

---

**CEDR Transnational Road Research Programme  
Call 2016: Environmentally Sustainable Roads: Surface-  
and Groundwater Quality**

funded by Austria, Finland,  
Germany, Ireland, Norway,  
Netherlands and Sweden



**MICROPROOF**  
**Micropollutants in Road RunOff**

**Review of available measurements of  
organic micropollutants, microplastics  
and associated substances  
in road run-off**

Deliverable 1.2  
April 2018

The Netherlands Organisation for Applied Scientific Research (TNO), the Netherlands  
Wageningen Marine Research (WMR), the Netherlands  
Aalborg University (AAU), Denmark  
M.P. Shulgin State Road Research Institute State Enterprise –  
DerzhdorNDI SE (DNDI), Ukraine

---

**CEDR Call 2016: Environmentally Sustainable  
Roads: Surface- and Groundwater Quality  
MICROPROOF  
Micropollutants in Road RunOff**

**Review of available measurements of organic  
micropollutants, microplastics and associated  
substances in road run-off**

Actual delivery date draft: 28/02/2018  
Actual delivery date final: 13/04/2018

Start date of project: 01/09/2017

**Author(s) of this deliverable:**  
Jes Vollertsen, Aalborg University, Denmark

PEB Project contact: Rob Hofman

Version: final, 04/2018

---

## Table of contents

1	Microplastic .....	1
1.1	Littering .....	1
1.2	Road marking wear .....	2
1.2.1	Composition of road markings .....	2
1.3	Brakes.....	3
1.3.1	Composition of brake linings .....	3
1.4	Tyre wear .....	4
1.4.1	Characterization of tyre materials .....	4
1.4.2	Size of tyre wear particles .....	5
1.4.3	Field measurements of tyre wear particles .....	5
1.5	Airborne microplastic.....	6
1.6	Microplastic in stormwater runoff from mixed catchments .....	6
2	Microplastic as vector for other pollutants.....	7
2.1	Tyre microplastic as pollutant vectors.....	7
2.1.1	Brake microplastic as pollutant vectors .....	8
2.1.2	Microplastic plastic from road markings as pollutant vectors .....	8
2.1.3	Microplastic from litter as pollutant vectors .....	8
3	Organic micropollutants in road runoff.....	8
4	References.....	10

This report addresses available measurements of organic micropollutants and microplastics originating from traffic associated activities and atmospheric deposition in relation to roads and highways. It also addresses problematic substances associated to the microplastic found here. It does so by reviewing the available scientific literature by searching recognized databases, namely Web of Science, Scopus, and Google Scholar. It further includes reports and grey literature in terms of reports and data collections from national road authorities.

## 1 Microplastic

Microplastic (MP) in road runoff can originate from abrasion of tyres, road markings, littering and waste dumping along the road, as well as from air borne deposition. Of these sources road markings and air borne depositions are probably the minor ones and tyre abrasion the major one (Sundt et al., 2014; Lassen et al., 2015; Verschoor et al., 2016). However, no study based on measurements in the field has compared the relative importance of these source and the ranking of the source strength hence remains a theoretical estimate only. Furthermore, only a few studies have quantified MP in road runoff, road dust, or soils close roads, and none have quantified all plastic materials. At the same time, the studies that have been conducted have applied vastly different methods which tend to make results difficult, if at all, comparable.

### 1.1 Littering

While littering and illicit waste dumping often is observed along roads and also will occur during construction work, there have been few studies that quantify the amount of plastic from these sources (Willis et al., 2017; Bläsing and Amelung, 2018). Kim et al. (2014) and Kim et al. (2016) quantified the amount of gross pollutants in runoff from highways. They found that 90% of the gross material was of natural origin while 10% was litter. Of the latter approx. half was metals and biodegradable materials such as plastics. Biodegradable litter consisted mainly of paper products. The loading with non-biodegradable litter (plastic and metal) ranged from 0.85 to 6.6 kg ha<sup>-1</sup> of catchment surface. The corresponding water phase concentrations of dry litter ranged from 0.03 to 5.5 mg/l.

Willis et al. (2017) studied the occurrence of marine debris in relation to the number of storm drains close by. This study showed that there was a correlation between the number of storm drains and litter. It showed that there was an increase in debris at sites closer to public roads and sites with higher population densities. However, whether this litter came via road runoff or via other pathways associated to anthropogenic activity cannot be deduced from that study.

Alam et al. (2017) studied the occurrence of gross solids captured in catch basin inserts from urban roads (inserts in gully pots) by screening down to 150 µm. They found that 93% of the solids on average were vegetation and 7% were litter, a category which comprised plastic, paper, cans, and miscellaneous items. The load of dry litter averaged to slightly above 1 kg/(ha year). Alam et al. (2017) also accumulated existing literature on gross solids captured by traps in catch basins. Also those studies found that the major fraction of gross solids was vegetation in origin.

Other studies have in general addressed how mismanaged plastic waste is conveyed from land to the oceans (Jambeck et al., 2015; Lebreton et al., 2017; Schmidt et al., 2017). While these studies conclude that land based sources are major and maybe even the largest, they do, however, not allow deduction of which fraction can be contributed to runoff from

highways and roads in rural areas. It hence remains largely unknown how significant the contribution of plastic litter (plastic solids > 5 mm) and secondary MP (< 5 mm) is to MP in road runoff, road dust, and nearby soils.

## 1.2 Road marking wear

Road markings contain polymeric binders and are hence categorized as plastic. Various polymeric binders are used in road markings, for example acrylates, alkyds, various latex and various resins (e.g. Kosto and Shall, 2008; Cruz et al., 2016, Hongkong Highways Department, 2016). Recent studies have shown paint and pigmented MP particles to be present in the environment (Imhof et al., 2016). That study did however not quantify whether or not the found particles could have originated from road markings. Horton et al. (2017) studied the abundance of large microplastic particles s (1 - 4 mm) in sediments of tributaries of the River Thames. They found significant amounts of fragments of thermoplastic road-surface marking paints downstream of a storm drain outfall receiving urban runoff. The amounts found could not be back-calculated to runoff concentrations but the study did show that thermoplastic road-surface marking paints do contribute to the load of microplastic on the environment. They also identified the presence of road marking particles on road surfaces upstream of the addressed storm drain.

The use of road markings differs between countries. Norway uses 320 ton/year to mark its roads, corresponding to some 0.060 g/(capita year) (Sundt et al., 2014). This use might be in the high end of what is used throughout Europe as the use of salt and spikes during winter increase the wear of the markings.

### 1.2.1 Composition of road markings

Road marking paints are typically a mix of glass beads, filler, and pigments, held together by a polymeric binder. The polymeric binders are for example acrylates, latex rosins and derivatives sometimes mixed with a plasticizer to make the paints less brittle. Typical composition of a thermoplastic road marking paint is found in Table 1. Depending on their color, road markings can also include for example pigments for red and yellow color.

**Table 1. Typical composition of thermoplastic road marking paint (after Conserva and Dupont, 2011)**

Function	Range [%weight]	Material
Binder	8-15	Hydrocarbon based resin
	1-5	Plasticizer
	0-5	Thermoplastic elastomer
Colouring	5-10	Pigments such as TiO <sub>2</sub> and ZnO
Fillers	15-20	Glass beads
	20-40	Aggregates

Various road marking paints are on the market. The binders (i.e. plastic) of these paints are typically polyvinyl acetates, acrylates, acrylic, alkyds, or various types of resins or latex in nature. A survey of data sheets on the web did though show that not all manufactures state which type of binder is used.

## 1.3 Brakes

Brake linings contain abrasives fibres, fillers, frictional additives or lubricants, and binders to hold everything together. The binders are polymers of a variety of modified phenol-formaldehyde resins (Chan and Stachowiak, 2004; Kukutschová et al., 2011). Wear of the brake linings create microparticles (Grigoratos and Martini, 2014), which must be categorized as microplastic as they contain polymeric binders.

Brake wear particles have been in focus in terms of their contribution to air pollution. Grigoratos and Martini (2014) made an extensive literature review on these particles and summarize that particles from “brake wear contributes 16-55% by mass to total non-exhaust traffic related PM10 emissions in urban environments, while in freeways this contribution is significantly lower (~3% by mass) due to lower braking frequency.” They further summarize that about half of the break wear particles are found in the PM10 fraction while the remaining is of smaller size. Wahid (2018) arrives at a similar conclusion in a review on automotive brake wear.

Kukutschová et al. (2011) showed that particles released from low-metallic brakes generated both nano and micro particles in all captured fractions (10 nm to 20 µm). They also found that wear particles in the nanometre range tended to agglomerate and that wear particles and agglomerates contained carbon black and graphitic particles.

Emission from brakes are highly variable and of course related to the applying the brakes during driving as well as the type of vehicle on the road. Typical emissions of PM10 particles from braking of light duty vehicles is some mg/(km vehicle) with substantial local variations (Grigoratos and Martini, 2014).

### 1.3.1 Composition of brake linings

Each brand of brake linings has its own formulation and the detailed composition is not readily available from the manufactures. The most abundant metals present in modern liners are though typically reported as Fe, Cu, and Zn (Bukowiecki et al., 2009). Thorpe and Harrisson (2008) compiled a summary of which metals are found in both brake linings and dust emitted from braking (Table 2).

**Table 2. Metals found in brake linings and dust emitted from braking in mg/kg (after Thorpe and Harrisson, 2008, and Grigoratos and Martini, 2014). The values for Pb are only valid for older brakes.**

Metal	Car brake linings	Car brake dust	Metal	Car brake linings	Car brake dust
Al	3765	330-2500	K	857	190-5100
As	<2.0-18	<2.0-11	Mg	6140	83,000
Ba	2638	5900-74,400	Mn	181-3220	620-5640
Ca	14,300	920-8600	Mo	0.4-215	5.0-740
Cd	<1.0-41.4	<0.06-2.6	Na	15,400	80
Co	6.4-45.8	12-42.4	Ni	3.6-660	80-730
Cr	<10-411	135-1320	Pb	1.3-119,000	4.0-1290
Cu	11-234,000	70-39,400	Sb	0.07-201	4.0-16,900
Fe	12,000-637,000	11,000-537,000	Zn	25-188,000	120-27,300

## 1.4 Tyre wear

The emission of micro-particles (microplastic) from tyre wear has been estimated in the range from 0.23 to 4.7 kg/(capita year), with a global average of 0.81 kg/(capita year) (Kole et al, 2017). So did for example Norén and Naustvoll (2010) estimate around 1 kg/(capita year) from Swedish roads while Essel (2014) estimate around 1.4 kg/(capita year) from German roads. Tyre abrasion can cause a mass loss of up to 10% during the lifetime of the tyre (Milani et al., 2004),

There is a general consensus that tyre wear is a substantial source for microplastic and in many cases also the largest source for microplastic particles discharges into the environment. So did for example Lassen et al. (2015) calculate that the emission of tyre wear particles constituted 55.8% of the total microplastic emission in Denmark. This percentage does, though, not cover the fragmentation of macroplastic (plastic litter) to microplastic in the environment.

Roads are the largest source of tyre microplastic particles followed by emission from artificial turfs and then airplane tyres. Most of this plastic load has been theorized to end up in either stormwater runoff or accumulating in surrounding soils. Tyre wear particles have also been estimated to contribute significantly to particulate matter (PM) in air (Grigoratos and Martini, 2014; RIVM, 2016).

### 1.4.1 Characterization of tyre materials

Tyres are made of a mixture of synthetic and natural rubbers. The tyre tread has a specific density of around 1.15 g/cm<sup>3</sup> (Heitzman et al., 1992). Sulphur is added for vulcanization and zinc to catalyse the process. The zinc and sulphur content of tyre rubber hereby becomes approx. 1-2% zinc (Evans and Evans, 2006; Gunasekara et al., 2000; Degaffe et al., 2011; Lee et al., 2011; Taheri et al., 2011) and 1% sulphur (Evans and Evans, 2006). Besides these substances, tyres also contain trace concentrations of problematic metals such as lead, copper, chromium, and nickel in the low µg g<sup>-1</sup> range or in the ng g<sup>-1</sup> range such as cadmium, arsenic, and mercury (Bocca et al., 2009).

**Table 3 Typical composition of tyre tread of a passenger car Ahlbom and Duus (1994) and Barbin and Rodgers (1994). After Wik and Dave (2009)**

Component/additive	Ingredients	Content (wt-%)
Polymer	Synthetic and natural rubbers	40–60
Filler (for reinforcement)	Carbon black and silica	20–35
Process oils/extender oils	Mineral oils	15–20
Vulcanisation system		
Vulcanisation agent	Sulphur	1
Vulcanisation activators	Zinc oxide	1.5
	Stearic acid	1
Vulcanisation accelerators	e.g. Sulphenamide or thiazoles	0.5
Protective agents	Antioxidants and antiozonants	1
Processing aids	Peptisers, plasticizers, and softeners	<1

### 1.4.2 Size of tyre wear particles

Tyres wear creates particles from sizes of some tenth of a millimetre and down, hence covering what often is referred to as micro (often defined as 1-5000  $\mu\text{m}$ ) and nano particles (often defined as 1-100 nm). The particles consist of both the tyre tread and the road material. While only tyre tread is viewed as a microplastic, the latter has been detected by spectroscopic means in ponds receiving road runoff (Liu et al., unpublished). The formation of particles with respect to size distribution has only been addressed by a limited number of studies. Some of these studies covered the particle range from the high nanometre range to the micrometre range while other covered the nanometre range (Kreider et al., 2010; Aatmeeyata et al., 2009; Dahl et al., 2006; Mathissen et al., 2011). Unfortunately no study has covered the whole range from low nanometre to high micrometre. The use of different metrics (such as particle mass versus numbers), application of different analytical methods, and substantial variation in experimental conditions further complicate the comparison and interpretation of the results. All in all the question which particle sizes are the most abundant is hence ambiguous.

### 1.4.3 Field measurements of tyre wear particles

Analytical quantification of tyre materials in environmental samples is quite demanding and still a major area of research within the field of microplastic quantification. The most widely used methods to quantify microplastic materials in general are FT-IR and Raman. These are however of limited value for tyre rubber. A major reason is that tyres contain carbon-black, which adsorbs most of the light used by these techniques. A further complicating aspect is that tyre rubber does not generate as sharp spectra peaks as many other plastic materials. In most cases the approach of choice for tyre particles in environmental samples is a range of thermoanalytical techniques. The major drawback of these techniques is that they only quantify the total polymer mass in the sample and are impractical to identify individual particles. On the other hand, their ability to quantify mass is significantly better than that of FT-IR and Raman, which basically only gives the material. Mass must then be deducted from an estimate of particle size, which can be rather tedious and imprecise.

One of the first attempts to quantify particles of tyre tread rubber dates back to Thompson et al. (1996). They used Styrene as a marker for qualitative analysis of road dust applying a pyrolyzer. Over the following decades there were further attempts to measure tyre tread rubber, but mainly in air samples. Saito (1989) measured tyre particles in piled particulate matter. They used a Curie-point pyrolyzer coupled to a GC-FID (gas chromatograph – flame ionization detector) to quantify styrene butadiene rubber (SBR) and isoprene (NR) which are both used in tyres (SBR commonly in cars and NR commonly in busses and trucks). They analysed the tyre material in road dust accumulated in and at a tunnel and at a highway in Japan. They found 75 – 920  $\mu\text{g SBR g}^{-1}$  and trace amounts to 1760  $\mu\text{g NR g}^{-1}$ . This summed up to the highest concentrations found 60 m inside the tunnel, totalling approx. 2700  $\mu\text{g tyre rubber g}^{-1}$ . Outside the tunnel the highest concentration was a bit lower, namely 2100  $\mu\text{g tyre rubber g}^{-1}$ . Depending on the actual content of rubber in the tyre particles (Table 3) this corresponds to approx. twice the mass as microplastic particles. Other studies used other markers to quantify the amount of tyre particles in environmental samples, such as 2-(4-morpholinyl) benzothiazole (24MoBT), benzothiazole (BT), 2-hydroxybenzothiazole (HOBT), and zinc. Wik and Dave (2009) compiled what data was available and found that the reported range was rather large, ranging from close to zero to 21% of dry road dust being tyre particles. Concentrations in soil close to roads ranged similarly, from zero to 11.7% of the dry mass. Estimates on road runoff contents of tyre particles ranged from 12 to 179  $\text{mg L}^{-1}$ . Some of these numbers seem unrealistic high, and cannot be representative for road dust or



road runoff on European roads. However, the results do indicate that particles of tyre tread are present in significant amounts in road dust, road runoff, and soils in the vicinity of roads.

Unice et al. (2012) applied a pyrolysis GC-MS method to quantify tyre tread particles in a soil sample and some sediment samples. The soil sample came from Japan was taken less than 5 m from a road with approx. 20,000 vehicles per day. It contained 2.3 mg g<sup>-1</sup> car tyre tread. Two sediment samples came from the USA, the Potomac River close to the district of Columbia. They contained around 0.09 and 0.5 mg g<sup>-1</sup> tyre tread, respectively. In a later study applying the same analytical method, Unice et al. (2013) investigated the occurrence of tire and road wear particles (TRWP) in watershed sediments in France, USA and Japan. They found concentrations in soil and sediment in the range 26-11,600 µg g<sup>-1</sup>. The same dataset is also reported in ChemRisk (2011).

All in all these studies make it clear that tyre tread particles can be found at high concentrations. In other words, there do exist hotspots where tyre tread can be present at considerable concentration.

### **1.5 Airborne microplastic**

Panko et al. (2013) used a pyrolysis GC-MS to quantify tire and road wear particles in air from Europe, Japan and the USA. The sampling locations covered a wide range of settings, going from rural to dense city. They found that the concentrations of these particles in the PM10 fraction were low. Averages ranged from 0.05 to 0.70 µg m<sup>-3</sup>, and constituted on average 0.84% of all PM10 in the samples. They found a weak correlation between parameters like traffic load and population density. However, the trends were not statistically significant and it hence is uncertain if those trends were real or not. Dall'Osto et al. (2014) studied tyre and road dust in the size range of 6-20,000 nm using Aerosol Time-Of-Flight Mass Spectrometry. They concluded that tyre wear particles in the tested road dust and atmospheric samples were internally. In other words, tyre material and road surface material created particles containing both source materials. They found that tyre particles contributed with 4% of London road dust, decreasing to zero for marine sites.

Prior to these studies, Lee et al. (1989) found 2.2 µg m<sup>-3</sup> in air from Seoul, Korea. For Tokyo, Japan, Kim et al. (1990) found that between 0.5 and 3% of the particulate matter in air consisted of tyre tread material. They found air concentrations of <1 to 100 µg m<sup>-3</sup>, depending on where the sample was taken. Concentrations were highest at street level, decreasing with increasing height. Yamaguchi et al. (1995) found airborne concentrations of tyre tread particles of 0.5-10.5 µg/m<sup>3</sup> along a highway in Japan. The tyre material could account for 0.4-6.3% of total airborne particles.

### **1.6 Microplastic in stormwater runoff from mixed catchments**

Measurements of microplastic in stormwater runoff from roads and highways are scarce if existing at all. The same is the case for stormwater runoff from mixed urban areas. At present the only published study is an application note on FT-IR imaging (Olesen et al., 2017). They analysed stormwater and sediments from an urban stormwater pond and found 5.2 10<sup>5</sup> particles/kg dry sediment, equivalent to 26 mg/kg dry sediment. In the water samples they found 1.1 x 10<sup>2</sup> particles/L, equivalent to 4.5 µg/L. The plastic materials present were polyethylene, polypropylene, polyvinyl chloride, polystyrene, polyurethane and zinc stearate coated particles. That study did not address tyre particles as the applied technique was not suited here for.

## 2 Microplastic as vector for other pollutants

Plastic can contain additives that can be released from the solid phase to a surrounding liquid phase. With respect to road runoff, tyre rubber and brake liner particles are important materials, but plastic from littering and road markings can also contain additives which can leach from generated microplastic particles.

### 2.1 Tyre microplastic as pollutant vectors

Tyres contain a range of inorganic and organic micropollutants, of which the heavy metal zinc is the most abundant in terms of mass. Zinc contained in tyres can leach from the microplastic particles into the surrounding environment. Rodes et al. (2012) compiled 14 studies on zinc-leaching from tires and concluded that lower pH and smaller particle size favoured the leaching. They also found that leaching at some point seemed to reach a steady state. Most of the studies behind the review were, however, done on large particle sizes compared to what is found from tyre abrasion, and it is hence not clear how long fine tyre particles have to be submerged in water before the majority of the zinc has leached out. Selbes et al. (2015) investigated leaching of various substances from scrap tyres. They also found that the leaching of metals such as zinc was favoured at low pH. They investigated the leaching of dissolved organic carbon (DOC) and found that the tyre particles continued to release DOC for the one month of experiment duration, without any indication that the process had run to completion.

Part of the leached dissolved organic carbon will have been organic micropollutants such as 24MoBT and N-cyclohexyl-2-benzothiazolamine (NCBA) which are present in automobile tires as impurities of the applied vulcanisation accelerators (Pan et al., 2012). In road dust from China and India, these researchers found 24MoBT and NCBA within the range of 3.40-151 ng g<sup>-1</sup> for and nd-56.9 ng g<sup>-1</sup>, respectively. Similarly did Kumata et al. (2002) find 24MoBT and NCBA concentrations in runoff water from 15 to 417 ng L<sup>-1</sup> and 22 to 508 ng L<sup>-1</sup>, respectively. They found that most of the NCBA was present in the particulate phase (>0.7) while most of the 24MoBT was present in the dissolved phase, an observation which they ascribed to the octanol-water partitioning of these two substances.

Li et al. (2010) studied the leaching and outgassing of organic micropollutants from crumb rubber material made of scrap tyres. They found that volatile BT was the substance present at highest level in the headspace of all studied samples, in the range of 8.2–69 ng g<sup>-1</sup>. They did, though, find that BT leaching into a water phase was limited. They found a total amount of BT in recycled tyre rubber at 48 µg g<sup>-1</sup>. They found a range of polycyclic aromatic hydrocarbons (PAHs) and antioxidants to be present in the µg-range (ethylnaphthalene (1-MeNA) 1.0 µg g<sup>-1</sup>; 2-methylnaphthalene (2-MeNA), 2.1 µg g<sup>-1</sup>; fluoranthene (Flu), 19 µg g<sup>-1</sup>; naphthalene (NA), 1.1 µg g<sup>-1</sup>; phenanthrene (Phe), 4.6 µg g<sup>-1</sup>; pyrene (Pyr), 9.0 µg g<sup>-1</sup>; butylated hydroxyanisole (BHA), 24 µg g<sup>-1</sup>; butylated hydroxytoluene (BHT), 0.36 µg g<sup>-1</sup>; 4-tert-octylphenol (4-t-OP), 48 µg g<sup>-1</sup>).

Depaolini et al. (2017) studied the PAH content of 25 types of granulated recycled tyre rubber. They found the sum of 15 common PAHs in the range of 37-65 µg g<sup>-1</sup> for these samples.

### 2.1.1 Brake microplastic as pollutant vectors

Filip et al. (2002) estimated that some 147 million vehicles in the USA released some 30,000 ton of break wear particles. These microplastic particles contain both metals (Thorpe and Harrisson, 2008; **Table 2**) and organic micropollutants (Rogge et al., 1993). The most abundant organic micropollutants identified by Rogge et al. (1993) in brake lining dust were polyglycol ethers (mainly from hydraulic fluids). Other substances found in trace amounts included alkanes, alkanic acids, PAHs, oxy-PAHs, benzaldehydes, benzoic acids, and oleic acids.

### 2.1.2 Microplastic plastic from road markings as pollutant vectors

Road marking paints can contain Phthalates, alkylphenols and their ethoxylates, bisphenol A, alkyd resins (Aznar et al. 1997; Staples et al., 1998; Andersson and Sörme, 2004; Markiewicz et al., 2017). However, many different road marking materials are used across Europe, and there hence might be significant difference between countries, regions, and from road to road. The significance of road marking paints for the pollutant mass flow is though not well understood.

### 2.1.3 Microplastic from litter as pollutant vectors

Seitz and Winzenbacher (2017) took grab samples of water from 4 basins that receive road runoff and analysed them for a range of organic micropollutants. Among other substances they found melamines which are widely used in the production of certain plastics such as melamine resin used in for example kitchen utensils. It seems likely that this substance would have originated from littering. Otherwise no link between plastic litter and organic micropollutants in runoff have been established.

## 3 Organic micropollutants in road runoff

Besides the microplastic associated sources, road runoff can contain organic micropollutants generated from traffic, construction materials, and atmospheric deposition. Markiewicz et al. (2017) reviewed the emission of organic micropollutants related to traffic and roads. They found a large number of these substances associated to traffic and roads and ranked them as priority pollutants according to their environmental impacts and mass flow. They found the following priority order: PAHs > alkanes C20 - C40 > alkylphenols > phthalates > aldehydes > phenolic antioxidants > bisphenol A > oxygenated-PAHs > naphtha C5 - C12 > amides > amines. They selected PAHs for a substance flow analysis and found that of a total annually emitted load of PAH of 5.8–29 kg/ha, only 2-6% ended up in stormwater runoff. Especially the PAHs can originate from quite many sources, and so did for example Brandt et al. (2001) show experimentally that PAHs could leach from bitumen and asphalt. Grung et al. (2017) performed a data register study to identify the amounts of organic micropollutants in products related to motorized transport in Norway. They found that the products held hazardous substances present in problematic amounts. The most important prioritized compounds were methyl tertiary butyl ether, benzene, tetrachloroethylene, hydrazine, medium-chain paraffins, tetraborates, nonylphenols and its ethoxylates, decamethylcyclopentasiloxane, and the tetraborate orange lead.

Many of these substances have not or only sporadically been measured in stormwater runoff. The group of organic micropollutants which have be monitored most frequently is PAH. Tromp et al. (2012) found PAH in road runoff from a highway in The Netherlands to 2.4  $\mu\text{g L}^{-1}$  with fluoranthene being the PAH contributing the most, followed by Chrysene. In a study of runoff from a highway in Oslo, Norway, Vollertsen et al. (2009) found total PAH as flow weighted average concentrations over one full year of monitoring to be 1.8  $\mu\text{g L}^{-1}$ . Brongers

(2010) reports measurements of PAH from a Dutch highway and found PAH generally significantly below  $1 \mu\text{g L}^{-1}$ , albeit with some outliers as high as  $6 \mu\text{g L}^{-1}$ . Best et al. (2002) compiled a number of studies and concluded that PAH was in the range  $0.5 - 1.5 \mu\text{g L}^{-1}$  in runoff from the investigated roads. Velsen (1997) investigated water from 4 Dutch tunnels and found PAH in the tunnel runoff of  $0 - 1.1 \mu\text{g L}^{-1}$ . Tromp (2005) analysed highway runoff from a Dutch highway and found 11-PAH in an average concentration of  $3.2 \mu\text{g L}^{-1}$  with fluoranthene being the PAH contributing the most, followed by pyrene. Berg et al. (2009) measured PAH in runoff in a wet ditch (canal) where the runoff water had passed a grassed strip before entering the canal. They found that the PAH in the water seldom exceeded the detection limits. These ranges of data on PAH in highway runoff indicate that typical levels are somewhere between below detection limits and a few  $\mu\text{g L}^{-1}$ .

Besides measurements of PAHs in the runoff itself, quite some data are available on concentrations in road dust, soils close to roads, and stormwater pond sediments. For example did Velsen (1997) find  $12-160 \mu\text{g g}^{-1}$  of 16-PAH in road dust from two Dutch tunnels. A Danish survey covering 70 wet detention ponds receiving highway runoff show that PAH in dry sediments typically was in the range  $0-2 \mu\text{g g}^{-1}$  (Grauert et al., 2012a; Grauert et al., 2012b). They also conclude that PAH in sediments of reference lakes were in the same range as the stormwater ponds. A similar conclusion was drawn by Stephansen (2014) when studying PAH in stormwater ponds and natural shallow lakes.

For road dust did for example Zhang et al. (2017) study the relation between street pavements and PAH in 6 German cities. The highest solid phase concentration was associated with a road with high traffic load ( $36 \mu\text{g g}^{-1}$ , while the highest area concentration (surface load) was found on a natural stone-paved pedestrian path ( $35 \mu\text{g m}^{-2}$ ). The spread in surface load of the 6 sites were nearly 2 orders of magnitudes. Their study also reviewed comparable references for surface loads and found that reported values were in the range of  $0-9600 \mu\text{g g}^{-1}$ , with typical values somewhere in the range of 1 to  $100 \mu\text{g g}^{-1}$ . Majumdar et al. (2017) reviewed a large number of studies on PAH in road dust. They found that concentrations ranged many orders of magnitude, but still with typical values very roughly in the range 1 to  $100 \mu\text{g g}^{-1}$ .

Lutz (2017) estimated the load of PAH from 14 sections of a Swizz highway to lay between 40.5 and  $70.9 \text{ g/ha year}$  based on runoff characteristics and the usage of the highway. They then calculated the emission of PAH onto the local receiving waters. The sampled sediments in that receiving waters and found PAH to peak at 5 cm depts. With  $6 \mu\text{g g}^{-1}$ . In the surface sediments they found  $2 \mu\text{g g}^{-1}$  while PAH was below  $1 \mu\text{g g}^{-1}$  at 10 cm or deeper. Pyrene accounted the largest part of the PAHs (15-23% of total PAH), followed by fluoranthene (13-28%) and phenanthrene (5-14%).

For other organic micropollutants than PAH, the number of field measurements become sporadic. One of these studies is the previous mentioned study by Seitz and Winzenbacher (2017) where grab samples were taken of water from 4 basins that receive road runoff, a large number of organic micropollutants were detected. The highest median concentrations they found were: Tolyltriazole  $2.3 \mu\text{g L}^{-1}$ ; Desphenyl-chloridazon  $1.2 \mu\text{g L}^{-1}$ ; Hexamethoxymethylmelamine  $0.66 \mu\text{g L}^{-1}$ ; Methyl-desphenyl-chloridazon  $0.34 \mu\text{g L}^{-1}$ ; Melamine  $0.25 \mu\text{g L}^{-1}$ ; 2-Hydroxybenzothiazole  $0.17 \mu\text{g L}^{-1}$ ; 2-(Methylthio)-benzothiazole  $0.11 \mu\text{g L}^{-1}$ ; 2-Mercaptobenzothiazole  $0.11 \mu\text{g L}^{-1}$ ; Cyclamate  $0.10 \mu\text{g L}^{-1}$ ; Benzotriazole  $0.10 \mu\text{g L}^{-1}$ . The benzothiazoles most likely originate from tyre abrasion while the pesticide metabolites (Desphenyl-chloridazon; Methyl-desphenyl-chloridazon) most like originate from atmospheric deposition. The sweetener cyclamate might originate from littering (e.g. soda bottles) while the Melamines probably originate from plastics.

## 4 References

- Ahlbom, J., & Duus, U. (1994). *Nya hjulspår- en produktstudie av gummidäck (in swedish)* No. Report 6/94). Solna: Swedish Chemicals Agency.
- Alam, M. Z., Anwar, A. H. M. F., Sarker, D. C., Heitz, A., & Rothleitner, C. (2017). Characterising stormwater gross pollutants captured in catch basin inserts. *Science of the Total Environment*, 586, 76-86.
- Andersson, Å., & Sörme, L. (2004). *Substansflödesanalys – av alkylfenoler och alkylfenoletoxilater i Stockholms stad 2004 (substance flow analysis - of alkylphenols and alkylphenol in the city of Stockholm 2004)* (ISSN: 1653-9168)
- Aznar, A., Caprari, J., Meda, J., & Slutzky, O. (1997). Study of formulation variables of thermoplastic reflecting materials for traffic marking. *Journal of Coatings Technology*, 69(868), 33-38.
- Berg, G. A., Hunneman, H., & Langemeijer, H. D. (2009). *Emissie van verontreiniging door run-off en verwaaiing van dunne deklagen: Pilot noordoostpolder* No. A307104) Rijkswaterstaat, dienst Verkeer en Scheepvaart.
- Best, J. H. d., Vergouwen, A. A., & Schipper, P. N. M. (2002). Afstroming en verwaaiing bij provinciale wegen - literatuur overzicht Grontmij Advies & Techniek bv; Energionderzoek Centrum Nederland (ECN).
- Bläsing, M., & Amelung, W. (2018). Plastics in soil: Analytical methods and possible sources. *Science of the Total Environment*, 612, 422-435.
- Bocca, B., Forte, G., Petrucci, F., Costantini, S., & Izzo, P. (2009). Metals contained and leached from rubber granulates used in synthetic turf areas. *Science of the Total Environment*, 407(7), 2183-2190.
- Brandt, H., & De Groot, P. (2001). Aqueous leaching of polycyclic aromatic hydrocarbons from bitumen and asphalt. *Water Research*, 35(17), 4200-4207.
- Brongers, I. (2010). Jaarverslag 2009 monitoring WVOvergunning A27. The Netherlands: Rijkswaterstaat - Ministerie van Verkeer en Waterstaat.
- Bukowiecki, N., Gehrig, R., Lienemann, P., Hill, M., Figi, R., Buchmann, B., et al. (2009). PM10 emission factors of abrasion particles from road traffic Swiss Association of Road and Transportation Experts (VSS).
- Chan, D., & Stachowiak, G. (2004). Review of automotive brake friction materials. *Proceedings of the Institution of Mechanical Engineers Part D-Journal of Automobile Engineering*, 218(D9), 953-966.
- ChemRisk, L. L. C. (2011). TRWP global sampling project - Summary report. Pittsburgh, PA, USA: ChemRisk LLC.
- Conserva, V., & Dupont, M. (2011). Kraton polymers boost functional life of thermoplastic road marking paints Kraton Polymers LLC.

- Cruz M, Klein A, Steiner V (2016). Sustainability assessment of road marking systems. 6th Transport Research Arena April 18-21, 2016. Transportation Research Procedia 14 (2016) 869 – 875.
- Dahl, A., Gharibi, A., Swietlicki, E., Gudmundsson, A., Bohgard, M., Ljungman, A., et al. (2006). Traffic-generated emissions of ultrafine particles from pavement-tire interface. *Atmospheric Environment*, 40(7), 1314-1323.
- Dall'Osto, M., Beddows, D. C. S., Gietl, J. K., Olatunbosun, O. A., Yang, X., & Harrison, R. M. (2014). Characteristics of tyre dust in polluted air: Studies by single particle mass spectrometry (ATOFMS). *Atmospheric Environment*, 94, 224-230.
- Depaolini, A. R., Bianchi, G., Fornai, D., Cardelli, A., Badalassi, M., Cardelli, C., et al. (2017). Physical and chemical characterization of representative samples of recycled rubber from end-of-life tires. *Chemosphere*, 184, 1320-1326.
- Essel, R. (2014). Einsatzmengen von mikroplastik in der kosmetischen industrie und schätzung des eintrags aus anderen quellen. nova institute, köln 1st of july 2014” by sundt et al. (2014). Unpublished manuscript.
- Filip, P., Weiss, Z., & Rafaja, D. (2002). On friction layer formation in polymer matrix composite materials for brake applications. *Wear*, 252(3-4), 189-198.
- Grauert, M., Larsen, M., & Mollerup, M. (2011). Sedimentanalyser fra 70 regnvandsbassiner - fokus på miljøfremmede stoffer (analysis of sediments from 70 wet detention ponds - focus on micropollutants) No. 191 - 2011). Copenhagen, Denmark: The Danish Road Authority.
- Grauert, M., Larsen, M., & Mollerup, M. (2012). Quality of sediment in detention basins - mapping of the danish national road network. *Transport Research Arena 2012*, 48, 393-402.
- Grigoratos, T., & Martini, G. (2014). Non-exhaust traffic related emissions – brake and tyre wear PM (Type: EUR - Scientific and Technical Research Reports. Luxembourg: Publications Office of the European Union.
- Grung, M., Vikan, H., Hertel-Aas, T., Meland, S., Thomas, K. V., & Ranneklev, S. (2017). Roads and motorized transport as major sources of priority substances? A data register study. *Journal of Toxicology and Environmental Health-Part A-Current Issues*, 80(16-18), 1031-1047.
- Heitzman, M. (1992). Design and construction of asphalt paving materials with crumb rubber No. Transportation Research Record No. 1339). Washington, DC: Transportation Research Board.
- Hongkong Highways Department, (2016). Guidance notes on road markings. Resarch & Development Division, Hongkong Highways Department, RD/GN/036A
- Horton, A. A., Svendsen, C., Williams, R. J., Spurgeon, D. J., & Lahive, E. (2017). Large microplastic particles in sediments of tributaries of the river thames, UK - abundance, sources and methods for effective quantification. *Marine Pollution Bulletin*, 114(1), 218-226.

- Jambeck, J. R., Geyer, R., Wilcox, C., Siegler, T. R., Perryman, M., Andrady, A., et al. (2015). Plastic waste inputs from land into the ocean. *Science*, 347(6223), 768-771.
- Kaul, A. D. S., & Sharma, M. (2009). Traffic generated non-exhaust particulate emissions from concrete pavement: A mass and particle size study for two-wheelers and small cars. *Atmospheric Environment*, 43(35), 5691-5697.
- Kim, L., Kang, J., Kayhanian, M., Gil, K., Stenstrom, M., & Zoh, K. (2006). Characteristics of litter waste in highway storm runoff. *Water Science and Technology*, 53(2), 225-234.
- Kim, L., Kayhanian, M., & Stenstrom, M. (2004). Event mean concentration and loading of litter from highways during storms. *Science of the Total Environment*, 330(1-3), 101-113.
- KIM, M., YAGAWA, K., INOUE, H., LEE, Y., & SHIRAI, T. (1990). Measurement of tire tread in urban air by pyrolysis-gas chromatography with flame photometric detection. *Atmospheric Environment Part A-General Topics*, 24(6), 1417-1422.
- Kole, P. J., Lohr, A. J., Van Belleghem, F. G. A. J., & Ragas, A. M. J. (2017). Wear and tear of tyres: A stealthy source of microplastics in the environment. *International Journal of Environmental Research and Public Health*, 14(10), 1265.
- Kosto KB, Schall DC (2008). Low-temperature waterborne pavement markings paints: A road assessment of this low-VOC option. *JCT CoatingsTech*, July 2008
- Kreider, M. L., Panko, J. M., McAtee, B. L., Sweet, L. I., & Finley, B. L. (2010). Physical and chemical characterization of tire-related particles: Comparison of particles generated using different methodologies. *Science of the Total Environment*, 408(3), 652-659.
- Kukutschova, J., Moravec, P., Tomasek, V., Matejka, V., Smolik, J., Schwarz, J., et al. (2011). On airborne nano/micro-sized wear particles released from low-metallic automotive brakes. *Environmental Pollution*, 159(4), 998-1006.
- Kumata, H., Yamada, J., Masuda, K., Takada, H., Sato, Y., Sakurai, T., et al. (2002). Benzothiazolamines as tire-derived molecular markers: Sorptive behavior in street runoff and application to source apportioning. *Environmental Science & Technology*, 36(4), 702-708.
- Lassen, C., Hansen, S. F., Magnusson, K., Norén, F., Hartmann, N. I. B., Jensen, P. R., et al. (2015). Microplastics occurrence, effects and sources of releases to the environment in denmark environmental No. Denmark Environmental project No. 1793). Copenhagen, Denmark: The Danish Environmental Protection Agency.
- Lebreton, L. C. M., Van der Zwet, J., Damsteeg, J., Slat, B., Andrady, A., & Reisser, J. (2017). River plastic emissions to the world's oceans. *Nature Communications*, 8, 15611.
- LEE, Y., KIM, M., & WHANG, K. (1989). Simultaneous determination of natural and styrene butadiene rubber tire tread particles in atmospheric dusts by pyrolysis-gas chromatography. *Journal of Analytical and Applied Pyrolysis*, 16(1), 49-55.
- Li, X., Berger, W., Musante, C., & Mattina, M. I. (2010). Characterization of substances released from crumb rubber material used on artificial turf fields. *Chemosphere*, 80(3), 279-285.

- Liu, F., Olesen, K. B., & Vollertsen, J. (2018). Microplastic in stormwater ponds. in preparation. Unpublished manuscript.
- Lutz, H. (2017). Evaluation der gewässerbelastungen durch ableitungen von autobahnabwasser im bereich des zweckverbandes ARA untermarch. Wallisellen, Switzerland: AfU Schwyz Zweckverband ARA Untermarch Gemeinde Wangen.
- Majumdar, D., Rajaram, B., Meshram, S., Suryawanshi, P., & Rao, C. V. C. (2017). Worldwide distribution of polycyclic aromatic hydrocarbons in urban road dust. *International Journal of Environmental Science and Technology*, 14(2), 397-420.
- Mark, J. E., Erman, B., & Eirich, F. R. (Eds.). (1994). *The science of rubber compounding* (2nd ed.). San Diego: Academic Press.
- Markiewicz, A., Bjorklund, K., Eriksson, E., Kalmykova, Y., Stromvall, A., & Siopi, A. (2017). Emissions of organic pollutants from traffic and roads: Priority pollutants selection and substance flow analysis. *Science of the Total Environment*, 580, 1162-1174.
- Mathissen, M., Scheer, V., Vogt, R., & Benter, T. (2011). Investigation on the potential generation of ultrafine particles from the tire-road interface. *Atmospheric Environment*, 45(34), 6172-6179.
- Milani, M., Pucillo, F., Ballerini, M., Camatini, M., Gualtieri, M., & Martino, S. (2004). First evidence of type debris characterization at the nanoscale by focused ion beam. *Materials Characterization*, 52(4-5), 283-288.
- Norén, F., & Naustvoll, L. -. (2010). Survey of microscopic anthropogenic particles in skagerrak No. TA, 2779). Oslo, Norway: Klima- og forurensningsdirektoratet Norge.
- Olesen, K. B., Alst, N. v., Simon, M., Vianello, A., Liu, F., & Vollertsen, J. (2017). Analysis of microplastics using FTIR imaging (Application Note No. Publication number: 5991-8271EN) Agilent Technologies.
- Pan, S., Sun, Y., Zhang, G., Li, J., Xie, Q., & Chaktaborty, P. (2012). Assessment of 2-(4-morpholinyl) benzothiazole (24MoBT) and N-cyclohexyl-2-benzothiazolamine (NCBA) as traffic tracers in metropolitan cities of china and india. *Atmospheric Environment*, 56, 246-249.
- Panko, J. M., Chu, J., Kreider, M. L., & Unice, K. M. (2013). Measurement of airborne concentrations of tire and road wear particles in urban and rural areas of france, japan, and the united states. *Atmospheric Environment*, 72, 192-199.
- Rhodes, E. P., Ren, Z., & Mays, D. C. (2012). Zinc leaching from tire crumb rubber. *Environmental Science & Technology*, 46(23), 12856-12863.
- Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G., & Simoneit, B. R. T. (1993). Sources of fine organic aerosol .3. road dust, tire debris, and organometallic brake lining dust - roads as sources and sinks. *Environmental Science & Technology*, 27(9), 1892-1904.
- Russ, A., & Russ, E. (2006). *The composition of a tyre: Typical component No. Project code: TYR0009-02*. Oxon, UK: The Waste & Resources Action Programme.
- Saito, T. (1989). Determination of styrene butadiene and isoprene tire tread rubbers in piled particulate matter. *Journal of Analytical and Applied Pyrolysis*, 15, 227-235.



- Schmidt, C., Krauth, T., & Wagner, S. (2017). Export of plastic debris by rivers into the sea. *Environmental Science & Technology*, 51(21), 12246-12253.
- Seitz, W., & Winzenbacher, R. (2017). A survey on trace organic chemicals in a german water protection area and the proposal of relevant indicators for anthropogenic influences. *Environmental Monitoring and Assessment*, 189(6), 244.
- Selbes, M., Yilmaz, O., Khan, A. A., & Karanfil, T. (2015). Leaching of DOC, DN, and inorganic constituents from scrap tires. *Chemosphere*, 139, 617-623.
- Staples, C., Dorn, P., Klecka, G., O'Block, S., & Harris, L. (1998). A review of the environmental fate, effects, and exposures of bisphenol A. *Chemosphere*, 36(10), 2149-2173.
- Stephansen, D. A. (2014). Levels of environmental pollutants and their effects on aquatic ecosystems in wet detention ponds receiving stormwater runoff. Unpublished PhD, Aalborg University, Aalborg, Denmark.
- Sundt, P., Schulze, P. -, & Syversen, F. (2014). Sources of microplastics-pollution to the marine environment. Asker, Norway: Mepex Consult AS for Norwegian Environment Agency.
- Thorpe, A., & Harrison, R. M. (2008). Sources and properties of non-exhaust particulate matter from road traffic: A review. *Science of the Total Environment*, 400(1-3), 270-282.
- Tromp, K. (2005). Helofyteninfiltratiesystemen voor zuivering van wegwater - onderzoek naar het milieurendement van een helofyteninfiltratiesloot langs de A1 in 't gooi Ministerie van Verkeer en Waterstaat, wegendistrict Amsterdam, regio NoordHolland.
- Tromp, K., Lima, A. T., Barendregt, A., & Verhoeven, J. T. A. (2012). Retention of heavy metals and poly-aromatic hydrocarbons from road water in a constructed wetland and the effect of de-icing. *Journal of Hazardous Materials*, 203, 290-298.
- Unice, K. M., Kreider, M. L., & Panko, J. M. (2013). Comparison of tire and road wear particle concentrations in sediment for watersheds in france, japan, and the united states by quantitative pyrolysis GC/MS analysis. *Environmental Science & Technology*, 47(15), 8138-8147.
- Unice, K. M., Kreider, M. L., & Panko, J. M. (2012). Use of a deuterated internal standard with pyrolysis-GC/MS dimeric marker analysis to quantify tire tread particles in the environment. *International Journal of Environmental Research and Public Health*, 9(11), 4033-4055.
- Velsen, A. F. M. v. (1997). Bemonstering tunnelafstroomwater. Utrecht, The Netherlands: MTI Milieutechnologie.
- Verschoor, A., Poorter, L. d., Dröge, R., Kuenen, J., & Valk, E. d. (2016). Emission of microplastics and potential mitigation measures abrasive cleaning agents, paints and tyre wear. No. RIVM Report 2016-0026). Bilthoven, the Netherlands: National Institute for Public Health and the Environment, The Netherlands.
- Vollertsen, J., Astebol, S. O., Coward, J. E., Fageraas, T., Nielsen, A. H., & Hvitved-Jacobsen, T. (2009). Performance and modelling of a highway wet detention pond designed for cold climate. *Water Quality Research Journal of Canada*, 44(3), 253-262.

- Wahid, S. M. S. (2018). Automotive brake wear: A review. *Environmental Science and Pollution Research*, 25(1), 174-180.
- Wik, A., & Dave, G. (2009). Occurrence and effects of tire wear particles in the environment - A critical review and an initial risk assessment. *Environmental Pollution*, 157(1), 1-11.
- Willis, K., Hardesty, B. D., Kriwoken, L., & Wilcox, C. (2017). Differentiating littering, urban runoff and marine transport as sources of marine debris in coastal and estuarine environments. *Scientific Reports*, 7, 44479.
- Yamaguchi, T., Yamazaki, H., Yamauchi, A., & Kakiuchi, Y. (1995). Analysis of tire tread rubber particles and rubber additives in airborne-particulates at a roadside. *Japanese Journal of Toxicology and Environmental Health*, 41(2), 155-162.
- Zhang, J., Hua, P., & Krebs, P. (2017). The influence of surface pavement on the distribution of polycyclic aromatic hydrocarbons (PAHs) in urban watershed. *Water Air and Soil Pollution*, 228(9), 318.