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MICROPROOF
Micropollutants in Road RunOff

Review of literature on organic micropollutants, microplastics and associated substances in road run-off

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1 Introduction

This report describes the literature review on specific contaminants (organic micropollutants, microplastics and associated substances) in road run-off water. The report has been prepared as part of the CEDR Call 2016 project, “Environmentally Sustainable Roads: Surface- and Groundwater Quality, MICROPROOF, Micropollutants in Road Run-off.

The report gives an overview of the current knowledge on main contaminants and their emission sources (related to traffic and roads) on secondary roads and highways (outside city limits).

Emissions from traffic and roads are very divers and include exhaust emissions, abrasion of tyres, brakes and road surface, leakage of engine oils and diffuse emissions from street furniture. Identification and quantification of the different sources has been subject (and still is) of scientific research. This literature review summarises the current state of play and aims to pinpoint the main pollutants which will be investigated in detail in following work packages of the project.

The assessment of the different emission sources also includes the identification of the possible pollutants from each source. Where possible, the concentrations of the different pollutants in road run-off is described, including any details on the environmental load. Special attention is paid to the so called microplastics. The definition we use in this study for this container concept is: Microplastics contain all plastic particles smaller than 5 mm, insoluble and not or slowly degradable. Microplastics include plastic particles from biogenic origin and rubber particles.

The following paragraphs describe the consecutive steps in the identification of main sources and contaminants in road runoff. A complete list of discussed pollutants is presented in Annex A.

2 Methods of literature research

This report is the result of literature research into peer reviewed literature. In cases / subjects where no scientific research was available (and or not conclusive), grey literature was taken into account.

The main literature search-engine we used, was Scopus (www.scopus.com). A straightforward search protocol was tried initially, but did not deliver any substantial results. For instance, a search on “tyre wear run-off” did result only in 5 hits of which most were rather old (youngest 2011 and eldest 1990) and most references are reporting about metals (which are not subject of this study). Therefore, by necessity, the search process had to be more elaborate (trial and error). Taken the most resent known articles (such as Markiewicz et al., 2017 and Wik and Dave, 2009) we defined new search keywords. Once relevant new substances had been discovered, the search was widened in other search arenas such as ResearchGate (www. researchgate.net) and Google scholar (https://scholar.google.com/). Eventually we found over 200 articles. This report does not cover all these articles. Only those which are directly relevant with respect to the scope of this this work package are elaborated. All articles and other literature are shared with all project partners, to enable usage in other work packages.

3 Sources and chemical speciation

Water is one of the most important transport media for the pollutants which are generated by activities on the road networks. Soil and water are the main receptors of these pollutants. Man, animals and plants are dependent on water of good quality, and legislation typically puts much emphasis on the protection of groundwater and surface water. Given the dense road network and rapidly increasing traffic, protecting the environment, from road and traffic pollutants and securing a good water quality, is an area of increasing concern to road planners and engineers.

Figure 1 schematically depicts the sources and pathways of road related pollutants to the environment.

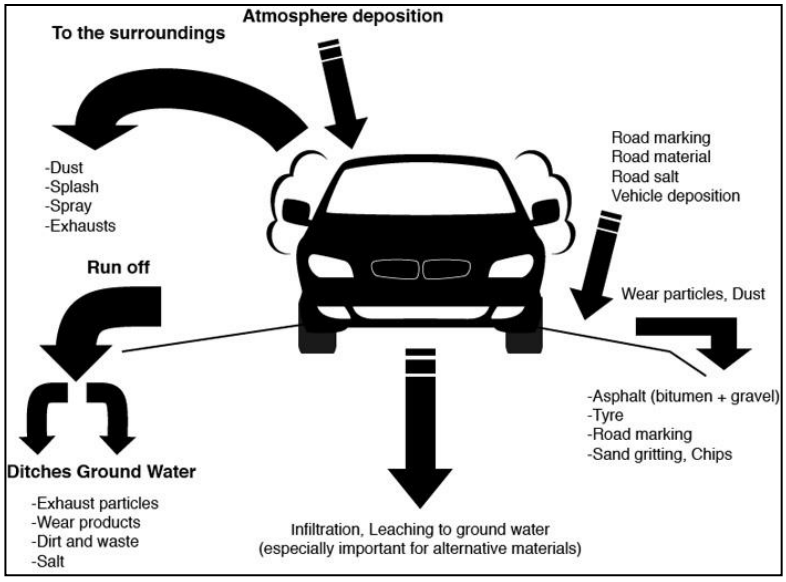

Figure 1 Sources and pathways of road-side pollution (source: Roadex network, Swedish Road Administration)

The following primary sources of organic micropollutants and microplastics to the road are the most relevant:

- Tyres
- Asphalt and concrete
- Brakes
- Brake fluids
- Road markings
- Car coatings
- Corrosion inhibitors
- Automotive coolants
- Fuels, oils and lubricants
- Others

Littering is also a major source microplastics to the environment, but it is no subject in this study.

In principle, all these components will lose mass during use. This implies that all constituting substances can be found in road run-off. Amongst them many substances which theoretically can be harmful to the surrounding road-side ecosystems. Electric vehicles do not cause

exhaust emissions, and emissions from brake lining from electric cars might be lower than emissions from brake lining from regular combustion cars (if the electric vehicle uses regenerative braking). All of the other emissions will also occur from electric vehicles.

To be able to quantify the risk of a certain substance it is necessary to know:

- the actual releases to the environment
- the fate of the substance after release and;
- the potential ultimate exposure of organisms living in receiving surface waters that have to be protected under the Water Framework Directive.

This report describes the analysis of the possible pollutants released by the above-mentioned emission sources.

In the following paragraphs, reported emissions of organic micropollutants and microplastics per source will be summarized. Furthermore, the reported measured data will be listed and interpreted. The number of literature references elaborating the source characteristics of emissions of organic micropollutants and microplastics are rather scarce, compared to the sources detailing the emissions of metals from road activities. This fact will limit the basis for solid conclusions.

3.1 Tyres

3.1.1 Microplastic emissions from tyres

Tyres consist of rubber (natural and synthetic rubber), carbon black, silicium compounds, sulphur, zinc and different types of chemicals. Evans and Evans (2006) showed differences in tyre composition for passenger cars, trucks and off-road. However, all tyres contain rubber, carbon black and other additives. Tyre particles are generated during driving and braking because of friction between the tyre and the road surface. The total tyre particle is considered a microplastic (and not only the rubber content).

Many European countries estimate the microplastic emissions from tyre wear. Worn rubber particles from tyres represent the microplastics. Emissions are calculated from an emission factor multiplied by an activity rate. A variety of emission factors is used in different countries depending on the type of vehicle and driving behaviour (see Table 1). Emission factors are derived from specific measurement of the reduction of mass during the life time of tyres. The general assumption is that the total mass loss (during the life span of a tyre) is released into the environment. Given the distance over which the tyre was used, the emission per km driven can be calculated. The largest (and heaviest) vehicles are responsible for the highest release of tyre particles per kilometre. No differences in wear of winter tyres and summer tyres is reported. Only when winter tyres are used in summer, an elevated level of tyre particle release can be expected. Driving behaviour will also influence the release of tyre wear particles. The reported emission factors in Table 1 are generic values and do not differentiate according to driving behaviour.

Table 1 Emission factors of tyre wear from various literature sources in mg/km.

	Passenger cars	Light commercial	Commercial / trucks	Bus	Motorcycle	Average
GRPE, 2013 [1)]	132	204	712			
Pant and Harrison, 2013						100
Lassen et al., 2015						90-150
Gustafsson, 2001	50			700		
Klein et al., 2017 (rural)	85	102	546	267	39	
Klein et al., 2017 (highway)	104	125	668	326	47	
Sundt, et al., 2014						270
Hillenbrand, et al., 2005	90		700	700	45	
Azarov, et al., 2013	130	320	1500			

1) Emission factors from GRPE (2013) are originally reported as emission factor per wheel. In this table, the emission factors are multiplied by 4.

Another more generic approach is to express the emission per capita. Kole et al. (2017) estimated 0.23 - 4.7 kg tyre particles emitted per capita. The lowest emissions are estimated for India (0.23 kg/capita) and China (0.55 kg/capita), while the highest emission is estimated for the USA (4.7 kg/capita). The difference is mainly caused by the larger number of cars and trucks in the USA and the longer distances they travel per vehicle. For European countries, the emission varies between 0.52 kg/capita (in the Netherlands) and 1.5 kg/capita (in Norway). The low emission in the Netherlands is caused by the use of porous asphalt, in which a part of the tyre wear particles will be trapped (and removed by the periodic cleaning of the road surface). Since this does not influence the emission (but only the pathway to the environment), it is better to exclude this value in the comparison. When excluding the emission from the Netherlands, the emission in European countries varies between 0.81 kg/capita (in Italy) and 1.5 kg/capita (in Norway).

3.1.1.1 Tyre wear particles in road run-off

Tyre particles are expected to be the largest source of microplastics (Sundt et al., 2014; Lassen et al., 2015; Verschoor et al., 2016; Magnussen et al., 2017; Essel et al., 2015). Since rubber particles have not been measured very often, other pollutants could be used as an indicator. Wik and Dave (2009) provided a literature review on rubber concentrations that were measured using different markers (Zinc, Styrene butadiene rubber, Natural rubber, Benzothiazoles, 2-(4-morpholinyl)benzothiazole, 2-hydroxybenzothiazole, N-cyclohexyl-2-benzothiazolamine). In this study, concentrations of tyre wear particles in road run-off varied between 12 mg/l and 179 mg/l, with multiple measurements in the range of 87 mg/l – 97 mg/l.

Measurement data on zinc (as a possible tracer of tyre particles) are reported more frequently. The use of Zinc as tracer is questionable as it is also emitted from safety fences, brakes and zinc gutters (Mangani et al., 2005; Huber et al., 2016; Legret and Pagotto, 1999). For example, Charters et al. (2016) measured zinc concentrations from galvanised roofs that were higher than the zinc concentrations from road run-off. But since rubber particles have not been measured in surface waters, zinc concentrations could be used as a first indicator.

Reported Zinc concentrations in road run-off vary between an average total zinc concentration of 847 µg/l for a busy road in Munich (Helmreich et al., 2010), 400 µg/l on a highway in Italy (average value for dissolved and undissolved zinc together from Mangani et al., 2005) and 356 µg/l on a motorway in Nantes France (Legret and Pagotto, 1999).

It was noted that concentrations of metals in road run-off were higher during the cold season compared to the summer period (Helmreich et al., 2010, Magani et al., 2005, Legret and Pagotto, 1999).

Passenger car tyres consist for approximately 1% of zinc oxide (Milani et al., 2004; Lassen et al., 2015). Combining the average zinc concentration from the above-mentioned studies with a zinc oxide content of 1% in tyres, this results in a tyre wear concentration of 36-85 mg/l in road run-off. Since the above-mentioned concentrations partly consist of zinc from other sources, the actual tyre wear concentrations are expected to be lower.

In soils at European roadsides, highest zinc concentrations were measured in the top soil layer at the first 5 meter beside the road (Werkenthin et al., 2014). Also, Radziemska et al. (2015) concluded that average zinc concentration in the soil was highest close to the road. At 25-meter distance, the zinc content was reduced with 96% compare to the level close to the road (Radziemska et al., 2015). This distance dependency is expected to be valid for tyre particles.

Abassi et al. (2017) investigated microplastics and microrubber in street dust samples in Iran with average concentrations of 210-1658 microplastic particles per 10 grams dust and 44-782 microrubber particles per 10 grams dust.

3.1.1.2 Tyre wear particles in surface waters

Microplastic concentrations in surface waters are reported in many studies (Leslie et al. (2017), Lechner et al. (2014), Faure et al. (2015)). However, most of these studies do not contain data specific for microplastics from tyre wear and microplastic from road markings.
Only a few studies indicate that the measured microplastic concentrations are linked to tyre wear:

- Wik and Dave (2009) reported on three studies (Reddy and Quinn, 1997; Kumata et al., 2000; Ni et al., 2008) that measured tyre wear particles in river water with concentrations varying between 0.5 mg/l and 3.6 mg/l.
- Norén and Naustvoll (2010) reported the presence of a large number of black particles (median: 41 particles per litre) in Norwegian waters (Skagerrak) which could be rubber particles or road wear particles.

In paragraph 3.1.1.1, tyre wear concentration was estimated using the zinc concentration as a proxy for tyre particles. For concentrations in receiving waters, this will not be possible, because these waters are influenced by many other sources than traffic. For example, Fronczyk (2016) indicated that differences in measured zinc concentration in the road drainage system around Warsaw were caused by differences in traffic intensity and influences from other locations (e.g. a nearby parking lot).

Transport of microplastics to surface water and sea and the fate of microplastics are modelled in several studies (Siegfried et al., 2017; Besseling et al., 2017). Siegfried et al. (2017) concluded that 42% of the modelled microplastics exported by rivers to the sea are synthetic polymers from tyre and road wear particles (TRWP). This study only considered microplastics released via effluents of centralized sewage systems.

Besseling et al. (2017) modelled the fate of microplastics in freshwater systems. It was discussed that a substantial retention of tyre dust in freshwater may occur due to the size of the tyre dust particles.

3.1.2 Organic substances other than PAH in tyres

In this subparagraph a distinction will be made between total loss of tread (the part of the tyre which is in contact with the road surface) from tyres and the tread formulation that gives an indication of substances lost to the environment.
Most literature references on tyre wear mainly discusses the airborne tyre particulates, which is only a very small fraction of total tyre wear. Only a few literature sources were found about organic micropollutants that are contained in tyre treads (Unice et al., 2015; Baumann and Ismeier, 1998; Wik, 2007). Table 2 shows the organic substances contained in tyres, tyre tread and in Tyre and Road Wear Particles (TRWP).

Table 2 Organic substances contained in tyres and rubber tread (mg/kg)

Chemical	Short name	Function	Cas-no	Tyre formulation		Uncured rubber tread	Cured rubber tread	Fresh TRWP
				(1)	(2)	(3)	(3)	(4)
N-Cyclohexyl-2-benzothiazole	CBS	Vulcani-zation accelerator	95-33-0	2600	5000	1400	2.1	<1
N-tert-Butyl-2-benzothiazolesulfenamide	TBBS		95-31-8	1100				
2,2'-Dithiobis(benzothiazole) (R)	MBTS		120-78-5	900			2.1	<1
1,3-Diphenylguanidine	DPG		102-06-7		5000	1400	650	310
Benzothiazole (R)	BT		95-16-9				<10	35
2-Mercaptobenzothiazole (R)	MBT		149-30-4				9.4	7.5
2-Methylbenzothiazole (R)	MeBT		120-75-2				na	
Cyclohexylamine (R)	CHA		108-91-8				69	33
2-Methylthiobenzothiazole (R)	MeSBT		615-22-5				<3	<4
2-Benzothiazolesulfonic acid (R)	BTSO3H		21465-51-0				na	
2-Benzothiazolone (R)	BTON		934-34-9				5.2	20
N-cyclohexyl-1,3-benzothiazol-2-amine (R)	NCBA		28291-75-0				-	2
Aniline (R)			62-53-3				11	2
Diphenylurea (R)			102-07-8				na	
N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenylenediamine	6-PPD	Antioxi-dants	793-24-8	5700	8000	2200	1200	1000
N-Isopropyl-N'-phenyl-1,4-phenylenediamine	IPPD		101-72-2	800				
Nμ-(p-Phenylene)ditoluidine	DTPD		620-91-7	200				
(1,4-dimethylpentyl) phenylenediamine	77PD		3081-14-9	300				
Poly(1,2-dihydro-2,2,4-trimethylquinoline)	TMQ		26780-96-1	1600				
Wax					7000			
4-Aminodiphenylamine (R)	4-ADPA		101-54-2				26	17
4-Nitrosodiphenylamine (R)	4-sDPA		156-10-5				na	
4-Nitrodiphenylamine (R)	4-NDPA		836-30-6				na	na
Diphenylamine (R)	DPA		122-39-4				1	2.1
4-Hydroxydiphenylamine (R)	4-HDPA		122-37-2				<5	42
N-butylaniline (R)			1126-78-9				na	
N-phenylformamide (R)			103-70-8				na	
Bis(triethoxysilylpropyl) tetrasulfide (R)	SI69	Coupling agent	40372-72-3		15000			
Sulphur	S	Cross linking agent	7704-34-9	7000	6000			
Stearic acid	SAD	Accelerator activator	57-11-4	7500	6000			
Zinc oxide	ZnO		1314-13-2	21500	6000			

(R) indicates possible reaction product of concern
Data from: (1) Baumann and Ismeier (1998), table 9.31; (2) Unice et al. (2015), table 1; (3) Unice et al. (2015), table 2; (4) Unice et al. (2015), table S6.

The release of these substances to the environment is only partial because some of the tyre tread ingredients, especially the vulcanization accelerators, will react to other products during the vulcanization process. Baumann and Ismeier (1998) were certainly aware of this phenomenon and report a number of reaction products that could be of environmental concern. The study presents the results of several measurements concerning leaching experiments with fresh tyre wear materials that were produced with a belt grinding machine using new and used tyres of both passenger cars and truck tyres. Also, uncured rubber tread mixtures were leached. Various types of grinding belts were used in order to produce wear particles with different particle size spectra. The leaching experiments were executed both with distilled water and artificial “acid rain” being distilled water maintained at pH=4 by means of Nitric acid. The relevant results are summarised in Table 3.

Table 3 Measured concentrations in leachate of artificial tyre wear materials in distilled water and in artificial acid rain. Several measurements were below the detection limit. Data from Baumann and Ismeier, 1998 (Tables 9.34 and 9.35).

Chemical	Short name	Cas-no	Distilled water		“Acid rain” (pH=4)	
			Average (SD) (µg/L) [1]	Detection limit (µg/L) # below DL [2]	Average (SD) (µg/L) [1]	Detection limit (µg/L) # below DL [2]
Mercaptobenzothiazol	MBT	149-30-4	414 (334)	0.5 (9/14)	144 (181)	0.5 (5/11)
Benzothiazol	BT	95-16-9	550 (357)		402 (336)	
Methylbenzothiazol	MeBT	120-75-2	254	2 (13/14)	83	2 (12/13)
2-Methylthio benzothiazole	MeSBT	615-22-5	87 (72)		37 (28)	
N-Isopropyl-N'-phenyl-1,4-phenylenediamine	IPPD	101-72-2	33 (10)	15 (5/13)	94 (63)	15 (5/13)
N-(1,3-dimethylbutyl)-N’-phenyl-1,4-phenylenediamine	6PPD	793-24-8	40 (29)	10 (5/14)	1685 (3147)	10 (3/12)
N,N'-ditolyl- and N,N'-diphenyl-p-phenylenediamine	DPPD/ DTPD	74-31-7 / 620-91-7		80 (14/14)		80 (13/13)
Aniline		62-53-3	14 (14)		13 (14)	
Dicyclohexylamine	DCHA	101-83-7	134 (173)		185 (218)	
Cyclohexylamine	CHA	108-91-8	543 (877)	1 (4/14)	434 (1017)	1 (4/13)

1) This column shows the average concentration. The standard deviation (SD) is shown in brackets.
2) This column shows the detection limit (DL) concentration. The number of samples below the detection limit compared to the total number of samples in shown in brackets.

The results of these experiments show that organic substances in measurable quantities are leached with water from in laboratory produced tyre wear materials (see Table 4). Also MBT, IPPD, 6PPD, DPPD/DTPD and CHA were included in the leaching study reported by Baumann and Ismeier (1998), but measurements of these pollutants were below the detection limit.

Table 4 Measured concentrations in road run-off at the start or during a rain event (W1-W7), a rain reservoir (W8) and road-side snow samples which were sampled 14 days after a snow event (W9-W11). Data from Baumann and Ismeier, 1998 (Tables 9.38, 9.39, 9.40, 9.41).

	Chemical	**Benzothiazol (µg/L)**	**2-Methylthio benzothiazole (µg/L)**	**Methyl Benzothiazole (µg/L)**	**Aniline (µg/L)**	**Dicyclohexylamine (µg/L)**
		BT	MeSBT	MeBT		DCHA
	Casno	95-16-9	615-22-5	120-75-2	62-53-3	101-83-7
Sample number	Time after start rain					
W1	At start	< 2	< 2	< 2	< 8	
W2	After 15 min	< 2	< 2	< 2	< 8	
W3	After 30 min	< 2	< 2	< 2	< 8	
W4	At start	5.68	4.34	< 2	< 2	< 35
W5	After 30 min	6.37	7.90	< 2	< 2	< 35
W6	At start	7.7	2.57	< 2	< 2	< 35
W7	After 30 min	11.8	5.13	< 2	< 2	< 35
W8	Rain reservoir	5.17	2.69	< 2	< 2	< 35
W9	Snow after 14 days	71.2	15.9	14.2	33.9	53.6
W10	Snow after 14 days	9.9	< 2	<2	4.01	43.5
W11	Snow after 14 days	34.9	< 2	8.7	19.9	50.2

The results of these measurements show that some substances that were found in the tyre wear leachate in the laboratory also could be found back in run-off and snow samples that were collected near a busy road. The results of W4/W5 and W6/W7 indicate that during a rain event the concentrations of substances become higher over time. The higher concentrations in snow samples, compared to run-off samples, can be an indication that, most probably, a substantial part of the substances is bound to (organic) particles which are accumulated in the snow.

Benzothiazoles were also detected in several other studies (Grung et al., 2017; Seitz and Winzenbacher, 2017; Kloepfer et al., 2005; Reddy and Quinn, 1997). Benzothiazoles also were detected in run-off water from roads in rather low concentrations, taken from effluents of purification basins and overflow basins. Seitz and Winzenbacher (2017) measured concentrations in run-off water from roads: 2-Hydroxybenzothiazole (0.17 µg/L), 2-(methylthio)-benzothiazole (0.11 µg/L), 2-Mercaptobenzothiazole (0.11 µg/L).

Highest concentrations in direct street run-off water were found by Kloepfer et al., 2005. In the first flush a benzothiazole concentration of 74 µg/L was found (for BTSA, OHBT, BT, MTBT and MBT together). The dominant component was benzothiazole-2-sulfonate (Casno. 941-57-1) (60%), followed by 2-hydroxybenzothiazole (Casno. 934-34-9) (25-30%) and benzothiazole (Casno. 95-16-8) (8-13%). The fluxes of benzothiazoles from the study area into surface water during the rainfall event that was monitored in this study were 152 $\mu g/m^2$ for benzothiazole-2-sulfonate, 54 $\mu g/m^2$ for 2-hydroxybenzothiazole, and 15 $\mu g/m^2$ for benzothiazole. These findings indicate that emissions of these substances (related to tyre

wear) may have some implications for the quality of surface waters. Within the broad spectrum of benzothiazoles the exact choice of substances to be measured is important.

Reddy and Quinn (1997) measured benzothiazoles in leachate of crumb rubber material which is used in CRM modified asphalt (CMA). The leach test consisted of 5 times 24 hours of leaching with water followed by centrifuging the leachate (water). Total amount of substances in the leachate from the rubber material amounted to 100 mg/kg Benzothiazole (Casno 95-16-9), 36 mg/kg 2-Hydroxybenzothiazole (Casno 934-34-9) and 2 mg/kg 2-Morpholinobenzothiazole (Casno 4225-26-7). These results were substantially higher than the results of Baumann and Ismeier (1998), indicating that the method of extraction is extremely important.
Reddy and Quinn (1997) also measured benzothiazole concentrations in urban run-off, in water and sediment of settling ponds, in urban particulate matter and in road dust. Results are shown in Table 5.

Table 5 Measured concentrations in environmental media (Reddy and Quinn, 1997, figure 1 and table 2)

Environmental medium	**BT** **Benzothiazole** **Casno 95-16-9**	**OHBT** **Hydroxybenzothiazole** **Casno 934-34-9**	**24MoBT** **2-Morpholinobenzothiazole** **Casno 4225-26-7**
Leaching from CRM in 5 x 24h (mg/kg)	100	36	20
Urban run-off (ng/L)	378-1210 (D*) 46.6-152 (P*)	721-6910 (D) 60-114 (P)	198-278(D) <10 (P)
Highway settling pond water (ng/L), n=7	<50 (D)	50-516 (D)	5-13.5 (D)
Highway settling pond sediment (µg/kg)	<20	<20	1.16 – 1.31
Urban particulate matter (µg/kg)	393-813	696-893	63.2-107
Road dust highway (µg/kg)	149	90.2	1.68
Road dust residential (µg/kg)	78.7	24.6	2.45

CRM = Crumb Rubber Material, D = dissolved, P = particle bound

It can be seen in Table 5 that far most of the benzothiazoles are dissolved in water and that only a small part is bound to particles. This has consequences for the environmental distribution.

Comparison of the results of the above-mentioned studies is hampered, as different substances are measured in the studies. The common component in all studies is Benzothiazole. The concentrations of Benzothiazole in highway run-off measured by Baumann and Ismeier (1998) of 5.7-11.8 µg/l are somewhat higher than the concentrations measured by Kloepfer et al. (2005) of 1-5 µg/l and Reddy and Quinn (1997) of 0.4-1.2 µg/l.

3.1.3 PAH in tyres

A review of Polycyclic Aromatic Hydrocarbons (PAH)-content in tyres was provided by ten Broeke et al. (2007). See Table 6 for PAH content as presented in various literature references. Grung et al. (2017) concluded that most of the 50 identified PACs (Polycyclic Aromatic Compounds) in road tunnel particulate matter are not regularly monitored.

Table 6 Measured contents of PAH in various tyre tread (mg/kg)

PAH-component	Directive 2005/69/ EC	PC	HD	PC 13% HA-oil	PC	HD	PC	PC
		Nilsson et al., 2005		KEMI, 2003 BLIC, 2002	Baumann and Ismeier, 1997		Edeskär, 2004	Källqvist, 2005
Fluoranthene		9.4	15.4	1.4	7.4	3.8	4.3	7.5
Pyrene		24.2	33.2	3.3	14.0	3.5	17.0	23.5
Benzo(a)fluorene				0.1				
Benzo(a)anthracene	X	0.8	0.9	4.4	1.0	0.7	8.5	1.3
Chrysene	X	5.5	5.3	51.3	7.0	2.3	6.0	2.2
Benzo(b+j+k)fluoranthene	X	1.8	2.1	4.2	3.8	1.9	5.8	3.0
Benzo(b)fluoranthene	X	6.4	6.4	9.5	6.4	6.4	3.3	2.4
Benzo(e)pyrene	X	5.5	5.9	14.7				
Benzo(a)pyrene	X	1.3	2.6	1.7	3.0	0.4	3.0	2.1
DiBenzo(a,j)anthracene				0.6				
DiBenzo(a,h)anthracene	X	1.2	0.8	0.7	0.1	0.2	0.5	1.1
Indeno(1,2,3-c,d)pyrene		2.3	1.0	0.8	0.1	0.4	0.2	0.8
Benzo(ghi)perylene		12.9	7.3	2.3	0.5	2.4	6.0	3.6
Antanthrene				0.9				
Naphtalene		1.6	4.5	1.6	2.7	4.5	0.6	0.4
Acenaphtene					0.1	1.0	0.3	0.2
Acenaphtylene					0.4	0.3	5.6	0.6
Fluorene					0.1	4.4	0.2	0.4
Phenanthrene		4.3	2.3	4.3	4.2	2.3	4.3	5.5
Anthracene		0.8	0.1	0.8	0.7	0.1	0.8	2.0

PC = Passenger cars, HD = Heavy Duty vehicles (Trucks and Lorries)

It has to be noted that concentrations of PAH were measured in tyres before EU-regulation (Directive 2005/69/EC) became into force by 1-1-2010. The average concentrations could have been lowered by about a factor 10 according to ten Broeke et al. (2007).

According to Directive 2005/69/EC it is prohibited to place on the market, tyres (and treads for rethreading), containing extender oils, exceeding the limits of 1 ppm for benzo(a)pyrene and/or 10 ppm total of the 8 following polycyclic aromatic hydrocarbons (PAHs):
- Benzo(a)pyrene
- Benzo(e)pyrene
- Benzo(a)anthracene
- Chrysene
- Benzo(b)fluoranthene
- Benzo(j)fluoranthene
- Benzo(k)fluoranthene
- Dibenzo(a,h)anthracene.

In principle low-PAH extender oils are available and could lower the PAH-concentration with 98% (Null, 1999). A number of authors (Favraux, 2013 and Pan et al., 2016) however are in doubt whether the effect of the Directive 2005/69/EC is completely as was expected before because non-dedicated analytical methods for PAH-concentrations (e.g. ISO 21461) cannot assess that the above-mentioned target values for individual PAH in tyres will be met in practice. Table 7 shows the PAH-content of 50 tyres that were bought in San Antonia (TX, USA) and were produced after 2010.

Table 7 PAH-content of tyres produced after 1 January 2010 (Elaborated results of Pan et al., 2016)

Parameter	Unit	All tyres	Tyres Bay-H% > 0.35 %	Tyres Bay-H% <= 0.35 %	Tyres BaP < 1 ppm and 8-PAH < 10 ppm
Number of tyres		50	9	41	6
Bay-H [1)] (%)	avg	0.23	0.62	0.14	0.14
	sd	0.20	0.13	0.07	0.03
Benzo(a)pyrene (BaP) (ppm)	avg	11	22	9	0.8
	sd	12	10	11	0.2
8-PAH[2)] (ppm)	avg	58	194	28	3.4
	sd	88	121	34	0.9

1) Bay-H% indicates the percentages of bay region hydrogens in a sample solution. This is used as a measure for the amount of aromatic hydrocarbons in the sample.
2) 8-PAH includes the PAH mentioned in Directive 2005/69/EC: Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(j)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Benzo(e)pyrene, Dibenzo(a,h)anthracene.

It can be seen in Table 7 that 41 of 50 tyres did comply to Directive 2005/69/EC applying ISO 21461 criterion Bay-H% <= 0.35. However, of these 41 tyres, only 6 tyres in reality complied with the criteria of Directive 2005/69/EC (BAP < 1 ppm and 8-PAH < 10 ppm). From these results it can be concluded that the real reduction, as a consequence of Directive 2005/69/EC, is much lower than could be expected, because an indirect analytical method is accepted as a means of compliance check. Instead of 98% reduction (1 - 3.4 / 194 = 0.98) of 8-PAH-emission, the real reduction might be somewhere between 70% (1 - 28 / 194 = 0.7) and 85% (1 – 58 / 194 = 0.85).

A check by ETRMA (ETRMA, 2012) revealed that 10% of the tyres did not meet the limit values set by Directive 2005/69/EC applying ISO 21461 criterium Bay-H% > 0.35 %. These were almost entirely imported tyres.

The total PAH-load of traffic areas in Germany by the MONERIS-model (Fuchs et al., 2010) was estimated 11.9 g/ha/yr. Of this load 5.1 g/ha/yr was attributed to abrasion (mostly tyre wear). After 2012 according to Fuchs et al. (2010), by the effect of Directive 2005/69/EC the contribution of abrasion could have been lowered to a load 0.4 g/ha.yr. Regarding the results presented in Table 7, it was concluded that a PAH reduction of 98% was probably not retrieved, and it would more likely be a reduction of 70%-85%. This would mean that PAH load from abrasion of 1 g/ha.yr might be a more realistic value.

3.2 Asphalt and concrete

In literature, no emissions from microplastics and organic micropollutants from concrete road surfaces have been reported. This chapter will therefore focus on emissions from asphalt.

3.2.1 Microplastic emissions from asphalt

To improve the qualities of asphalt, polymers are added to asphalt (more specific to bitumen). According to Robinson (2005), different types of polymers that are added to bitumen are:

- Elastomers (synthetic polymer rubber polymers like styrene-butadiene-styrene (SBS), styrene-butadiene-rubber (SBR), styrene-ethylene-butadiene-styrene (SEBS), polybutadiene rubber (PB))
- Plastomers (Ethylene-ethyl-acetate (EVA))
- Natural rubber

Magnussen et al. (2017) made an estimation of the microplastic emission from asphalt in Sweden. Magnussen et al. (2017) describes that asphalt consist for 5-6% of bitumen. About 5% of the bitumen is mixed with 5% polymers. This results in a polymer concentration in the asphalt of 5.5% * 5% * 5% = 0.014%. It is estimated that 110 kton of asphalt is abraded per year in Sweden (Gustafsson, 2001). Compared to the yearly Swedish use of asphalt of 5000-7000 kton, this implies that yearly 1.8% of the applied asphalt is abraded.
This results in a microplastic emission factor of 0.014% * 1.8% = 0.00025% (2.5 kg microplastic per kton applied asphalt). Studded tyres increase the wear of asphalt (Gustafsson and Eriksson, 2015).

In Sundt et al. (2014), it is indicated that polymers (Styrene Butadiene (SBR) and Styrene Ethylene Butylene Styrene Copolymer (SEBS)) are added to some bitumen in order to improve the properties of asphalt. The use is limited, because it is rather expensive. Exact figures are not known in Norway.

The emissions of microplastics from asphalt are expected to be relatively small, compared to microplastic emissions from tyres. Nevertheless, Norén and Naustvoll (2010) reported the presence of a large number of black particles (median: 41 particles per litre) in Norwegian waters (Skagerrak) which could be rubber particles or road wear particles.

3.2.2 PAH in asphalt

Markiewicz et al. (2017) indicated that potential emitted substances from bitumen/asphalt include phthalates, alkylphenols and alkylphenol ethoxylates, polycyclic aromatic hydrocarbons, amides, amines, bisphenol-A and antioxidants. Wess et al. (2004) described several studies that measured PAH leaching from asphalt. In these studies, the PAH concentrations were either below the detection limit, or below drinking-water limits.

Coal tar-based asphalt contains more PAH than bitumen-based asphalt. In most EU-countries the application and reuse of coal tar containing asphalt mixes has been prohibited and abandoned. Total PAH-content of coal tar containing asphalt varied between 0.7 g 10-PAH/kg asphalt (Rood et al., 1995), 1.5 gram 10-PAH/kg asphalt (Denier van der Gon, 2008) and 3.8 mg 16-PAH/kg road dust (Rogge et al., 1993), while the highest detected 16-PAH content in Sweden was over 5 gram 16-PAH/kg asphalt (Andersson-Sköld et al.,2007, Sweden).
Concentrations of individual PAHs in bitumen have been measured by Brandt and de Groot (2001) and are presented in Table 8.

Table 8 PAH-content of bitumen (from Brandt and de Groot, 2001)

PAH	Sample A (mg/kg)	Sample E (mg/kg)	Sample G (mg/kg)
Naphthalene	2.7	3	2.5
Acenaphthene	0.2	0.7	Below DL
Fluorene	0.3	0.4	0.4
Phenanthrene	1.8	2	1.1
Anthracene	0.2	0.2	0.1
Fluoranthene	0.9	0.8	0.3
Pyrene	0.9	1	0.3
Benzo(a)anthracene	0.7	0.2	Below DL
Chrysene	2.4	1	0.5
Benzo(b)fluoranthene	1	0.7	0.4
Benzo(k)fluoranthene	0.4	0.3	Below DL
Benzo(a)pyrene	0.7	0.5	Below DL
Dibenz(a,h)anthracene	0.5	0.3	Below DL
Benzo(g,h,i)perylene	2	2	0.8
Indeno(1,2,3-c,d)pyrene	0.5	0.2	Below DL

Below DL = Below detection limit

The wear of PAH from coal tar containing road in the Netherlands was estimated by Denier van der Gon, 2008 between 2919 kg/yr (1990) and 1724 kg/yr (2006) and 0 kg in 2015. When applying a total area of about 100,000 ha of asphalt paved area in the Netherlands, 20-30 grams/ha.yr of 10-PAH could have been released between 1990 and 2006. It was estimated by Denier van der Gon, 2008 that about 10% of the total wear directly could be transported to surface waters. This would have resulted in total emissions of 2-3 g 10-PAH/ha.yr. As a consequence, the total contribution of the asphalt-component would have been about half of the wear component as indicated by Fuchs et al. (2010), who calculated 5.1 g 16-PAH/ha/yr.

3.3 Brakes

Brakes contain a variety of components that are subject to wear when braking. Kole et al. (2017) describes the content of the brake pads and counterparts:

- Brake pads
  - binders (phenol-formaldehyde resins)
  - fibres (copper, steel, brass, potassium titanate, glass, organic material and Kevlar)
  - fillers (barium and antimony sulphate, magnesium and chromium oxides, silicates, ground slag, stone and metal powders),
  - lubricants (graphite, ground rubber, metallic particles, carbon black, cashew nut dust and antimony trisulphide)
  - abrasives (aluminium oxide, iron oxides, quartz and zircon).
- Counterparts:
  - cast iron and sometimes composites

3.3.1 Microplastic emissions from brakes

There is no literature on actual measurements of emissions of microplastics from brakes. Kole et al. (2017) estimated that microplastic emissions from brake wear is about 8% of the microplastic emission from tyre wear, because the PM10 emission factor of brake wear is approximately 3-8 mg PM10/km (Grigoratos, et al., 2015), while the emission factor of tyre wear is approximately 132 mg PM10/km (GRPE, 2013).

3.3.2 Organic micropollutant emissions from brakes

Markiewicz et al. (2017) indicated that potential emitted substances from brake linings include polycyclic aromatic hydrocarbons, oxygenated PAHs, polyglycol ethers, benzaldehydes, benzoic acids, oleic acids and n-alkanoic acids. Rogge et al. (1993) provided a comprehensive list of organic compounds. Brake lining particles contain 530 mg n-alkanoic acids per kg brake lining particles, 879 mg polyalkylene glycol ethers per kg brake lining particles, and many other substances with a lower percentage (Rogge et al., 1993). The 16-PAH content of brake lining was measured at 16 mg/kg brake lining (Rogge et al., 1993).

3.4 Brake fluids

3.4.1 Organic micropollutant emissions from brake fluids

Brake fluids are used to build up pressure in the brake cylinders to push brake pads onto the brake disks. Brake fluids consist of solvent (60-90 % polyglycolethers), lubricant basis (5-30 % polyglycols) and additives (2-5% corrosion inhibitors and antioxidants)[1].

Polyglycols are used as lubricants in proportion of up to 30% in brake fluids. Polyglycols have a high viscosity, and therefore, it is necessary to dilute them with a product with low viscosity (polyglycol ethers). Corrosion inhibitors are added to protect the brake system metals from corrosion, and antioxidants are needed to reduce the oxidative decomposition of the organic constituents and to retard the formation of acidic decomposition products and resins. An example composition of brake fluid is presented in Table 9.

[1] Source: https://www.lubricants.total.com/brake-fluid-composition

Table 9 Brake fluid examples of composition for 3 example brake fluids and a comparative example, as presented in US Patent 6339050 B1 regarding brake fluid composition for an automobile (%m/m)

			Examples in US Patent 6339050 B1			
Function	**Substance**	**Casno**	**1**	**2**	**3**	**Compara-tive**
Base fluid	Polyethylene glycol monomethyl ether	9004-74-4	-	-	-	20
	Triethylene glycol monoethyl ether	112-50-5	23	20	22	15
	Polyalkylene glycol		6.8	2	7.8	8
	Polyethylene monobutyl ether	9004-77-7	21	22	20	20
	Polyethylenepropylene glycol monomethyl ether		28	24	22	
	Boric-acid-ester		19	23	25	36
Corrosion inhibitors	Tributyl phosphate	126-73-8	0.6	0.2	0.8	-
	Benzotriazole	95-14-7	0.2	0.2	0.2	0.25
	Tolyltriazole	29385-43-1	-	-	-	0.1
	Triethanol amine	102-71-6	0.3	0.4	0.5	-
	Cyclohexyl amine	108-91-8	-	-	-	0.25
	Dibutyl amine	111-92-2	-	-	-	0.2
Antioxidant	Dibutylhydroxy toluene	128-37-0	0.3	0.45	0.55	-
	Bisphenol A	80-05-7	-	-	-	0.2
Total			99.2	92.25	98.85	90

Table 9 shows that corrosion inhibitors and antioxidants in brake fluid contain several compounds of high environmental relevance (triazoles and bisphenol A). Table 9 provides only an example composition. Other compositions are possible, and their constituents can potentially find their way to the environment from leakages of the brake system. The probability of such leakages is low as the level of brake fluid in cars is monitored in modern cars. The quantity of emissions of brake fluids is not known at this moment.

3.5 Road marking

3.5.1 Microplastic emissions from road marking

Different types of road marking exist: road paint, thermoplastic marking, preformed thermoplastic, preformed polymer tape and epoxy resins. Part of the road paints and thermoplastic markings consist of polymers and therefore the wear products are considered a microplastic when released. When resin/polymers from natural/biogenic origin are used, the released wear particles are also considered a microplastic, because it has the same properties as microplastic with non-biogenic resin components.
The durability of the different road markings differs and the wear depends on the traffic intensity, climate and road maintenance conditions (e.g. effect of snowploughs on the different types of road marking). Therefore, the type of road marking differs per country in Europe.

A few countries made an estimation of microplastic emissions from road markings.
Lassen et al. (2015) estimated microplastic emissions from road marking in Denmark. In Denmark, mainly thermoplastic markings are used. These markings consist of plastic

polymer (0.5-2%), resin (10-15%), fillers (50%), glass beads (30%) and titanium dioxide (5-10%). It is assumed that the microplastic particles consist of the plastic polymer, resin and titanium dioxide, which make up 15-27% of the thermoplastic road marking (Lassen et al., 2015). In Lassen et al. (2015), it is assumed that 15-43% of the applied road marking is emitted. Combined with the percentage microplastics in thermoplastic marking of 15-27%, this results in an emission factor of 2-12% of the applied amount of thermoplastic marking.

Sundt et al. (2014) estimated microplastic emission from road marking in Norway. In Norway, both thermoplastic marking and road paint are used. The study assumed that the annual consumption of polymers road paint reflects the annual abrasion. Only the polymers are considered a microplastic in this study, which is 1-5% of the thermoplastic material. Based on the data from Sundt et al. (2014), Kole et al. (2017) estimated a microplastic emission from wear of road marking of about 5% of the microplastic emission from tyre wear. This figure is based on the estimated amount of road marking wear in Norway (320 ton/year) and the estimated tyre wear of 7040 ton/year (Sundt et al., 2014).

Magnussen et al. (2017) estimated microplastic emissions from road marking in Sweden. In Sweden, both road paint and thermoplastic markers are used. The emission is calculated based on the same assumptions as the Norwegian study on microplastics (Sundt et al., 2014), scaled to the road length.

Concentrations of road marking particles in run-off have not been measured in many studies. Horton et al. (2017) measured concentrations of microplastics in tributaries of the river Thames. At one of the sites, a large concentration of thermoplastic road marking was observed.

3.5.2 Organic micropollutant emissions from road marking

Markiewicz et al. (2017) indicated that potential emitted substances from road paints include phthalates, alkylphenols and alkylphenol ethoxylates, bisphenol A and alkyd resin. Emissions of these pollutants from road markings have not been quantified.

3.6 Car coatings

3.6.1 Microplastic emissions from car coating

Car coatings consist of (polyurethane or acrylic) lacquers, plasticizers and pigments that can wear down and then released as a microplastic to the environment. So far, no estimates of microplastic emission from this source have been reported. It can be expected that this emission source will be much lower than the microplastic emission from tyres.

3.6.2 Organic micropollutant emissions from car coatings

Markiewicz et al. (2017) indicated that potential emitted substances from undercoating and paint/lacquer of vehicles include phthalates, polycyclic aromatic hydrocarbons and alkylphenols and alkylphenol ethoxylates.

Except plasticizers and fire retardants, also some monomers of lacquers might be of importance with respect of water quality. One substance (Hexa(methoxymethyl)melamine (HMMM), Casno 3089-11-0) has drawn special attention because it has been measured in several German rivers in substantial amounts. The compound occurred in 60 of 117 water samples from three river systems, with concentrations ranging between 10 and 880 ng/L. It was expected that HMMM would not be released to the environment, because HMMM is incorporated in synthesized products. Next to industrial point sources the compound is

probably released by leaching of car coatings that contain unincorporated HMMM (Dsikowitsky and Schwarzbauer, 2015).

3.7 Corrosion inhibitors

3.7.1 Organic micropollutant emissions from corrosion inhibitors

Benzotriazoles are widely used as corrosion inhibitors and are almost ubiquitously measured in road run-off, wastewaters and wastewater treatment plant effluents in relative high concentrations.
It should be noted that benzotriazoles are used in many other applications (amongst others in industrial cooling water and boiler systems, in car coolants, in car lubricant oils and in dishwashing tablets and metal detergents). So benzotriazoles in run-off cannot exclusively be attributed to corrosion inhibitors.

Substances that were measured include 1H-Benzotriazole (Casno 13351-73-0), Methyl-Benzotriazole (Casno 29385-43-1), 4-Methyl-Benzotriazole (Casno 29878-31-7), 5-Methyl-Benzotriale (Casno 136-85-6) (Loos, et al., 2013). Concentrations in WWTP-effluents vary roughly between 1 and 20 µg/L.
Benzotriazoles also were detected in road run-off water from roads in rather high concentrations taken from effluents of purification basins and overflow basins. Seitz and Winzenbacher (2017) found Tolyltriazole (Casno 29385-43-1) 2.3 µg/L and Benzotriazole (Casno 95-14-7) 0,1 µg/L.
Leaching of derivates of Benzotriazoles to groundwater in significant concentrations was measured by Trček et al. (2018). This makes that these components are of importance with respect of the protection of drinking water resources.

3.8 Automotive Coolants

3.8.1 Organic micropollutant emissions from automotive coolants

Automotive coolants are the transport medium of engine heat to the environment or to the car interior for heating purposes. Because the medium gets hot and is passing several engine parts consisting of different materials (copper, iron, solders, rubbers), the coolant must compromise many characteristics (resist high temperatures while not boiling and not being corrosive). Basically, the coolant consists of the cooling fluid (ethylene glycol or propylene glycol > 90%) and some additives (a combination of inorganic and organic substances 5-10%).

The history of automotive coolants reflects both the coping with many technical and later also environmental issues (see Lijima, et al., 2002). A comprehensive list of possible constituents of coolants is also presented by Ijima, et al. (2002), and shown in Table 10. It has to be noted that sodium chromate, triethanolamine and nitrite have been banned (at least in some countries) and most probably are not in use any more. Organic substances that still could be relevant for water quality are Benzotriazole, Mercapto benzothiazole (MBT), Tolytriazole (TT) and silicate stabilizers. In environmental samples, triazoles are frequently found in rather high concentrations. This makes that emissions of coolants from road traffic are potential contaminants in road run-off. However, as the level of coolants in cars is monitored constantly it is not expected a major source.

Table 10 Substances used in automotive coolants (total 5-10% m/m), as presented in Lijima et al. (2002)

	Substance	Casno	Remark
Inorganic inhibitor	Phosphoric acid	7664-38-2	
	Sodium monohydrogen phosphate	7558-79-4	Anode type
	Sodium polyphosphate	10361-03-2	Anode type
	Sodium borate	1303-96-4	Cathode type
	Sodium boric acid	1330-43-4	
	Sodium carbonate	497-19-8	
	Sodium hydroxide	1310-73-2	
	Sodium nitrite	7632-00-0	Anode type
	Sodium molybdate	10102-40-6	Anode type
	Sodium nitrate	7631-99-4	
	Sodium silicate	1344-09-8	Anode type
	Zinc nitrate	19154-63-3	Anode type
	Sodium chromate	7775-11-3	Anode type (now out of use)
Organic inhibitors	Sodium benzoate	532-32-1	Anode type
	p-tert-Butyl sodium	1716-12-7	Anode type
	Triethanolamine	102-71-6	Adsorption type
	Benzotriazole	95-14-7	Film-forming type
	Mercapto benzothiazole (MBT)	149-30-4	Film-forming type
	Tolytriazole (TT)	29385-43-1	Film-forming type
	Organic acid (Sebacic acid, Terephthalic acid)	111-20-6;100-21-0	
	Polymethacrylate (PMMA)	80-62-6 (polymerproduct)	Dispersal of scale
	Polyalcohol		Antifoaming agent
	Silicate stabilizer	R-Si(OH)3	Silicate precipitate inhibitor

3.9 Fuels, oils and lubricants

3.9.1 Organic micropollutant emissions from leakage of fuels, oils and lubricants

Markiewicz et al. (2017) indicated that potential emitted substances from leakage of fuels, oils and lubricants by road traffic include polycyclic aromatic hydrocarbons, phthalates, alkylphenols and alkylphenol ethoxylates, naphtha and bisphenol A.

Klein et al (2017) reported an average leakage loss of 10 mg lubricant oil per kilometre. It is expected that older vehicles have more leakage than younger vehicles. Mikhailova (2014) analysed petroleum products in the roadside area in Ukraine. In this study, it was determined that in the soils of roadside area accumulate up to 80% of petroleum products and near 20% of petroleum products are subject to evaporation. Furthermore, it was concluded that the

concentration of petroleum products in soils in the vicinity (1 m) of investigated highways was 3-24 times higher than the optimal permissible concentration value. Thus, leakage of petroleum products could be a relevant source for water bodies as well.
Lovinetska et al. (2015) concluded that with increasing distance from the road (from 5 meter to 15 meter distance from the road), the petroleum content of the soil decreased 10-20 times. Deltares and TNO (2016) estimated that 20% of the emitted engine oil will end up in surface water, while the other 80% of the emitted engine oil will remain in the soil.

Leakage of fuels, oils and lubricants could be a source of PAH. The PAH content of lubricant oil, as used in the Netherlands' Emission Inventory, is presented in Table 11.

Table 11 PAH content of lubricant oil (Deltares and TNO, 2016)

PAH	mg/kg lubricant oil
Anthracene	20.2
Benzo(a)Anthracene	26.7
Benzo(a)Pyrene	12
Benzo(b)Fluoranthene	13.9
Benzo(ghi)Perylene	47.6
Benzo(k)Fluoranthene	15.3
Chrysene	45
Phenantrene	135.1
Fluoranthene	39.4
Indeno (1,2,3-c,d)Pyrene	8.1
Naphtalene	220
Acenaphthene	5.3
Acenaphthylene	3.8
Dibenzo(ah)anthracene	0.9
Fluorene	42.9
Pyrene	88.5

3.10 Other sources related to road transport

3.10.1 PAH in car exhaust gases and other sources

Besides the above elaborated sources, exhaust gases from traffic also contribute to near road deposition of PAH. The deposition on individual (near)road surfaces is dependent on traffic intensity, traffic composition, traffic speed, road- and environmental conditions. Nevertheless, as a consequence of EU-regulation, exhaust emissions of PAH have been reduced within the EU around one order of magnitude during the last few decades (Shen, 2011).

The implication would be that both direct input from abrasion (tyre and brake wear) and indirect input via atmospheric deposition and exhaust could have been lowered with about a factor 10 compared to the 1990's levels.

3.10.2 Phthalates and nonylphenols from various sources

In a recent monitoring study, phthalates and nonylphenolic substances, previously seldom analysed in run-off, were detected in high concentrations in storm water and urban sediment (Björklund et al., 2009). These substances are considered as undesirable in water environments because of their potential of endocrine disrupting effects. Therefore, it seems to be relevant to consider long term effects of such components within roadside environments.

In a follow-up study (Björklund, 2010), a substance flow analysis was executed whereby emission factors concerning phthalates and nonylphenol (NP) and ethoxylates (EO) substances were estimated based on a combination of literature, interviews and interpreting the results of the measurements (see Table 12).

Table 12 Emission factors of selected phthalates and NP/EOs from identified sources in urban catchments (from Björklund, 2010)

Source	**Unit**	**Substance and CAS number**				
		DBP di-n-butyl phthalate 84-74-2	DEHP di(2-ethylhexyl) phthalate 117-81-7	DINP diisononyl phthalate 28553-12-0	DIDP diisodecyl phthalate 26761-40-0	NP/EOs nonylphenol and its ethoxylates 104-40-5/ 9016-45-9
Vehicles	µg/veh.km	$3.5\ 10^{-4}$	42	160	70	28
Tyre wear	µg/veh.km	-	$7.8x10^{-7}$	$7.8x10^{-7}$	$7.8x10^{-7}$	$2.6x10^{-6}$
Concrete	$mg/m^2.yr$	-	-	-	-	80
Atmospheric deposition	$µg/m^2.yr$	100	600	600	600	110
Roofing and cladding	$mg/m^2.yr$	16	470	450	300	$3.2x10^{-6}$
Flexible PVC	$mg/m^2.yr$	15	280	400	240	$4.6x10^{-6}$

Within the study of Björklund (2010), vehicles, concrete and roofing and cladding appeared as the main sources of phthalates and NP/EOs to both water and other sinks (such as soils and sludges). Depending on area characteristics, other sources than vehicles (atmospheric deposition) may be more important.

In urban areas the contribution of atmospheric input seems to be rather limited (Gasperi et al., 2014). They showed by measurements that local sources of Bisphenol A (BPA), Alkylphenol ethoxylates (APnEOs) and polybrominated diphenyl ethers (PDBEs) is dominating the contribution of atmospheric input to three very different French urban catchment areas. The same conclusion may hold for road-side environments as well. Confirmation by measurements in road-side environments however is lacking.
Pooled concentrations in storm water in three French catchments are presented in Table 13.

Table 13 Pollutant concentration (ng/l) in storm water of three French urban catchments, (Gasperi, et al., 2014)

Substance	Casno	Mean	SD
Bisphenol A (BPA)	80-05-7	552	510
4-tert-octylphenol (OP)	140-66-9	61	37
Octylphenol monoethoxylate (OP1EO)	51437-89-9	23	25
octylphenol diethoxylate (OP2EO)	2315-61-9	10	11
nonylphenol (NP)	104-40-5	359	228
Nonylphenol monoethoxylate (NP1EO)	9016-45-9	347	543
Nonylphenol diethoxylate (NP2EO)	20427-84-3	164	216
Nonylphenol monocarboxylate (NP1EC)		466	1,179

A comparison of concentration of micropollutants in storm water effluents of several types of areas including one traffic area (road effluent) within the city of Berlin was made by Holsteijn (2014). The concentrations of substances that indicate a possible significant contribution of traffic are presented in bold in Table 14.

Table 14 Concentrations of micropollutants (µg/L) in stormwater of various areas within the city of Berlin (Holsteijn, 2014)

Substance		Casno	Traffic	Residen-tial old	Residen-tial new	Offices zone	Commer-cial zone
TCCP	Tris(1-chloropropan-2-yl) phosphate	13674-84-5	0.13	0.43	0.44	0.24	0.36
OHBT	2-Hydroxybenzothiazole	934-34-9	**0.81**	0.38	0.32	0.30	0.35
DIDP	diisodecyl phthalate	26761-40-0	**8.60**	4.60	1.48	2.33	14.5
DEHP	di(2-ethylhexyl) phthalate	117-81-7	**2.27**	2.26	<LOD	0.63	1.86
PAH16	Polycyclic aromatic hydrocarbons		**2.8**	0.66	0.60	0.56	0.66
TSS (mg/L)	Total suspended solids		**280**	82.8	47.5	57.4	67.3

From Table 14 it can be concluded that not only a marker of tyre wear (OHBT = 2-hydroxybenzothiazole) but also several flame retardants like DIDP and DEHP might be emitted in significant amounts by road traffic.

Concentration measurements of organic micropollutants in literature are mainly focussed on PAHs (Best et al., 2002; Berg et al., 2009; Krein and Schorer, 2000; Magani et al., 2005; Tromp, 2005; Tromp et al., 2012; Velsen, 1997; Vollertsen, 2009). Other concentration measurements are done for petroleum products (Epoyan et al., 2014; Veremeyev et al., 2015; Parshine, 2013), benzothiazoles (Kloepfer et al., 2015) and a selection of pollutants by Seitz and Winzenbacher, 2017.

Many studies reported measured concentrations in the environment, but it is often not clear from which source (traffic, industry or any other source) the pollutants are. On the other hand, there are several modelling studies trying to model the amount of pollutants entering inland or marine surface waters. Data from these studies can be linked to the sources, but it does not contain any measured data. Some examples of measured concentrations of organic micropollutants:

- Gasperi et al., 2009 measured priority pollutants in the river Seine in France. The main PAHs that were found in the Seine sediments were fluoranthene, pyrene, benzo(a)pyrene and benzo(b)fluoranthene, while the main PAHs that were found in the Seine surface water were naphthalene, benzo(k)fluoranthene and fluoranthene. These compounds are present in tyres and could have been released by tyre wear. However, Gasperi et al. (2009) also indicated that these compounds could be related to combustion sources like diesel- and gasoline-powered vehicles.
- Gustafsson et al. (2017) measured environmental concentrations of 172 organic chemicals in Swedish coastal waters, including PAHs, octylphenol, nonylphenol, benzothiazole and BPA.
- Mikkelsen et al. (1996) studied infiltration systems for road run-off and concluded that the pollutant concentration decreased with increasing depths. Groundwater pollution from road run-off may therefore be limited.

4 Conclusion

Emissions from traffic and roads include exhaust emissions, abrasion/wear of tyres, brakes and road surfaces, leakage of engine oils and diffuse emissions from street furniture. Also, car coatings, brake fluids, corrosion inhibitors and automotive coolants are potential sources of contaminants in road run off. Important substances herein are Benzotriazoles, Benzothiazoles, Alkylphenols and Bisphenol A and possibly also some melamine compounds. Because some substances are polar (like triazoles) and rather persistent, protection of surface waters and groundwater could become an important environmental issue. The relevance of road traffic to the release of brominated diphenylethers (BDE's) is unknown.

In general, there are not enough measurements available to have an indication of the importance of emissions of other organic substances than PAH with respect to road-side environments. The emissions of PAHs are diminished with about one order of magnitude within the last 25 years. The emissions of PAH by tyres however should be controlled by proper measurements techniques. Therefore, it is obvious that road-side measurements on other substances than PAH are urgently needed.

Abrasion of tyres is one of the largest sources of pollutants to the environment. Tyre particles are also a vector for other pollutants to the environment, like PAHs, several benzothiazoles and amines.

Tyres, but also road markings, brakes and asphalt, are a source of microplastics. Tyres are responsible for the largest amount of microplastics, while microplastic emissions from road markings, brakes and asphalt are a factor of 10 lower than microplastic emissions from tyres. Tyres, brakes, roads, engine oils, car coatings, brake fluids, corrosion inhibitors and automotive coolants contain a large set of different organic compounds that are released during the use of vehicles.

Literature on microplastics and organic micropollutants in road run-off are scarce. Only PAHs in road run-off have been reported in multiple studies, while other organic micropollutants have only been reported occasionally.

Literature on microplastics and organic micropollutants in surface water is available, but it is often not clear what the source of these pollutants is. It is therefore difficult to indicate the share of traffic as a source for microplastics and organic micropollutants in surface water.

Some models have been reported in literature to estimate the amount of microplastics from various sources in surface water. Data from these literature sources could be used as an alternative when actual measurement data is lacking.

This study revealed a variety of organic micropollutants that are released from road transport to the environment, but it was concluded that the number of actual measurements is limited. It is recommended to perform more measurements in road run-off on organic micropollutants and microplastics. The following pollutants could be relevant for water quality and could be measured more frequently in road run-off and/or surface water:

- Tyres: Benzothiazoles (benzothiazole, mercaptobenzothiazole, benzothiazolone, hydroxybenzothiazole, benzothiazole-2-sulfonate), amines (cyclohexylamine, dicyclohexylamine, hydroxydiphenylamine, aminodiphenylamine), aniline
- Brakes and brake fluid: polyglycol ethers, Boric-acid-ester, Tributylphosphate, Triethanolamine
- Car coatings: hexa(methoxymethyl)melamine, nonylphenol ethoxylates, octylphenolethoxylates, bisphenol A
- Coolants: benzotriazole, tolyltriazole, mercapto benzothiazole, Sodium borate, Sodium Boric acid
- Other: diisodecyl phthalate, di(2-ethylhexyl)phthalate

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Annex A: Substances

This annex provides a list of the substances that are presented in the report (Table 15) and an overview of the PAHs that are included in the several PAH groups mentioned in this report (Table 16).

Table 15 List of substances presented in this report, including CAS numbers

Chemical	Short name	CAS number
(1,4-dimethylpentyl)phenylenediamine	77PD	3081-14-9
1,3-Diphenylguanidine	DPG	102-06-7
1H-Benzotriazole		13351-73-0
2-(methylthio)-benzothiazole	MTBT	615-22-5
2,2′-Dithiobis(benzothiazole)	MBTS	120-78-5
2-Benzothiazolesulfonic acid	BTSO3H	21465-51-0
2-Benzothiazolone	BTON	934-34-9
2-Hydroxybenzothiazole	OHBT	934-34-9
2-Mercapto benzothiazole	MBT	149-30-4
2-Methylbenzothiazole	MeBT	120-75-2
2-Methylthiobenzothiazole	MeSBT	615-22-5
2-Morpholinobenzothiazole	24MoBT	4225-26-7
4-Aminodiphenylamine	4-ADPA	101-54-2
4-Hydroxydiphenylamine	4-HDPA	122-37-2
4-Methyl-Benzotriazole		29878-31-7
4-Nitrodiphenylamine	4-NDPA	836-30-6
4-Nitrosodiphenylamine	4-sDPA	156-10-5
4-tert-octylphenol	OP	140-66-9
5-Methyl-Benzotriale		136-85-6
Aniline		62-53-3
Benzothiazole	BT	95-16-9
Benzothiazole-2-sulfonate	BTSA	941-57-1
Benzotriazole		95-14-7
Bis(triethoxysilylpropyl)tetrasulfide	SI69	40372-72-3
Bisphenol A	BPA	80-05-7
Boric-acid-ester		
Cyclohexyl amine	CHA	108-91-8
Di(2-ethylhexyl)phthalate	DEHP	117-81-7
Dibutyl amine		111-92-2
Dibutylhydroxy toluene		128-37-0
Dicyclohexylamine	DCHA	101-83-7
Diisodecyl phthalate	DIDP	26761-40-0
Diisononyl phthalate	DINP	28553-12-0

Di-n-butyl phthalate	DBP	84-74-2
Diphenylamine	DPA	122-39-4
Diphenylurea		102-07-8
Hexa(methoxymethyl)melamine	HMMM	3089-11-0
Mercapto benzothiazole	MBT	149-30-4
Methylbenzothiazole	MeBT	120-75-2
Methyl-Benzotriazole		29385-43-1
N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenylenediamine	6-PPD	793-24-8
N,N'-ditolyl- and N,N'-diphenyl-p-phenylenediamine	DPPD/DTPD	74-31-7 / 620-91-7
N-butylaniline		1126-78-9
N-cyclohexyl-1,3-benzothiazol-2-amine	NCBA	28291-75-0
N-Cyclohexyl-2-benzothiazole	CBS	95-33-0
N-Isopropyl-N'-phenyl-1,4-phenylenediamine	IPPD	101-72-2
Nonylphenol	NP	104-40-5
Nonylphenol and its ethoxylates	NP/EOs	104-40-5/9016-45-9
Nonylphenol diethoxylate	NP2EO	20427-84-3
Nonylphenol monocarboxylate	NP1EC	3115-49-9
Nonylphenol monoethoxylate	NP1EO	9016-45-9
N-phenylformamide		103-70-8
N-tert-Butyl-2-benzothiazolesulfenamide	TBBS	95-31-8
Nμ-(p-Phenylene)ditoluidine	DTPD	620-91-7
Octylphenol diethoxylate	OP2EO	2315-61-9
Octylphenol monoethoxylate	OP1EO	51437-89-9
Organic acid (Sebacic acid, Terephthalic acid)		111-20-6;100-21-0
Phosphoric acid		7664-38-2
Poly(1,2-dihydro-2,2,4-trimethylquinoline)	TMQ	26780-96-1
Polyalkylene glycol		
Polyethylene glycol monomethyl ether		9004-74-4
Polyethylene monobutyl ether		9004-77-7
Polyethylenepropylene glycol monomethyl ether		
Polymethacrylate	PMMA	80-62-6
p-tert-Butyl sodium		1716-12-7
Sodium benzoate		532-32-1
Sodium borate		1303-96-4
Sodium Boric acid		1330-43-4
Sodium carbonate		497-19-8
Sodium chromate		7775-11-3
Sodium hydroxide		1310-73-2
Sodium molybdate		10102-40-6
Sodium monohydrogen phosphate		7558-79-4

Sodium nitrate		7631-99-4
Sodium nitrite		7632-00-0
Sodium polyphosphate		10361-03-2
Sodium silicate		1344-09-8
Stearic acid	SAD	57-11-4
Sulphur	S	7704-34-9
Tolyltriazole	TT	29385-43-1
Tributyl phosphate		6131-90-4
Triethanol amine		102-71-6
Triethylene glycol monoethyl ether		112-50-5
Tris(1-chloropropan-2-yl) phosphate	TCCP	13674-84-5
Zinc nitrate		19154-63-3
Zinc oxide	ZnO	1314-13-2

Table 16 PAH per PAH group

PAH	CAS number	16-PAH	10-PAH	8-PAH
Acenaphthene	83-32-9	X		
Acenaphthylene	208-96-8	X		
Antanthrene	191-26-4			
Anthracene	120-12-7	X	X	
Benzo(a)anthracene	56-55-3	X	X	X
Benzo(a)fluorene	238-84-6			
Benzo(a)pyrene	50-32-8	X	X	X
Benzo(b)fluoranthene	205-99-2	X		X
Benzo(b+j+k)fluoranthene	205-99-2, 205-82-3, 207-08-9			
Benzo(e)pyrene	192-97-2			X
Benzo(g,h,i)perylene	191-24-2	X	X	
Benzo(j)fluoranthene	205-82-3			X
Benzo(k)fluoranthene	207-08-9	X	X	X
Chrysene	218-01-9	X	X	X
Dibenzo(a,h)anthracene	53-70-3	X		X
Dibenzo(a,j)anthracene	224-41-9			
Fluoranthene	206-44-0	X	X	
Fluorene	86-73-7	X		
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	
Naphthalene	91-20-3	X	X	
Phenanthrene	85-01-8	X	X	
Pyrene	129-00-0	X		