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MICROPROOF
Micropollutants in Road RunOff

**Pathways of organic micropollutants
and microplastics in road borders**

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1 Introduction

While research on microplastic occurrence and impacts has focused on the marine environment, very little is known about their release from land-based activities and the pathways from the source to soil, sediments and water. Also for organic micropollutants, little is known about the pathways from the source to soil, sediments and water. The different traffic related sources of microplastics and organic micropollutants are described in previous Microproof reports 1.1, 1.2 and 1.3.

In this report the different pathways of microplastics and organic micropollutants from traffic related sources to open water will be elaborated. Figure 1 gives a comprehensive overview of the possible pathways via which road dust (and the incorporated pollutants) eventually can end up in the aquatic environment (adapted from Vogelsang, et al., 2018).

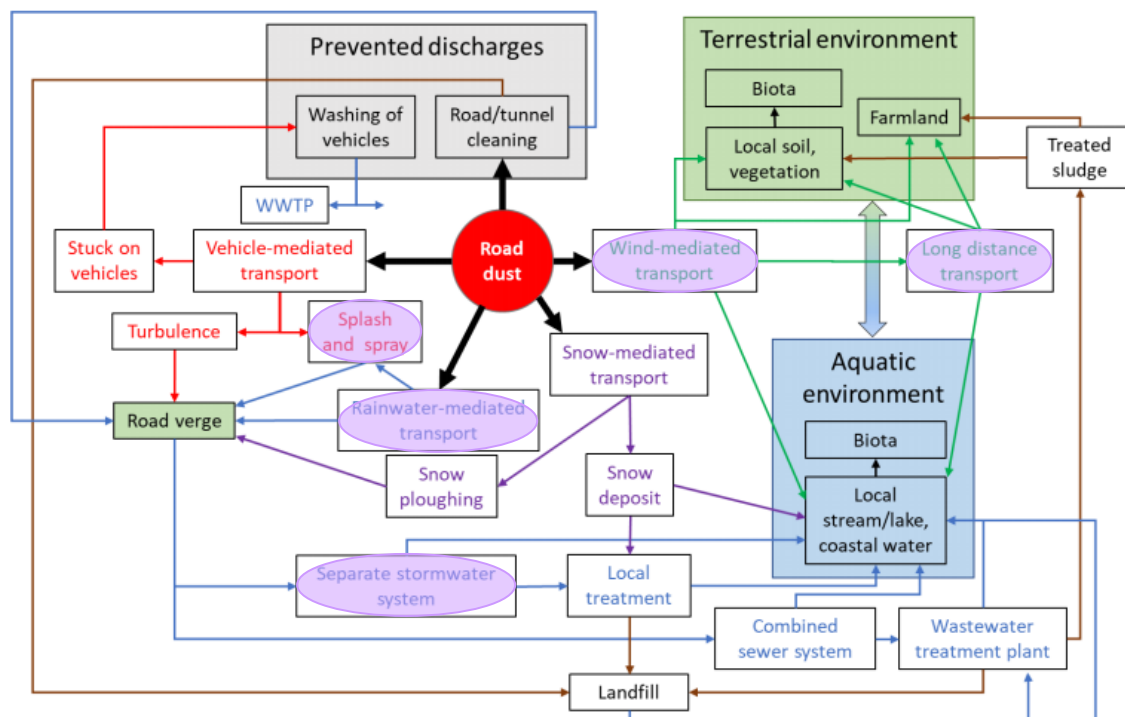


Figure 1 Potential main pathways for microplastics in road dust to reach aquatic (blue) and terrestrial (green) environments and prevented discharges (grey), presented by Vogelsang, et al., 2018. The purple circles indicate which pathways are discussed in this report.

Pollutants can be transported from the road into the environment via several pathways. Most pathways are relatively short, but atmospheric transport can be responsible for large distances. Different potential distances are discussed in literature varying between 10-250 meter (Werkenthin et al., 2014) and distances up to 50 kilometer (Kole et al., 2017). Quantities of pollutants deposited at 30 meter from the road are usually at the background deposition level (TRL, 2002). Since the concentrations resulting from the large distances are relatively small, this study will focus on the pathways in the close vicinity of the road.

Although quantitative information about microplastics and organic micropollutants entering the inland water system land is scarce, the general principles of the possible pathways are explained in the next chapters. The pathways are described in Chapter 2, while the fate of a selection of pollutants is explained in chapter 3.

2 Pathways

Pollutants which are caused by roads and traffic can be found in the soil or in the aquatic environment. Many factors impact the pathways of pollutant transportation; therefore, it is difficult to define the general status of the transportation process. Figure 2 provides a schematic overview of 6 different transportation routes from the road to surface waters. These routes are:

1. Direct airborne dispersion
2. Resuspension or wind dispersion (dry)
3. Splash and spray (wet)
4. Direct runoff
5. Discharge after treatment
6. Groundwater

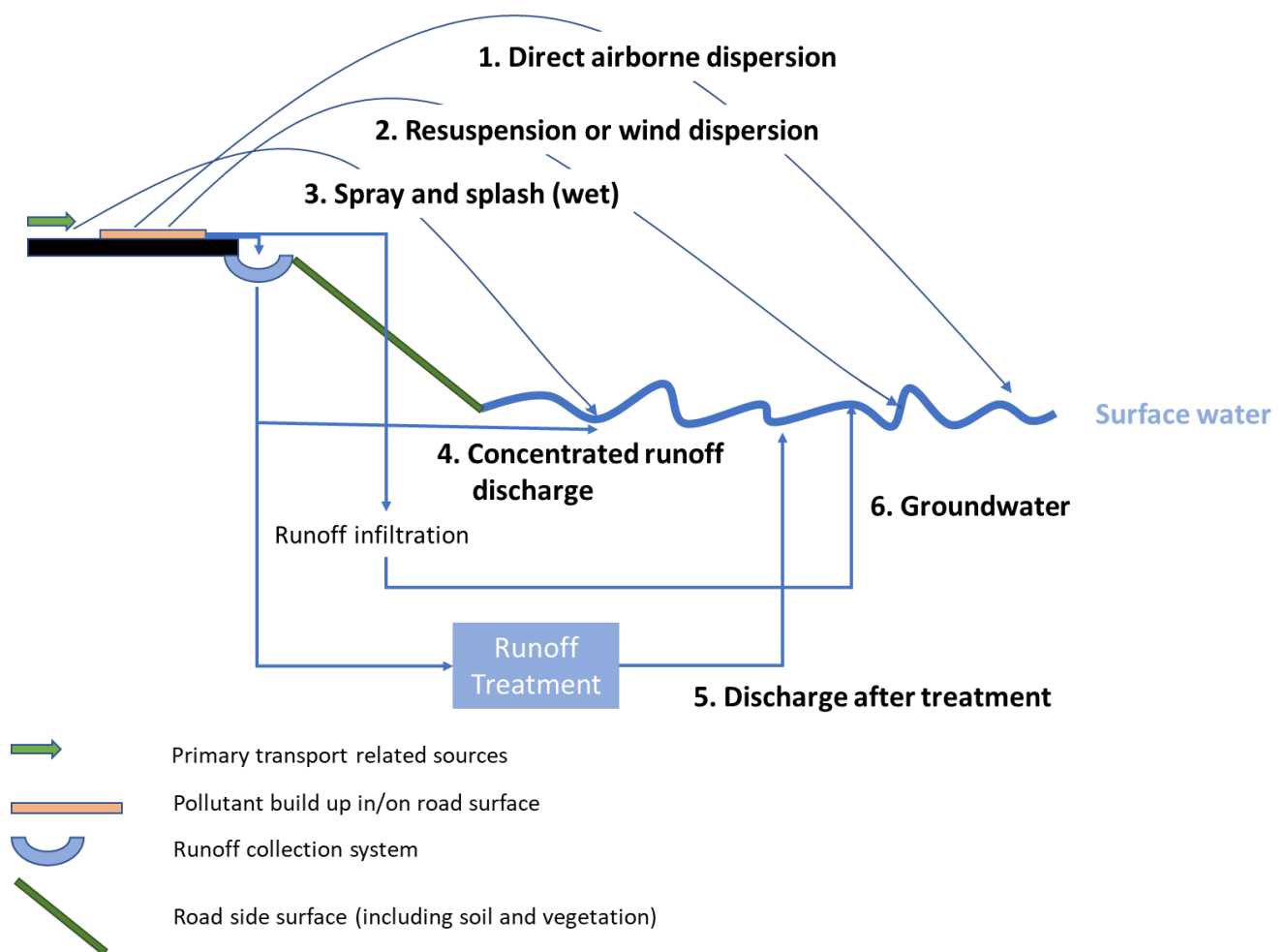


Figure 2 Transportation of pollutants within the proximity of the road verge

Paragraph 2.1 discusses the atmospheric dispersion, which includes direct airborne dispersion, resuspension or wind dispersion (dry) and splash and spray (wet). Direct runoff is discussed in paragraph 2.2, discharge after treatment is discussed in paragraph 2.3 and the transportation route via groundwater is discussed in 2.4.

2.1 Aerial dispersion

Pollutants can be transported from the road via aerial dispersion. Pollutants are either directly released to the atmosphere or are dispersed in the atmosphere by turbulence from moving traffic.

A large part of the pollutants is transported of the roads by aerial dispersion. Pollutants transport in run-off waters as an important pathway of environment contamination was described theoretically by Folkesson et al. (2009). Aerial dispersion could be a significant pathway to move pollutants from the road to a nearby surface water body, as is shown in the following studies:

- De Best et al. (2002) reported that 46-92 % of the pollutants are removed from the roads via drift, while 8-54 % of the pollutants are removed from the road via runoff.
- Boller et al. (2006) reported that 36 % of water is removed from a road via runoff and 64 % is removed via drift and spray.
- The POLMIT study (TRL, 2002) estimates 35 % to be transported by run-off. The other fraction of 65 % probably is re-emitted by air.
- Van Duijnhoven et al. (2013) reported that the percentage of heavy metals that is removed via runoff from a road with regular asphalt is between 17% and 43%, while the remaining 57% - 83% is removed by spray

These studies only analysed how pollutants are removed from the road. It does not necessarily mean that aerial dispersion also has the largest contribution to the amount of (road-related) pollutants that enter a water body.

The share of pollutants that is transported of the road by aerial dispersion depends foremost on the following factors:

- *Type of asphalt:* The use of porous asphalt ensures that water will be drained from the road surface fast and no puddles can form on the road. This will reduce the amount of pollutants that could be transported of the road via splash and spray. Pollutants will be partially retained in the open pores and the other part will be removed via runoff.
- *Presence of an emergency lane:* If an emergency lane is present, part of the pollutants in splash and spray or from atmospheric dispersion and deposition will end up on the emergency lane. In general, no vehicles drive on the emergency lane, and therefore, no resuspension or splash will occur on the emergency lane. This results in a larger amount of pollutants to be transported via runoff and a smaller amount of pollutants to be transported via splash and spray and dispersion/deposition.
- *Topographic features:* The presence of hills, trees or man-made objects will obstruct wind and thereby it will obstruct aerial dispersion of pollutants. This will reduce the amount of pollutants that are transported via atmospheric dispersion.
- *Weather conditions:* Wind may contribute to long distance transport of airborne particles directly to terrestrial and aquatic environments. During strong gusts of wind, the distance increases but the concentration of pollutants decreases. Light wind causes local areas of pollutants settling in the road environment (TRL 2002).

Type of asphalt and presence of emergency lane

The effect of asphalt type and the presence of an emergency lane is shown in a study by de Best et al. (2002). This study reported the share of pollutants that is transported via runoff and via drift from a road with different types of asphalt. A highway with porous asphalt results in a reduced amount of pollutants that is transported to the surrounding environment. This is caused by the open structure of the road, where more water and pollutants are caught. This will increase the evaporation and it will reduce the amount of splash, resulting in a reduced amount of pollutants that will be transported from the road via atmospheric dispersion (see Table 1). The share of pollutants that is transported via drift is lower for porous asphalt than for regular asphalt (except for PAH).

From Table 1, it appears that the proportion of pollutants that is released via drift is higher on secondary roads (with regular asphalt) than on highways (with porous asphalt). This is probably caused by the presence of the emergency lane on highways. Part of the pollutants that are transported from the highway by splash or spray, will deposit on the emergency lane, and the pollutants will be transported from the emergency lane via runoff.

Table 1 Transported amount of PAH, zinc and mineral oil on three different roads via drift (mg/week/m road). Data from de Best et al. (2002).

	PAH		Metals		Mineral oil	
	Drift (mg)	Drift (%)	Drift (mg)	Drift (%)	Drift (mg)	Drift (%)
Highway with regular asphalt	2.5	79%	2.3 - 84	50 - 78%		
Highway with porous asphalt	0.8	94%	0.2 - 7	24 - 46%		
Secondary road with regular asphalt	0.3	93%	0.65 - 24.3	87 - 98%	55.2	80%

Topographic features

The effect of topographic features is shown in a study by Schipper et al. (2003). In this study, PAH was measured in runoff and wet deposition on two secondary roads (without an emergency lane) with regular asphalt. The road borders of one road are open and there are no trees or other obstacles that could influence the amount of wet deposition, while the other road lies in an area with forests. The road without trees shows that more pollutants are transported via spray, while the road that lies in the forest shows that most pollutants are transported via runoff (see Table 2). (Schipper et al., 2003).

Table 2 Amount of PAH16 and Zinc in runoff (at the road side) and wet deposition (deposited between 0-6 meter from the road side) from two locations (mg/meter road surface/year) as measured in Schipper et al. (2003).

	Secondary road without trees		Secondary road with forest	
	Runoff	Wet deposition	Runoff	Wet deposition
PAH16	11 (37%)	19 (63%)	22 (88%)	3 (12%)
Zn	667 (49%)	706 (51%)	778 (60%)	522 (40%)

Schipper et al. (2003) also checked the effect of a wind break next to the road, to evaluate if this would reduce the amount of splash from the road. It was concluded that the wind break did only slightly influence the amount of splash. Possibly, this was due to the fact that the trees/bushes were still very small. The turbulence caused by road traffic could also be the reason for very small reducing effect of the wind break. Since forests do influence the transport of pollutants, it is expected that a full-grown wind break will probably ensure that most of the pollutants are deposited very close to the road.

Weather conditions

Precipitation and wind both influence the dispersion and deposition of pollutants. Strong winds will increase the travelled distance, but it will decrease the concentration in the atmosphere, and the deposition per hectare (as a result of the dilution). Wind is directly influenced by topographic features near the road (hills, forests, man-made objects). Rain and snow will increase the deposition of airborne particles, because precipitation collects pollution from the atmosphere and together this will rain down on the surface.

Deposition

Though tread wear particles up to 30 µm have been shown to be airborne (Cadle & Williams, 1978), particles >10 µm are not likely to stay airborne for a long period of time (Vogelsang et al., 2018). Smaller particles can stay airborne for longer periods of time (up to hours) and travel distances up to 50 km (Kole et al., 2017), although it depends on size and density of particles, and local conditions (Wagner et al., 2018).

TRL (2002) describes three types of deposition processes:

- Gravitational settling: settling of most of the particles greater than 25 µm in diameter;
- Dry deposition: settling of particles via dry deposition is dependent upon the concentration gradient between the surface and the atmosphere and the factors associated with the properties of both the pollutant and the surface;
- Wet deposition: pollutants carried up into the clouds by convection motion may become droplet nuclei or be dissolved in cloud water and transported back to the surface via rain or snow. Pollutants can also be transported via splash and spray of water droplets from the road surface.

2.2 Direct runoff

During precipitation, part of the pollutants accumulated on the roadside and in the roadside area is transported with road runoff. This runoff might be gathered in gutters and then centralized discharged in open water or in any kind of water treatment before discharge in open water.

The intensity of precipitation impacts the volume of runoff and the amount of pollutants that are accumulated in the roadside area during the dry period. Vogelsang et al. (2018) describes that particles will only be transported from the road, when the precipitation intensity exceeded a certain threshold, which depends on the road layout and. Runoff caused by precipitation after a dry period can contain a significant amount of pollutants in a short period of time. This "first flush" of intense precipitation (peak load of pollutants) can have a negative impact on the biota inhabiting the water environment (TRL, 2002).

Runoff could either be transported to a water body untreated, or it can be treated with a treatment system, or by infiltrating the runoff into the brink. The treatment system and the infiltration into the brink will reduce the potential amount of pollutants that can be transported to a water body (see paragraph 2.3).

The share of pollutants that is transported from the road via runoff depends on the type of asphalt, the presence of an emergency lane, topographic features and weather conditions. De Best et al. (2002) analysed the share of pollutants that is transported from the road via runoff and via drift, including the effect of the use of porous asphalt. Porous asphalt results in a reduced amount of runoff and drift, because part of the pollutants is stored in the pores and is removed by cleaning (see Table 3). Most of the pollutants in runoff end up within 1 meter of the road in the soil (Schipper et al., 2003), and therefore most pollutants do not end up in surface waters.

Table 3 Transported amount of PAH, zinc and mineral oil on three different roads via runoff (mg/week/m road) and contribution of runoff in total transport (%). Data from de Best (2002)

	PAH		Metals		Mineral oil	
	Runoff (mg)	Runoff (%)	Runoff (mg)	Runoff (%)	Runoff (mg)	Runoff (%)
Highway with regular asphalt	0.67	21%	1.66 – 58.7	22 - 50%	No data	No data
Highway with porous asphalt	0.054	6%	0.63 – 8.1	54 - 76%	No data	No data
Secondary road with regular asphalt	0.024	7%	0.06 – 2.15	2 - 13%	14.2	20%

2.3 Discharge after treatment

The substances settling on the road surface lead to the saturation of the surface runoff by various pollutants and this is washed off with rain and melting water which can then be fed into drainages. These either drain directly to surface water or to a storm water treatment installation. Contaminants are removed by filtration, sorption to soil particles and/or biodegradation. Which treatment is best suited depends on the climatic and hydrological characteristics of the territory, as well as on the characteristics of the pollutants. Pollutants are divided according to their physical state (soluble, insoluble, colloidal systems) and chemical composition. In most common storm water treatment systems, the concentration of suspended particles can be reduced significantly. Removal efficiency is a.o. dependant on retention time and particle size and shape. For water-soluble pollutants, the removal efficiency is lower. In general, the potential load to the surface water is reduced by any treatment installation compared to direct inputs from runoff. However, the efficiency of any removal installation is dependent on correct design, climatological circumstances and pollutant loads. Reports from WP4 will focus on treatment systems in more detail.

2.4 Flow via soil and groundwater

Flow via soil and groundwater is a potential pathway of pollutants to nearby surface waters. The pollutants in runoff water infiltrating the soil is dependent on many factors, including the intensity of traffic, type of road and condition of the road surface, soil type, vegetation and verge maintenance. The infiltration of runoff over a long period of time can be potentially associated with their accumulation in soil and leaching to the groundwater. Typical parameters which determine the risk of groundwater contamination are: degradability and other chemical properties of the organic pollutants, soil type, pH of the soil (and precipitation), precipitation surplus, groundwater level. The typical local situation of the verge determines the risk of groundwater pollution with dissolved pollutant from run off.

Pollutant characteristics, like solubility, biodegradability, adsorption, has an influence on the potential of groundwater flow as a pathway. Soluble pollutants are more likely to be transported via groundwater than insoluble pollutants, and pollutants which can be bound to particulates in the soil are less likely to be transported.

Soil and groundwater characteristics also have an influence on the potential of groundwater flow as a pathway. In regions with a low groundwater table, the pathway via groundwater will be negligible. The soil characteristics, like soil type, pH, soil organic matter, influences the potential of pollutants to be bound to the soil. For example, Werkenthin et al. (2014) showed that pH and soil organic matter affect the immobilisation of metals. Werkenthin et al. (2014) concluded that high percolation rates occur only at the immediate road edge and that might be problematic in regions with acidic sandy soils and a high groundwater table.

In the Netherlands, a study was conducted on groundwater concentrations near highways (RIVM, 1993). They measured PAH concentrations in groundwater near several highways. It was concluded that the PAH concentrations were higher in groundwater close to the highway, while the concentration is lower further away from the highway. Probably, these PAH are originated from the highway, which means that PAH can be transported to the groundwater from roads. It should be noted that groundwater levels in the Netherlands are relatively high in most locations, and more PAH could therefore reach the groundwater.

Flow of pollutants via groundwater and soil to nearby surface waters could be a relevant pathway (depending on the circumstances), but direct runoff and aerial dispersion will be responsible for a larger share of pollutant transport to surface water.

3 Fate of pollutants

3.1 Organic micropollutants

Organic micropollutants (OMP) is an operational definition for a group of compounds, which are not covered by existing water quality regulations due to their lower concentrations (i.e., ng/L up to µg/L) but are thought to be potential threats to environmental ecosystems (Farré et al., 2008). OMP are also referred to micropollutants (MP) or emerging pollutants (EP). Over the last few decades, the occurrence of OMP in the aquatic environment has become a worldwide issue of increasing environmental concern (Luo et al., 2014). According to the NORMAN network (<http://www.norman-network.net>), at least 700 substances categorized into 20 classes, have been identified in the European aquatic environment (Farré et al., 2008). They encompass a diverse group of compounds, including pharmaceuticals, drugs of

abuse, personal-care products (PCPs), steroids and hormones, surfactants, perfluorinated compounds (PFCs), flame retardants, industrial additives and agents, gasoline additives, nanomaterials, and 1,4-dioxane and swimming pool disinfection by-products (DBPs), as well as their transformation products (TPs) (Farré et al., 2008).

To date, discharge guidelines and standards do not exist for most micropollutants. Some countries or regions have adopted regulations for a small number of micropollutants (Luo et al., 2014). For example, environmental quality standards for a minority of micropollutants (e.g. nonylphenol, bisphenol A, DEHP and diuron) are included in Directive 2008/105/EC (European Parliament and The Council, 2008).

OMP can undergo significant biodegradation and transformation in effluent-impacted surface waters and groundwater. Biodegradation depends on the presence of a community of organisms able to transform the contaminants through metabolic networks and the bioavailability of contaminants, especially in sediments and soil. The natural biodegradation can vary significantly between compounds and has not been specifically studied for many OMP (Geissen et al., 2015). Before further elaborating on fate of OMP, we first describe the type of OMP that are associated with road runoff.

3.1.1 OMP in road runoff

Several tyre components are associated with road runoff (tyre wear) (Wik & Dave, 2009; Wicke et al., 2016; Avagyan et al., 2013):

- Styrene butadiene rubber (SBR), the most commonly used rubber polymer in passenger car tyres;
- Benzothiazoles (benzothiazole and its derivatives) (BTs), used as vulcanisation accelerators, e.g. 24MoBT (2-(4-morpholinyl)benzothiazole), BT (benzothiazole), HOBT (2-hydroxybenzothiazole), and NCBA (N-cyclohexyl-2-benzothiazolamine). Note that the use of the vulcanisation accelerator that contains 24MoBT has declined drastically in the last two decades of the previous century;
- Extractable organic zinc (zinc vulcanisation accelerator complexes).


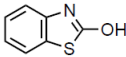
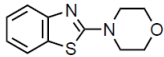
As this study is focussed on pollutants other than metals, the latter (Zn) is considered outside the scope of this study. SBR enters the environment as particles, and is described in the next section (microplastics).

Besides the components associated with road run-off there are some common tyre chemical additives that could be of concern. Common tyre chemical additives are the vulcanization agents 1,3-diphenylguanidine (DPG) and N-cyclohexylbenzothiazole-2-sulfenamide (CBS) and the antioxidant N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenylenediamine (6-PPD) (Unice et al., 2015).

3.1.2 Benzothiazoles

Main aspects determining the environmental fate of OMP are degradation, sorption at the sediment, and transport in the aqueous phase (Geissen et al., 2015). Important properties of main OMP in road run-off (i.e. BT, HOBT and 24MoBT) determining these processes are listed in Table 4 (from Reddy & Quinn, 1997).

Table 4 Chemical and physical properties of BT, HOBT, and 24MoBT at 25 °C in Distilled Water (from Reddy & Quinn, 1997)

	 BT	 HOBT	 24MoBT
CAS Registry No. ^g	95-16-9	934-34-9	4225-26-7
molecular mass	135	151	220
melting point (°C)	2	138	126–127
boiling point (°C)	231	360	NA
solubility in water (mol L ⁻¹)	2.2×10^{-2} ^a	4.6×10^{-3} ^b	$\sim 1 \times 10^{-3}$ ^c
vapor pressure (atm)	1.4×10^{-4} ^d	4.2×10^{-9} ^e	NA
molecular diffusivity in water (cm ² s ⁻¹)	1.0×10^{-5} ^f	9.7×10^{-6} ^f	8.0×10^{-6} ^f
molecular diffusivity in air (cm ² s ⁻¹)	0.095 ^g	0.090 ^g	0.074 ^g
octanol/water partition coefficient	98 ^h	58 ⁱ	420 ^j
organic matter/water partition coefficient [L (kg of om) ⁻¹]	60 ^k	40 ^k	180 ^k
Henry's law constant, K_H	2.6×10^{-4} ^l	3.8×10^{-8} ^l	2.3×10^{-11} ^m
molar absorptivity @ λ_{max} (L mol ⁻¹ cm ⁻¹)	1510 @ 296 nm ⁿ	3020 @ 287 nm ^o	NA ^p

^a Reference 8. ^b Determined in the laboratory as part of this study. ^c Estimated from the plot of K_{ow} versus water solubility of HOBT, 2-(methylthio)benzothiazole, 2-mercaptobenzothiazole, and 2-(thiocyanomethylthio)benzothiazole (from data listed in this table and in ref 8. ^d Estimated using equation 4–18 in ref 28. ^e Estimated using eqs 4–18 and 4–21 in ref 28. ^f Estimated with eq 9–30 in ref 28. ^g Estimated with eq 9–25 in ref 28. ^h Reference 8. ⁱ Reference 29. ^j The average of seven estimates obtained from the following software: ACD/LogP, Advanced Chemistry Development Inc., Toronto, ON; ClogP, Biobyte Corp., Claremont, CA; KOWWIN, Syracuse Research Corporation, Syracuse, NY; PrologP 5.1, CompuDrug Chemistry Ltd., Budapest, Hungary; Softshell Properties, Softshell, Inc., Grand Junction, CO. ^k Estimated using eq 11–24 in ref 28. ^l Estimated by dividing vapor pressure by water solubility and then dividing by RT. ^m Estimated by using Softshell Properties, Softshell, Inc., Grand Junction, CO. ⁿ Reference 30. ^o Reference 31. ^p NA, not available. ^g Supplied by the authors.

Another substance of which properties may be important because it is measured in substantial concentrations is benzothiazole-2-sulfonate (casno. 941-57-1) (Kloepfer et al., 2005).

In conventional waste water treatment plants (WWTP) the removal of BTs is mostly by biodegradation processes. However, in constructed wetlands biodegradation, photo degradation and plant uptake coexist and these have thus a high efficiency in removing BTs from the water phase (Matamoros et al., 2010).

A study on the transformation of BT in estuarine sediments found that BT was transformed more readily on sediments of high surface area under oxidized conditions vs. coarser sediments and those under reducing electrochemical conditions (Matamoros et al., 2010). Mixing was found to be the most significant variable in BT transformation rate, with constant stirring increasing observed degradation appreciably. Unstirred conditions showed greatly reduced BT transformation rates in all sediments, with half-lives on the order of 2200 to >4000 h (unstirred) vs. 640 to 1000 h in the continuously stirred systems (Matamoros et al., 2010).

Volatilisation

The volatilisation half-lives of BT, HOBT, and 24MoBT are 15 days, 235 years, and >1000 years in 1 m of stagnant water at 25 °C with the wind blowing at 10 m above the surface at 1ms⁻¹ (Reddy & Quinn, 1997). However, volatilization may be the important factor controlling the BT/HOBT in the environment. When the half-lives are recalculated at a water depth and speed of water more realistic of urban runoff (0.1 cm and 1 m s⁻¹, respectively), the half-lives become 30 min and 86 days, respectively (Reddy & Quinn, 1997). Pure 24MoBT was not studied but it was expected to be more resistant than BT and HOBT because it is more complex in structure, more hydrophobic (see Table 4) and because it was sometimes detected in water samples from the field, while BT and HOBT were not detected (Reddy & Quinn 1997).

Leaching

Leaching of benzothiazoles from crumbed rubber material was experimentally shown by Reddy and Quinn (Reddy & Quinn, 1997). The leaching of crumbed rubber material was executed by shaking of 4 gram of crumbed rubber material with 100 ML of water at 25 C during 24 hours per event. When crumbed rubber material was leached five consecutive times, approximately 50% of the total amount of these compounds in the material were removed or solubilized (Reddy and Quinn, 1997). This may give an indication of the total amount of benzothiazoles that will become bioavailable in time.

Adsorption

Because the low log Kow of BTs a moderately low retention into the organic matter should be expected (Matamoros et al., 2010). Organic matter / water partition coefficients of BTs are: 60; 40; and 180 L/kg for BT, HOBT, and 24MoBT, respectively (Reddy & Quinn, 1997).

Bioconcentration

A 42 day test for the degree of bioconcentration of BT in fish (*Cyprinus carpio*) showed a BCF (bioconcentration factor) value of 2.1 - 5.1 at a dose of 0.2 mg/l and a BCF value of > 4.1 - 7.5 at a dose of 0.02 mg/l (<https://echa.europa.eu/registration-dossier/-/registered-dossier/13176/5/3/2>).

Biodegradation

An ECHA dossier is available for BT, but not for HOBT or 24MoBT. According to the ECHA dossier (<https://echa.europa.eu/registration-dossier/-/registered-dossier/13176/5/3/2>) BT is readily biodegradable (0 % degradation after 7 days; 0 % degradation after 14 days; 58 % degradation after 21 days; 74 % degradation after 28 days).

Photolysis

Photolysis is probably not important in the environmental fate of BTs. Azizian et al. (2003) studied leachate from a mixture of crumb rubber material (shredded automobile tyres with a similar chemical composition to that of tyre particles) and asphalt and found that photolysis did not affect the BT concentration. BT was readily removed from the leachate by the environmental processes of soil sorption, volatilization, and biodegradation (Azizian et al., 2003). Benzothiazole can thus be considered a volatile and biodegradable compound, but resists the photolysis oxidation process (Azizian et al., 2003). Another study also suggests that direct photolysis of BT (and HOBT) will be a minor fate (Reddy & Quinn, 1997).

3.1.3 Chemical additives

As mentioned above, common tyre chemical additives are the vulcanization agents 1,3-diphenylguanidine (DPG) and N-cyclohexylbenzothiazole-2-sulfenamide (CBS) and the antioxidant N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenylenediamine (6-PPD) (Unice et al., 2015). Some properties of these substances are listed in Table 5. A laboratory study suggests that CBS, DPG and 6-PPD and their transformation products are unlikely to be persistent in the aquatic environment once released from TRWP (Unice et al., 2015).

Table 5 Estimated attenuation, release and availability factors for detected parent compounds and transformation products of CBS, DPG and 6-PPD (Unice et al., 2015).

Parent chemical	Detected chemical	Curing factor (f_c)	Wear factor (f_w)	Terrestrial aging factor - abiotic aging in soil (f_s)		Water release factor (f_l)	Environmental availability factor (f_A)	Fraction released to water (F_R)			Total fraction available (F_T)		
								$F_R = f_c \times f_w \times f_s \times f_l$			$F_T = f_c \times f_w \times f_s \times f_A$		
				0.1 years	0.8 years			0 years	0.1 years	0.8 years	0 years	0.1 years	0.8 years
CBS	CBS	0.0015	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a
	BT	0.025 ^b	1 ^b	0.51	0.13 ^c	0.37	0.37	0.0093	0.0048	0.0012	0.0093	0.0048	0.0012
	BTON	0.014 ^b	1 ^b	0.85	0.70	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a
	BTSO3H	0.039 ^d	1 ^d	0.91	0.73	1 ^d	1 ^d	0.039	0.036	0.029	0.039	0.036	0.029
	CHA	0.056 ^e	1 ^f	0.52	0.64	0.68 ^f	1 ^f	0.038	0.020	0.024	0.056	0.029	0.036
	MeSBT	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a
	MBT	0.0079	1 ^f	0.67	0.67	nc ^a	1 ^f	nc ^a	nc ^a	nc ^a	0.0079	0.0052	0.0052
DPG	MBTS	0.0015	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a
	NCBA	0.0014 ^b	1	0.89	0.50	0.10	0.65	1.4×10^{-4}	1.3×10^{-4}	7.1×10^{-5}	9.3×10^{-4}	8.3×10^{-4}	4.6×10^{-4}
	DPG	0.46	0.48	0.83	0.39	0.15	0.32	0.034	0.028	0.013	0.070	0.058	0.027
	Aniline	0.066 ^d	1 ^f	0.62	0.62	1 ^f	1 ^f	0.066	0.041	0.041	0.066	0.041	0.041
6-PPD	6-PPD	0.55	0.83	1	0.18	0.001	0.12	4.5×10^{-4}	4.5×10^{-4}	8.1×10^{-5}	0.055	0.055	0.010
	DPA	0.0010 ^b	1	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a
	4-ADPA	0.012	0.65	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a
	4-HDPA	0.019 ^b	1	0.43	nc ^a	0.0119	0.067	2.3×10^{-4}	9.7×10^{-5}	nc ^a	0.0013	5.5×10^{-4}	nc ^a
CBS	4-NDPA	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a	nc ^a
	ΣP + T	-	-	-	-	-	-	0.087	0.060	0.054	0.11	0.08	0.071
DPG	ΣP + T	-	-	-	-	-	-	0.10	0.069	0.054	0.14	0.10	0.068
	6-PPD	ΣP + T	-	-	-	-	-	6.8×10^{-4}	5.5×10^{-4}	8.1×10^{-5}	0.056	0.055	0.010

^a "nc" indicates the fraction was not calculated because analyte was not detected in TRWP, leachate and sediment incubators with the exception of MBTS, which was not analyzed in leaching tests or sediment incubators.

^b Amount present in cured tread estimated based on maximum detected concentration in TRWP.

^c The fraction remaining at 0.8 years was estimated based on 1/2 of the detection limit.

^d Amount present in cured tread estimated based on maximum detected mass of analyte leached from TRWP.

^e Amount present in cured tread estimated based on maximum detected mass of analyte in sediment incubator.

^f Calculated based on the maximum concentration measured in fresh TRWP, leached to water, and measured in sediment.

3.2 Microplastics

3.2.1 Tyre wear particles

Wear and tear from tyres significantly contribute to the flow of (micro-)plastics into the environment (Kole et al. 2017). Emissions and pathways depend on local factors like road type or sewage systems. It is estimated that 12% of the tyre and road wear particles (TRWP) ending up in the environment will eventually end up in surface waters (Kole et al., 2017). The relative contribution of tyre wear and tear to the total global amount of plastics ending up in our oceans is estimated to be 5–10% (Kole et al., 2017).

A summary and analyses of the existing knowledge on the occurrence of TRWP in the environment, and their ecotoxicological effects showed that tyre wear particles are present in all environmental compartments, including air, water, soils/sediments, and biota (Wik & Dave, 2009).

In the Seine watershed, France, sediment samples were collected upstream and downstream (or within) the population centers of Troyes, St. Dizier, Paris, and Rouen, with human populations varying from 30,000 persons in St. Dizier to 12 million in the Paris metropolitan area (Unice et al., 2013). The mean and median concentration of TRWP in sediment in the Seine watershed was measured by using pyrolysis GC/MS analysis 4500 µg/g d.w. and 4000 µg/g d.w., respectively. The maximum detected concentration of 11600 µg/g d.w. occurred near the center of the Seine River (depth = 3 m) downstream of the central Paris district and a major local bridge crossing within the larger metropolitan area.

The mean tread polymer concentration was measured in stormwater settling ponds near highways in Sweden using organic zinc as tyre tread marker (Wik et al., 2008). Based on 13 samples from 13 different locations the mean (minimum and maximum) concentration was

1600 (<150 to 9200) µg/g dry weight. TRWP concentration can be calculated as two times tread polymer concentration, based on the assumption that TRWP consists of 1:1 ratio of tread polymer:mineral encrustations (Wik et al., 2008).

Grain size may be an important general determinant of the quantity of TRWP in sediment (Unice et al., 2013). Study results indicated that sediment characterized by higher Total Organic Carbon (TOC) content and finer grain size are likely to contain higher amounts of TRWP as compared to more coarse and lower TOC content sediment (Unice et al., 2013).

3.2.2 Microplastics

TRWP are calculated to be the largest sources of microplastic in the European rivers, and account for 42% of the total exported microplastic load from land to sea (Siegfried et al., 2017).

The occurrence of microplastic in freshwater sediments has been experimentally confirmed (Besseling, 2018). The morphology (size, shape) and density of particles will influence their transport behaviour and fate in the aquatic environment (Kooi et al., 2018). Depending on the density and morphology of the particles, settling can occur. In a river system, this determines the fraction of the total amount of microplastics retained within the river, which thus is not exported at the river mouth. Retention fractions for TRWP (styrene butadiene rubber) were estimated by (Siegfried et al., 2017) to range between 0.75 and 0.9, based on spatially explicit hydrodynamic river model simulations as provided by (Besseling et al., 2017). The size of the modelled particles was 10-400 µm with a density of 1.2-1.3 g/cm³.

The specific gravity of a microplastic influences the floating ability of the particle in water (Besseling et al., 2017). The specific gravity of tyre rubber reported in literature ranges from 1.15 to 1.18 (Kole et al., 2017).

Nanoplastics (NPs) have not yet been measured in aquatic systems but fate model simulations are possible and have been performed (Koelmans et al., 2015).

A modelling study of micro- and nanoplastics in the river Dommel (the Netherlands) showed that the locations of peak concentrations in sediment were mainly related to the emission scenario and spatial properties of the river Dommel, whereas the height of these peak concentrations largely depended on particle size of either plastic or natural particles (Besseling et al., 2017). Small particles (<5 mm) reached their highest concentrations in the sedimentation area further downstream, whereas bigger particles settled earlier upstream (Besseling et al., 2017). A default upstream plastic mass concentration of 1 ng/L was used (Besseling et al., 2017). This concentration represents the average order of magnitude of published concentrations of microplastic in freshwater (Besseling et al., 2017).

Based on model simulations of the fate of different sizes of plastics in a river, it is suggested that the size of tyre dust (reported to range 60-80 µm) may imply substantial retention in freshwater (Besseling et al., 2017). Concentrations of black carbon (an important additive in car tyres) in freshwater sediments indeed have been shown to be high, i.e. median black carbon contents as a fraction of total organic carbon are 9% for sediments (Cornelissen et al. (2005) in (Besseling et al., 2017). However also other sources linked to combustion of fossil and non-fossil fuels have to be considered as sources of black carbon in fresh water sediments.

OSPAR (2017) reports the findings of two studies that have measured the concentration of microplastics in biota: one study measured concentrations in invertebrate species; and one study measured concentrations in fish. Microplastics were monitored in a number of invertebrate species of biota sampled in Lake Veere, Hoek van Holland, IJmuiden and

Amstel canal (OSPAR 2017). Microlitter was detected in most species with filter-feeders containing a significantly higher amount of particles compared to other functional groups. In bivalves the concentration was a thousand-fold higher compared to the surrounding sediment and water. Average concentrations ranged from 5820 to 73600 particles per kg dw. Of the microplastics found in biota, 28% were blue particles, 28% were black particles and 25% were fibres. Blue particles were found in 88% of the samples, black particles in 71% and in 94% of the samples fibres were present. Microplastics were also detected in fish sampled in French rivers (OSPAR 2017).

4 Conclusions

The traffic volume and its composition, type of road pavement, the territory of the road, natural and climatic conditions (amount of rainfall, wind direction and speed), geophysical conditions (relief, vegetation, type of soil, engineering - geological and hydrological conditions which in turn are characterized by the conditions of runoff, water evaporation, snow cover thickness and intensity of spring snow melting, depth of groundwater occurrence and features of their regime, regimes of surrounding rivers and streams) have a direct or indirect impact on the amount and spread of micro pollutants in the roadside environment.

Depending on several road characteristics, either runoff or drift is the most important pathway from roads to the environment. Runoff could be infiltrated in the brink and most pollutants will remain in the soil, except for pollutants with high solubility, which could be transported via groundwater. Runoff could also be treated in storm water treatment systems and the effluent is discharged in surface water. If pollutants are mainly transported by drift, then the storm water treatment system is not very useful. Pollutants will be deposited within a few 100 meters (or closer) from the road and could reach surface water without passing through the storm water treatment system.

A number of other climatic variables, namely the amount of precipitation, snowfall, intensity and wind character, play an important but poorly studied role in the propagation and redistribution of micropollutants. For example, depending on the temperature, the distribution of the air and atmospheric particles of the snow surface or water droplets, the speed of dry or wet precipitation which cause fractionation and precipitation of various compounds of these particles at different heights, is determined (Schmeller et al., 2018).

Treatment systems reduce the amount of pollutants that could potentially reach surface water bodies, but no specific treatment is now available to assure the complete removal of various micropollutants (Luo et al., 2014). After the discharge into the water, micropollutants are subjected to a variety of processes, including dilution and attenuation (biodegradation, sorption, volatilization and photolysis) (Luo et al., 2014). The smaller fraction is expected to be easily transported, while larger particles are kept more efficiently, as they settle in drainage channels and pits (Luo et al., 2014).

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