B. Note that highway comprise approx. 36% of the total estimated TWP emission in Germany (Tab. 3).

List of Tables

Table 1

General composition of tires (Baumann and Ismeier, 1998; Grigoratos and Martini, 2014; Wik and Dave, 2009)

Table 2

Morphologies of tire materials obtained under various sampling conditions.

Table 3

TWP emission in the EU (2014) calculated based on registered cars, in Germany (2014) and the USA (2010) calculated based on total traveled distances

[a]) tire abrasion rates (passenger cars, trucks & busses, trailer trucks): city: 120, 800, 1400 mg/km; highway: 70, 500, 1000 mg/km

[b]) includes trucks and trailer trucks

[c]) registered vehicles in the EU : 210x10^6 passenger vehicles; 36x10^6 trucks & trailer trucks; 1.5x10^6 busses

[d]) average distances travelled (passenger cars, trucks & trailer trucks, busses) in the EU 12,900, 39,000, 60,000 km/year (data adopted from Germany)

Table 4

Ecotoxicological studies on effects of TWP and tire material as well as leachates

Table 1

Category	Content [wt%]	Ingredients
Rubber/Elastomere	40-60	poly-butadiene, styrene-butadiene, neoprene isoprene, polysulphide
Reinforcing agent (filler)	20-35	Carbon black, silica, silanes
Process oils	15-12	mineral oils
Textile & metal net	5-10	
Vulcanization agent	1-2	ZnO, S, Se, Te Thiazoles, organic peroxides, nitrocompounds
Additives	5-10	Preservatives (halogenated cyanoalkanes), anti-oxidants (amines, phenols), desiccants (calcium oxides), plasticizers (aromatic and aliphatic esters), processing aids (mineral oils, peptisers)

Table 2

Sampling conditions	Morphology	Reference
Road runoff, road simulator, shredded tires	Elongated, circularity 0.83, aspect ratio 0.64	(Kreider et al., 2010)
Road simulator	Jagged, droplets, granules	(Gustafsson et al., 2008)
Road simulator, road runoff	Warped, porous	(Camatini et al., 2001)
Road runoff	Irregular	(Q. Wang et al., 2017)
Road simulator	Near spherical, elongated	(Dahl et al., 2006)

Table 3

region	**travel distance [x10^9 km/year]**			**tire wear emission rates [x10^3 t/year][a]**					
	urban	**rural road**	**highway**	**passenger cars**	**trucks[b] & busses**	**urban**	**rural**	**highway**	**total**
EU (2014)	n/a	n/a	n/a	264[c, d]	1,063[c, d]	n/a	n/a	n/a	1,327[c, d]
Germany (2014)	190	320	230	52	81	40	45	48	133
USA (2010)	4000	2000		500	620	750	370		1,120

Table 4

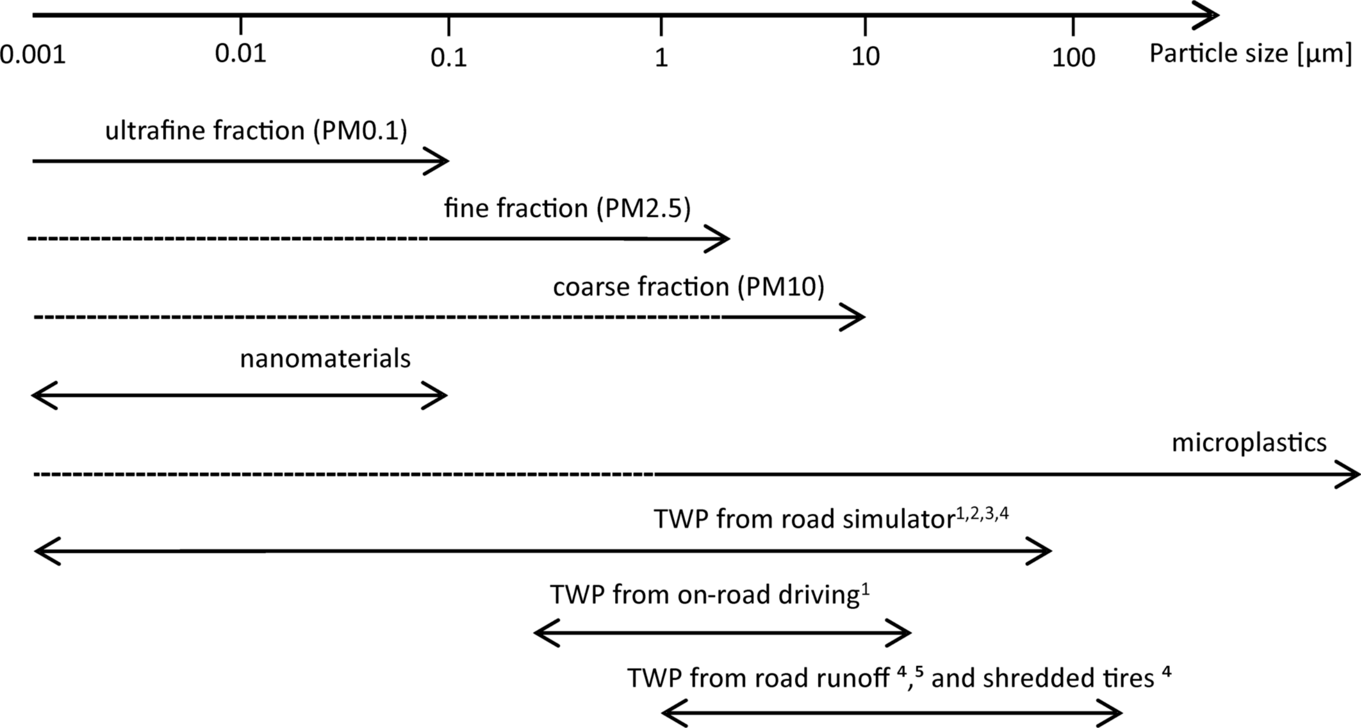
Particles	Tested material	Organisms	Effects	Study
	Leachtes (TWP removed)			
Ground tire material <590 µm	100 g/L, one week shaking; dilutions of 0.1-100%	*Aedes albopictus, Aedes triseriatus*	Significant effects on survivorship and rate of population increase observable at concentrations ≥100 mg/L; significant differences between species tolerance	(Villena et al., 2017)
Road simulator, <150 µm	Sediment spiked at 10 g/kg; preparation of elutriate (24h); exposure to elutriate and whole sediment	*Ceriodaphnia dubia,* *Pimephales promelas,* *Chironomus dilutus, Hyalella azteca*	*P. promelas, C. dubia, H. azteca*: no significant effects or differences to control groups *C. dilutus*: mild growth inhibiton (-20%), not significant	(Panko et al., 2013b)
Road simulator, <150 µm	Leachates with 625 – 5000 mg TWP /L; elutriate 72h; heating to 44 °C; Spiked sediment, TWP conc. of 100-10,000 mg/L	*Pseudokirchnerella subcapitata* *Daphnia magna* *Pimephales promelas*	Toxicity only observed for high-temp. leachates (44°C); presence of sediment had only minor effect on toxicity; TWP leachates incubated at room temperature, with or without sediment, were not toxic to *D. magna*	(Marwood et al., 2011)
End-of life car tires, abraded with steel file, <500 µm	0.5 g TWP / L sea water, 120 h leaching time	*Ulva lactuca*	Toxicity effects measured at an equivalent of 25 mg TWP /L sea water; measured by observance of chlorophyll-α fluorescence	(Turner and Rice, 2010)
Generated with rasp	0.01 – 10 g TWP /L Six consecutive leachings of the particles	*Daphnia magna,* *Ceriodaphnia dubia,* *Pseudokirchnerella subcapitata,* *Danio rerio*	min/max EC50 (g/L): *P. subcapitata*: 0.05 (1st leaching) 2.84 (6th leaching) *D. magna*: 0.37 (2nd leaching) 7.45 (2nd leaching) *C. dubia*: 0.01 (2nd leaching) 3.59 (6th leaching) *D. rerio*: no consistent toxicity was shown at tested concentrations Toxicity was reduced with sequential leachings; Different tires showed varying toxicity; *C. dubia* reproduction was most sensitive (at realistic environmental conditions)	(Wik et al., 2009)
Cryo fractured tire scrap	Soxhlet extraction (DCM); equivalents of 50 - 140 mg TWP/L in FETAX solution	*Xenopus laevis*	Toxicity observed at concentrations ≥80 mg/L; mortality, embryotoxicity, malformations of larvae EC50 144.6 mg/L tire debris organic extract	(Mantecca et al., 2007)
Abraded with rasp, from 25 tires	0.9 g TWP / 90 mL water; 44 °C, 72h	*Daphnia magna*	48h EC50: 0.5 - >10 g TP /L, depending on the tire Most toxic tire: 48h EC50 = 0.5 g TWP /L	(Wik and Dave, 2006)
Cryo fractured tire scrap	Water leachate: 50 g TWP /L and 100 g TWP /L, pH 3, 24 h; dilution series 1-100 %;	*Xenopus laevis*	Water leachate: 1-50% dilution not lethal, undiluted leachate (50 g TP /L) caused 80% mortality	(Gualtieri et al., 2005a)

	Organic extract: soxhlet extraction (DCM)		EC50 (50 g TWP /L): 40.2% EC50 (100 g TWP /L): 73.3 % Conclusion: leachates produced at 50 and 100 g TWP/L had teratogenic effects	
Road simulator particles, 10-80 µm	50-100 g TWP /L, shaking 24 h, dilution series 1-100 %;	*Raphidocelis subcapitata, Daphnia magna, Xenopus laevis*	EC50 (*R. subcapitata*): 13.81% leachate dilution 48 h LC50 (*D. magna*): 53.3% leachate dilution D. magna: after 5 days, all juveniles exposed to 10% concentration were dead Strong teratogenic effects in *X. laevis* (malformations); LC50 could not be calculated; undiluted leachate led to 80% mortality of *X. laevis*	(Gualtieri et al., 2005b)
No particles	chemical standards: benzothiazole, 2-mercaptobenzothiazole (MBT), 2-methylthiobenzothiazole (MTBT), 3,3′,5,5′-tetramethylbenzidine (TMBZ)	*Aedes albopictus*	Induction of microsomal cytochrome P450 monooxygenase activity (xenobiotic metabolizing enzyme) mainly by benzothiazole Increaed tolerance of the mosquitos to pesticides, since P450 is involved in insecticide detoxification	(Suwanchaichinda and Brattsten, 2002)
	TWP or road runoff sediment			
From tire scrap; <590 µm	TWP in aged sediment; 83.8 g TP / kg sed	*Rana sylvatica*	Measurable physiological outcomes: significant difference in hatching success and increased time to reach metamorphosis; no significant mortality	(Camponelli et al., 2009)
Sediments from road runoff detention systems	40 g sediment + 160 mL water; 24 h shaking; use of elutriate; Sediments from 18 road runoff detention systems were analysed. tire wear content in sediment <0.15 – 10.8 g TWP /kg ds (derived by organic Zn content, (Fauser et al. 1999))	*Hyalella azteca Daphnia magna, Ceriodaphnia dubia*	Toxicity strongly dependent on sample, but contaminant concentrations was hardly related to effects in bioassays;Toxicity is described as mobility after 48-72h exposure to sediment, sediment elutriate or site water and was strongly dependend on the sampling site. *H. azteca*, 72-h mobility: sediment 20-100 % site water: 90-100 % *D. magna*, 48h mobility: elutriate: 0-100 % site water: 0-100 % *C. dubia*, 48 h mobility; elutriate: 0-100% site water: 0 - 100 % chronic tox.: *C. dubia*, 9 day survival elutriate: 17-100 % 9-day young/female elutriate: 1-38	(Wik et al., 2008)
Grated rubber of 12 tires	72 h equilibration with water; conc. 0.25 – 16 g/L	*Daphnia magna*	Immobility was recorded after 24h and after 48h; tested tire samples showed strong differences in toxicity 24h EC50 0.29 – 32 g TWP /L	(Wik and Dave, 2005)

			48h EC50 0.125 – 2.41 g TWP /L	
	Complete tire or shredded tires			
No tire particles, rubber hose and rubber additives	Fish in glass tanks received water that flowed through 20 m rubber hose, time: 1 week; control: plastic hose	*Oncorhynchus mykiss*	Increase in EROD and GR activity = fish detoxification system no effect of rubber, but: effects of injected rubber additives (MBT) and (DPA) PAHs and benzothiazoles present in fish bile;	(Stephensen et al., 2005)
Whole tires with and without highly aromatic oils in the tread	Whole tire submerged in fish tanks with 400 L freshwater; addition of fish 1 day later	*Oncorhynchus mykiss*	Increase in in EROD activity, elevated antioxidant responses; hydroxylated PAH in the bile of fish indicates leakage from tire	(Stephensen et al., 2003)
Shredded tire chips, 1 cm³	Synthetic seawater, 140 g tire chips in 2.8 L sea water, varying salinities	*Allivibrio fischeri (Microtox bioassay)*	Toxicity effects were observed in all taxonomic orders; correlation between toxicity and salinity: toxicity decreases with increasing salinity; Interactions between salts and tire leachates were assumed	(Hartwell et al., 2000)
Shredded scrap tires	*Cyprinodon variegatus* *Palaemonetes pugio*	*Cyprinodon variegatus, Palaemonetes pugio*	96-h LC50s *C. variegatus* 10% leachate at 5‰ salinity 26% at 15‰ salinity 96-h LC50 *P. pugo* 63% at 5‰ salinity 96-h LOEC *C. variegatus* survival 12.5% at 5‰ salinity and 25% at 15‰ salinity 96-h LOEC for *P. pugio* survival 50% at 5‰ salinity Growth LOEC values: 12.5% at both salinities for *C. variegatus* 50% for *P. pugio* at 5‰ salinity	(Hartwell et al., 1998)
New tires, road-worn tires, tires from floating tire breakwater	Whole tires submerged in 300 L groundwater; up to 40 days leaching period = Equivalent to 27 – 42 g tire / L	*Oncorhynchus mykiss,* *Daphnia magna,* *Pimephales promelas,* *Photobacterium phosphoreum,* *Escherichia choli,* and others	Toxicity to O. mykiss 96h LC50 11.8 – 19.3 % v/v No toxicity to *D. magna* or *P. promelas* 10x concentrated leachate inhibited *P. phosphoreum* bioluminescence, enzymes in *E. coli* (β-galactosidase) and mitochondria (NADH-coenzyme Q reductase) Other screening tests revealed no toxicity (nematode lethality & mutagenicity, bacterial motility inhibition, bacterial colour production)	(Day et al., 1993)

Highlights

- Knowledge on TWP emissions, fate, and effects in the aquatic environment is reviewed.
- Knowledge gaps regarding environmental relevance of TWP are identified.
- TWP emissions entering the aquatic environment are below 20% of the total TWP emissions.
- There is hardly any information about TWP effects at environmentally relevant concentrations.


0.001
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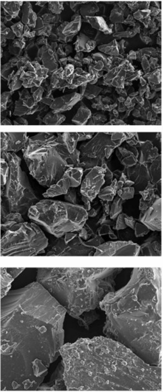
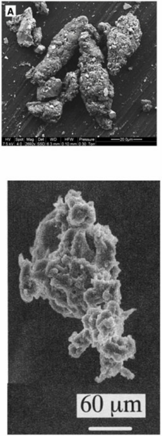
fine fraction (PM2.5)
coarse fraction (PM10)
nanomaterials
microplastics
TWP from road simulator1,2,3,4
TWP from on-road driving1
TWP from road runoff 4,5 and shredded tires 4

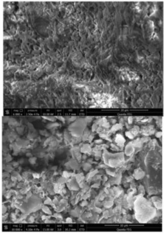
Shredded tire[1]

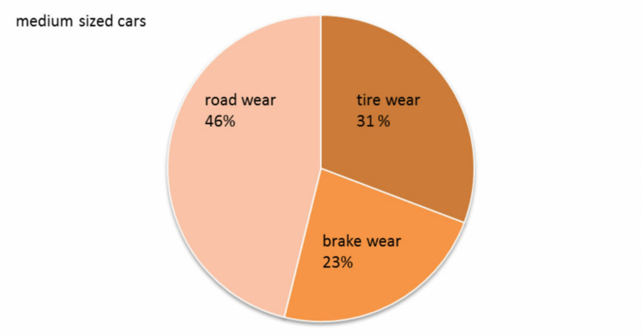


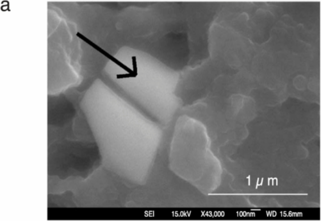
Road simulator[2,3]

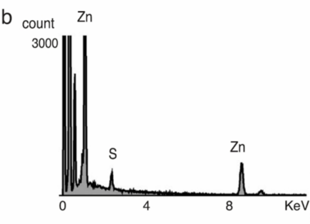


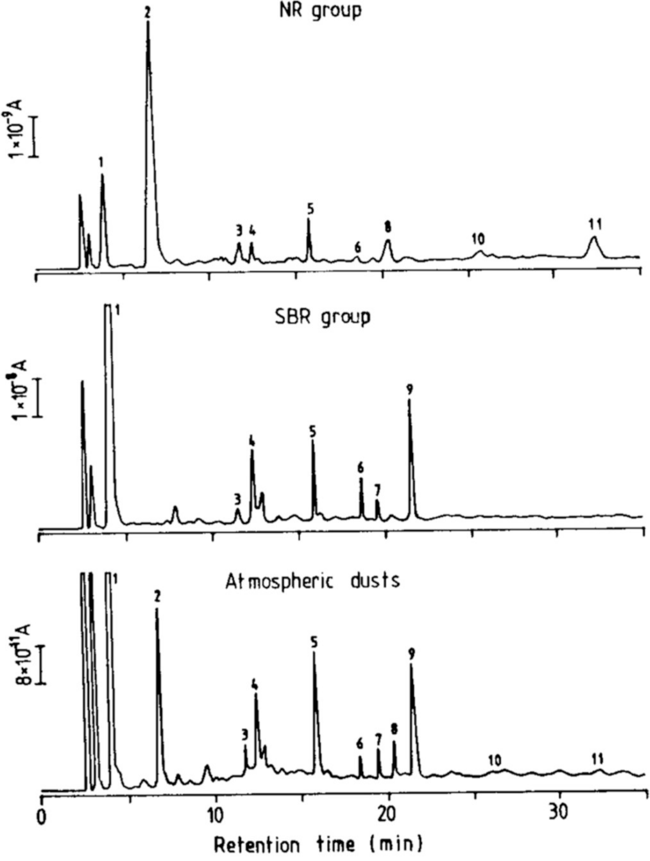
Road runoff[4]



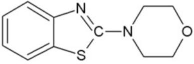

medium sized cars
road wear
46%
tire wear
31 %
brake wear
23%


a
1 μ m
SEI 15.0kV X43,000 100nm WD 15.6mm

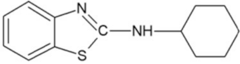

b
count
3000
Zn
S
Zn
0
4
8
KeV


NR group
1×10⁻⁹A
1
2
3
4
5
6
8
10
11
SBR group
1×10⁻⁸A
1
3
4
5
6
7
9
Atmospheric dusts
8×10⁻¹¹A
1
2
3
4
5
6
7
8
9
10
11
0
10
20
30
Retention time (min)

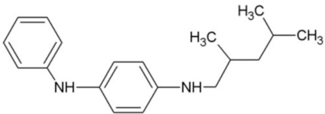
a)



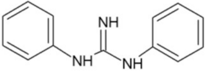
b)

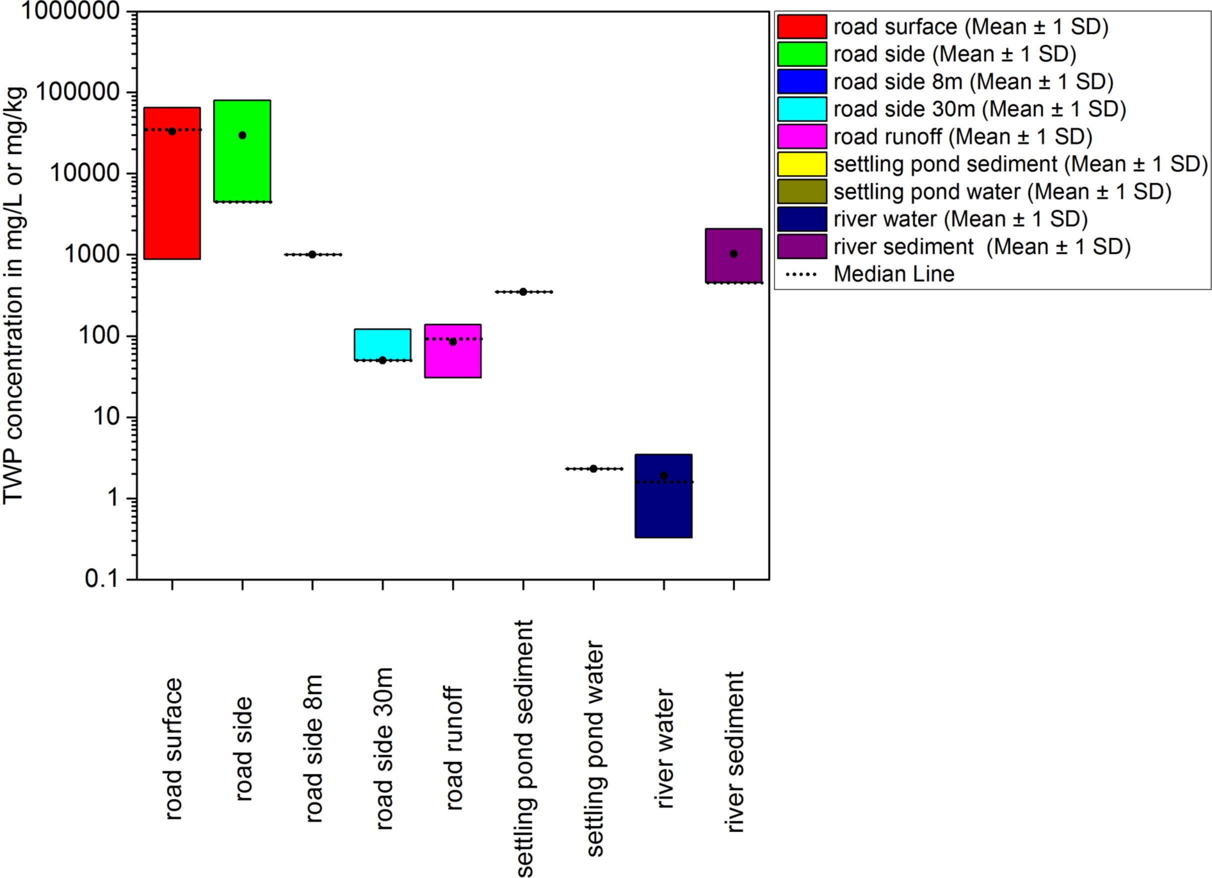


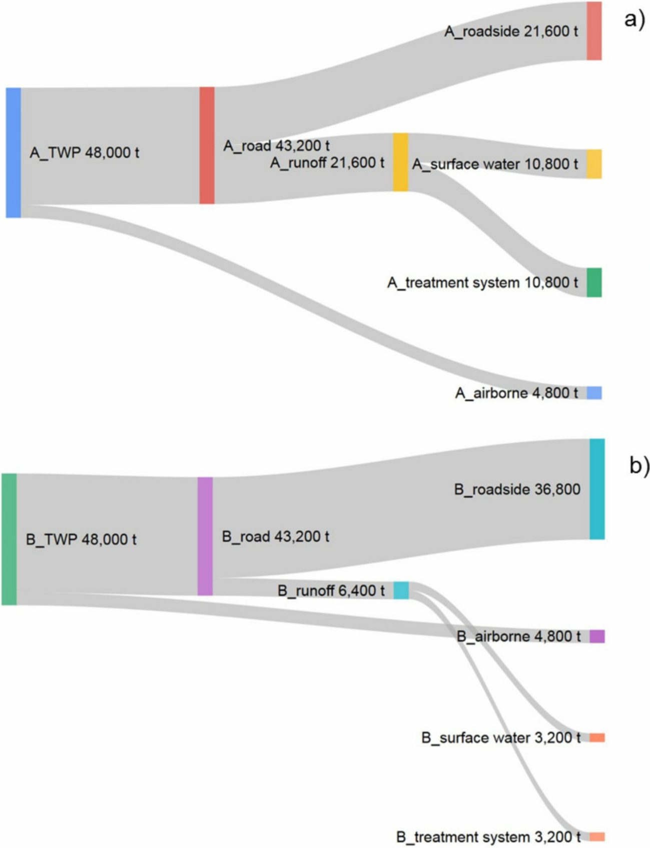
c)

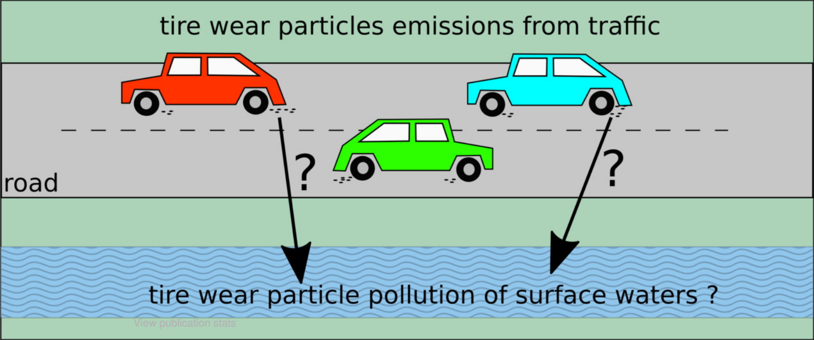


d)




1000000
100000
10000
1000
100
10
1
0.1
TWP concentration in mg/L or mg/kg
road surface
road side
road side 8m
road side 30m
road runoff
settling pond sediment
settling pond water
river water
river sediment
road surface (Mean ± 1 SD)
road side (Mean ± 1 SD)
road side 8m (Mean ± 1 SD)
road side 30m (Mean ± 1 SD)
road runoff (Mean ± 1 SD)
settling pond sediment (Mean ± 1 SD)
settling pond water (Mean ± 1 SD)
river water (Mean ± 1 SD)
river sediment (Mean ± 1 SD)
Median Line


a)
A_TWP 48,000 t
A_road 43,200 t
A_roadside 21,600 t
A_runoff 21,600 t
A_surface water 10,800 t
A_treatment system 10,800 t
A_airborne 4,800 t
b)
B_TWP 48,000 t
B_road 43,200 t
B_roadside 36,800
B_runoff 6,400 t
B_airborne 4,800 t
B_surface water 3,200 t
B_treatment system 3,200 t


tire wear particles emissions from traffic
road
?
?
tire wear particle pollution of surface waters ?