

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Colloidal Organic Pollutants in Road Runoff: Sources, Emissions and Effective  
Treatment Technologies

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Cover: Conceptual image of emulsions identified in road runoff

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## ABSTRACT

Thousands of organic substances circulate in our society and are diffusely emitted through traffic, combustion and leaching from constructions and building materials into the urban environment. The research in this PhD thesis focuses on road runoff as the highest concentrations of pollutants are frequently found in runoff from areas with high traffic intensity. Many organic pollutants (OPs) emitted from vehicles and traffic-related activities exhibit environmental persistence and a tendency to bioaccumulate and may have detrimental long-term effects on aquatic life. Road runoff contains a cocktail of both particulate and non-particulate OPs. Hydrophobic OPs such as higher petroleum hydrocarbons, phthalates, and polycyclic organic hydrocarbons (PAHs) are not exclusively bound to particles, but also present in runoff in colloidal and truly dissolved forms. These hydrophobic compounds can also form nano- and microsized emulsions that may carry pollutants in stormwater. Hence, it is of great importance to develop treatment technologies that can remove non-particulate OPs from contaminated stormwater. The overall aim of this PhD research was to evaluate the best options to manage the colloidal fraction of OPs in road runoff, including road dust, water and sediments. The research also included to study the sources, emissions and the transport processes of OPs in road runoff.

In Paper I approximately 1100 compounds were chosen for further studies after comprehensive screening and assessment. The results of the developed iterative selection process used for identifying and selecting priority pollutants in urban road environments showed the following priority order: PAHs > aliphates C<sub>20</sub>–C<sub>40</sub> > alkylphenols > phthalates > aldehydes > phenolic antioxidants > bisphenol A > oxygenated-PAHs > naphtha C<sub>5</sub>–C<sub>12</sub> > amides > amines. Among these, PAH-16 were chosen for a substance flow analysis (SFA), which was performed for a highway case study area. The SFA showed that the main sources of PAHs emitted in the area were vehicle exhaust gases, followed by tyre wear, motor lubricant oils, road surface wear, and brake linings. Only 2–6% of the total 5.8–29 kg/ha annually emitted PAHs end up in the stormwater sewer system.

Particle size distribution and zeta potential measurements was performed on simulated road runoff, using laboratory prepared mixtures of ultrapure water and specific OPs with and without addition of humic acid and iron colloids (Paper II). The aim was to provide an understanding of the transport routes of OPs in the environment, and to determine whether OPs are transported with nano- and microparticles in the form of emulsions. The following simulation mixtures were identified as potential emulsions: diesel (aliphates); alkylphenols (APs) and their ethoxylates (APEOs); diesel with APs and APEOs; phthalates, and a mixture of all OPs

(including PAH-16) with and without colloids. Most of the particles in the samples were found in the nano-range of 30–660 nm, and a smaller portion of particles <28% were found to be micro-sized.

In Paper III the potential of street sweeping to reduce the amounts of OPs and nano/microparticles reaching stormwater was investigated in a case study that included sampling road dust and washwater from a street sweeping machine, road dust before and after sweeping, and stormwater. The compound groups generally found in the highest concentrations in all matrices were aliphates  $C_5$ – $C_{35}$  > phthalates > aromates  $C_8$ – $C_{35}$  > PAH-16. The concentrations of aliphates  $C_{16}$ – $C_{35}$  and PAHs in washwater were extremely high at  $\leq 53,000$   $\mu\text{g/L}$  and  $\leq 120$   $\mu\text{g/L}$ , respectively, and the highest concentrations were found after a 3-month winter break in sweeping. The washwater contains a wide range of small particles, including nanoparticles in sizes from just below 1 nm up to 300 nm, with nanoparticles in the size range 25–300 nm present in the highest concentrations.

The design of an experimental car wash and subsequent laboratory analysis with a focus on OPs and particle size distributions was performed in Paper IV. The car wash experiment simulated high and a low intensity rain and carwash using conventional and eco-friendly detergents. Per driven km phthalates were emitted by 0.10–0.40  $\mu\text{g}$ , aliphates by 0.020–0.60  $\mu\text{g}$  and PAH-16 by  $2.5 \times 10^{-4}$ – $2.5 \times 10^{-3}$   $\mu\text{g}$ , and were the OPs emitted in largest amounts from all cars. The dominant phthalate was the high molecular weight di-iso-nonylphthalate (DINP) quantified up to 640  $\mu\text{g/L}$ . Nanoparticles in the size range 10–450 nm were also released in large amounts from the cars and the waters contained up to  $3.3 \times 10^6$  of particles per liter.

In Paper V a pilot plant using column bed-filters of sand as a pre-filter, in combination with sorption filters of granulated activated carbon, *Sphagnum* peat or *Pinus sylvestris* bark, was used to investigate the removal of non-particulate OPs from urban stormwater. Samples from the filter effluents were collected weekly; during or after rain events; and during stress tests when incoming water was spiked with contaminated sediment and petrol or diesel. All sorption filters showed efficient reduction of aliphatic diesel hydrocarbons  $C_{16}$ – $C_{35}$ , benzene, and the PAHs phenanthrene, fluoranthene, and pyrene during most of the operation time, which was 18 months. During the stress test events, all sorption filters showed 100% reduction of PAH-16, petrol and diesel aliphates  $C_5$ – $C_{35}$ .

The following recommendations are suggested to prevent further spread of OPs and nanoparticles to the urban environment: (1) Frequent street sweeping of the most polluted streets in urban areas should be introduced as soon as possible; (2) Frequent washing of vehicles in urban areas should be mandatory, especially during winter when emissions of exhaust gases and vehicle wear are greatest; (3) The final step for treating highly polluted stormwater must contain sorption filters to effectively remove OPs and especially OPs in colloidal forms. Future research should perform multi-criteria decision analyses to compare the treatment options studied in this research with other options to find the most sustainable solutions to remove OPs and nanoparticles from stormwater.

Keywords: stormwater, road runoff, colloids, organic pollutants, microparticles, nanoparticles, emulsions, sorption filters, street sweeping, vehicle wash, washwater, road dust, sweepsand.

## LIST OF PUBLICATIONS

This thesis is based on the work in the following papers:

- I. Markiewicz, A., Björklund, K., Eriksson, E., Kalmykova, Y., Strömvall, A-M., and 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. doi:[10.1016/j.scitotenv.2016.12.074](https://doi.org/10.1016/j.scitotenv.2016.12.074)
- II. Markiewicz, A., Strömvall, A-M., Björklund, K., and Eriksson, E. (2019). Generation of nano- and micro-sized organic pollutant emulsions in simulated road runoff. *Environment International* **133**. doi:[10.1016/j.envint.2019.105140](https://doi.org/10.1016/j.envint.2019.105140)
- III. Polukarova, M., Markiewicz, A., Björklund, K., Strömvall, A-M., Galfi, H., Andersson-Sköld, Y., Gustafsson, M., Järskog, I. and Aronsson, M. (2020). Organic pollutants, nano- and microparticles in street sweeping road dust and washwater. *Environment International* **135**, 105337. doi:[10.1016/j.envint.2019.105337](https://doi.org/10.1016/j.envint.2019.105337)
- IV. Markiewicz, A., Björklund, K. and Strömvall, A-M., (2020). Emissions of Organic Pollutants, Nano- and Microparticles from Vehicles during Rain and Car Wash Simulations. *Manuscript*.
- V. Markiewicz, A., Strömvall, A-M. and Björklund, K. (2020). Alternative sorption filter materials effectively remove non-particulate organic pollutants from stormwater. *Science of the Total Environment* **730**, 139059. doi:[10.1016/j.scitotenv.2020.139059](https://doi.org/10.1016/j.scitotenv.2020.139059)

Anna Markiewicz contribution the scientific papers:

Paper I: Participation in planning of the study, data collection, analysis and assessment of the data, wrote most parts of the paper, editing and revising after consultation with co-authors and external review.

Paper II: Participation in planning of the study, experimental work, analysis and assessment of the data, wrote most parts of the paper, editing and revising after consultation with co-authors and external review.

Paper III: Participation in planning of the study, help in experimental work, analysis and assessment of the data, wrote minor parts of the paper, co-editing and revising after consultation with co-authors and external review.

Paper IV: Participation in planning of the study, design and execution of experimental work, analysis and assessment of the data, wrote most parts of the paper, editing and revising after consultation with co-authors and external review.

Paper V: Participation in experimental work, analysis and assessment of the data, wrote most parts of the paper, editing and revising after consultation with co-authors and external review.

The author has contributed to the following work and publications, which are not appended to the thesis:

Järllskog I., Strömvall A-M., Magnusson K., Galfi H., Björklund K., Polukarova M., Garção R., Markiewicz A., Aronsson M., Gustafsson M., Norin M., Blom L. and Andersson-Sköld Y. (2020) Spreading of microplastic particles and pollutants from traffic in an urban area under construction. Under publication.

Polukarova M, Strömvall A-M., Järllskog I., Galfi, H., Magnusson K., Markiewicz A., Andersson-Sköld Y., Aronsson M., Gustafsson M., Garcao R., Norin M. and Blom L. (2020) Characterisation and Transport of Tyre and Bitumen Microplastics and Polycyclic Aromatic Hydrocarbons in Road Dust and Runoff SETAC Europe 30<sup>th</sup> Annual Meeting, Dublin Ireland.

Markiewicz, A., Björklund B. and Strömvall, A-M. (2017) A pilot study of sorption filters to remove non-particulate organic pollutants in stormwater, 14th IWA/IAHR Int Conf on Urban Drainage, Prague, Czech Republic

Wilén B-M., Markiewicz A. and Nilsson Å. (2010) Variation in dissolved oxygen concentration and its effect on the activated sludge properties studied at a full-scale wastewater treatment plant. In the proceedings of IWA World Water Congress & Exhibition, 19-24 September 2010 in Montreal

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# 1. INTRODUCTION

## 1.1 Background

Urbanization has contributed to degraded surface water quality, where inadequate stormwater management and pollution control have played an important role. Many environmental pollutants are transported from urban areas to receiving waters via surface runoff. Emissions of pollutants such as metals, organic pollutants (OP), and particles are particularly high in highly trafficked areas (Andersson-Sköld 2020, Björklund 2011, Hilliges et al. 2016, Huber et al. 2016, Müller et al. 2020). Stormwater management in urban areas has moved from quantity control and combined sewers to current strategies for quantity and quality source control, with an emphasis on the multiple benefits provided by blue-green infrastructure (Eckart et al. 2017). These stormwater management strategies have led to expanded opportunities and development of various technologies used to treat stormwater locally (Ellis and Lundy 2016). However, only a few percent of the stormwater generated in our urban environment is treated, and the treatment systems available today are not designed to effectively remove all pollutants. Therefore, research supporting development of more effective technologies and management strategies is urgently needed to meet the demands on a sustainable development of the urban environments.

The occurrence of OPs in the environment is a result of continuous increase in industrial production, combustion, traffic, farming and other human activities over the past decades. Organic pollutants are either unintentional by-products released into the environment, for example through combustion processes, or intentionally produced industrial chemicals. Many OPs are persistent to degradation, capable of bioaccumulation in fat tissue, and could travel long distances through water-air-soil systems and cause negative effects on animal and human health (UN-ECE 1998a). Apart from the most volatile substances, OPs emitted from nonpoint sources will settle on urban surfaces and subsequently be washed off by stormwater, into sewer systems and receiving waters. Particles arising from processes such as erosion, wear and tear of tyres, road surfaces and building materials are also of concern as these particles may contain substances subject to leaching, for example phthalates from PVC, alkylphenols from e.g. concrete and plastics (Björklund 2010, Lamprea et al. 2018) or PAHs and other organic chemicals leaching from tyre and road wear particles (Andersson-Sköld 2020, Kalbe et al. 2013, Unice et al. 2015), but also because many dissolved stormwater contaminants have an affinity for particles.

In the past years, OPs, including the most hydrophobic compounds, were shown to be present in dissolved and colloidal forms in stormwater, which suggests that the mobility, and consequently the toxicity and associated risks of the compounds, are potentially higher than previously assumed (Kalmykova et al. 2013). It has also been shown that the development of advanced stormwater treatment facilities will be necessary for retention of these forms of OPs (Kalmykova et al. 2014, Nielsen 2015). Indeed, the urban runoff quality is recognized as one of the most significant pressures on aquatic ecosystems worldwide (McGrane 2016). For this reason, it is vital that the dominant sources of OPs in urban areas are identified as this will

allow actions to be taken to improve surface water quality through control of the sources of emissions and ensure compliance with legal regulations and water quality standards, such as the European Water Framework Directive (EU 2000) and the American Clean Water Act (EPA 2002).

## 1.2 Aim and objectives

Traffic has been identified as one of the main sources of organic pollutants (OPs) in urban areas. Research findings show that a large part of the OPs is bound to nanoparticles such as colloids and/or emulsions, hence efficiently transported with the water phase in road runoff. This thesis describes research on evaluating the best options to manage the colloidal fraction of OPs in road runoff, including road dust, water and sediments.

The specific objectives of this thesis/research were to:

- Identify and quantify uses, sources, emissions and flows of selected OPs from vehicles, fuels, exhausts and road construction materials.
- Clarify generation and transportation processes of colloidal OPs in road-runoff, as this will highly affect treatment options.
- Investigate the efficiency of street sweeping and car wash for effective removal of OPs from vehicles in urban areas.
- Investigate the efficiency of alternative sorption filters for the removal of OPs from stormwater in pilot-plant studies.
- Suggest the best solutions for limiting the spread and removing OPs from roads and road runoff.

The result will be used as a basis for applicable preventative actions for pollution of OPs in urban areas, and for re-thinking treatment techniques for efficient removal of OPs, with emphasis on the colloidal fraction.

## 1.3 Thesis outline

The thesis is based on five papers appended and numbered as Paper I – V (Fig. 1). In Paper I, the sources, emissions and transport routes of OPs in the road and traffic environment is researched. In this paper, a model to prioritise and select OPs for further studies was developed. A substance flow analysis was also performed for polycyclic aromatic hydrocarbons (PAHs) in a highly trafficked case study area. In Paper II, the aim was to determine whether OPs are transported with nano- and microparticles in the form of emulsions. This research provides an understanding of the transport routes of OPs in the environment. Organic pollutants, nano- and microparticles in street sweeping road dust and washwater were identified in Paper III. The potential of street sweeping as a source control to reduce the amounts of OPs and nano/microparticles reaching stormwater was investigated in a case study. In paper IV, it was researched how carwash may contribute to reduced emissions of nanoparticles and OPs to road runoff. The aim was also to investigate how much of OPs that accumulate on cars during driving in the winter and how much of the sorbed pollutants that is rinsed off with precipitation. A pilot plant using column beds of sand as a pre-filter, in combination with sorption filters with

granulated activated carbon, *Sphagnum* peat or *Pinus sylvestris* bark, was used to investigate the removal of non-particulate OPs from urban stormwater in Paper V.

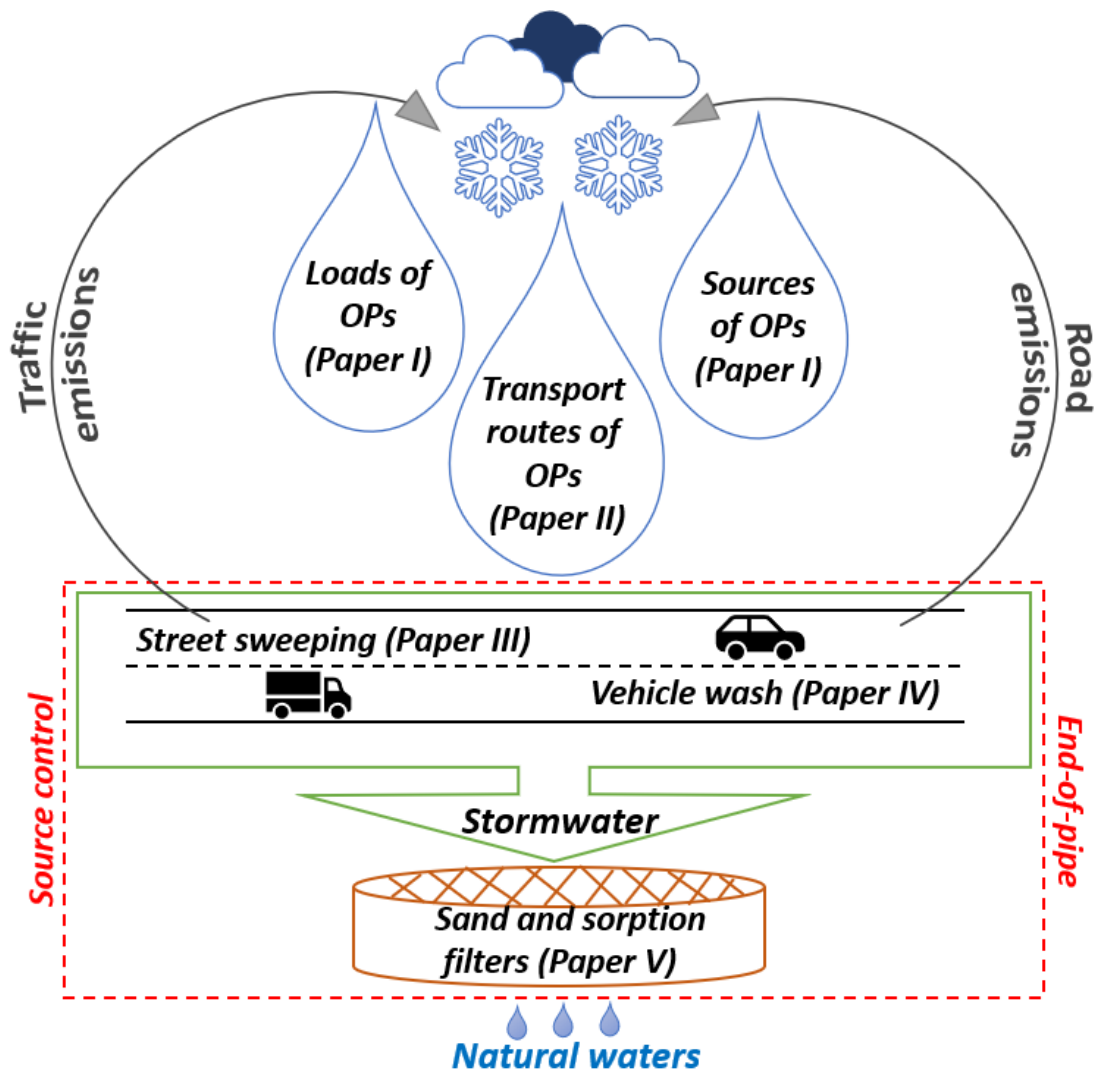
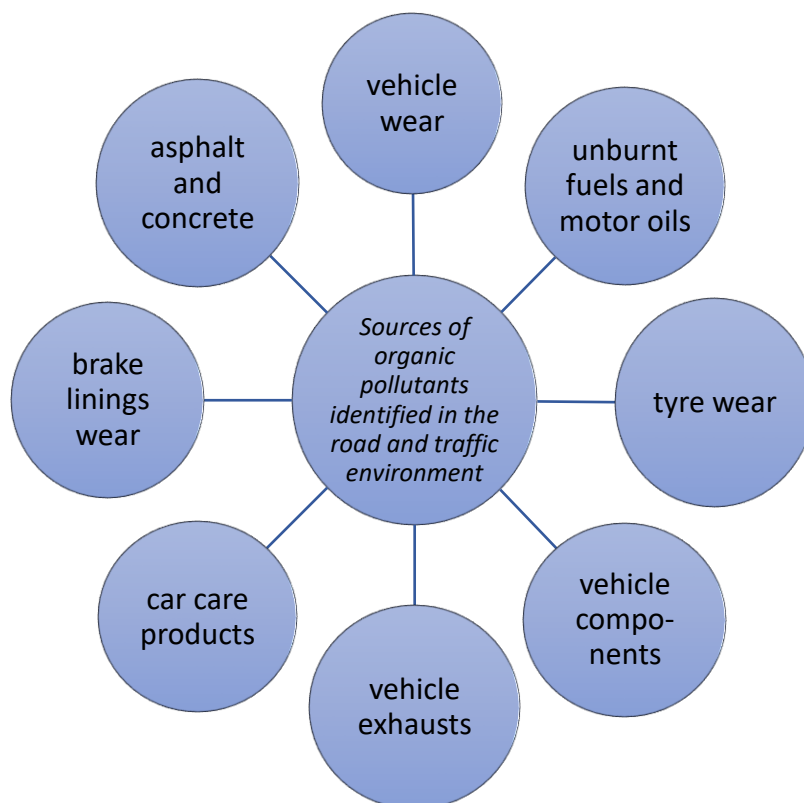


Fig. 1. Schematic presentation of the various part of the research in this thesis in the context of stormwater management.

## 2. THEORETICAL BACKGROUND

### 2.1 Sources of organic pollutants in road runoff

In Figure 2, the specific sources of organic pollutants identified in the road and traffic environment are presented, also see Paper I. The sources include vehicle parts, vehicle exhausts, asphalt and concrete materials, unburnt fuels and motor oils and car care products.



**Fig.2.** Sources of organic pollutants identified in the road and traffic environment (**Paper I**).

The composition of tyre rubber is complex, and often depends on quality demands as well as the vehicle for which it is designed. **Tyres** are believed to be a major source of OPs in road runoff; a broad spectrum of toxic and harmful substances are released as tyres wear (Andersson-Sköld 2020, Järleskog et al. 2020, Rogge et al. 1993). Several studies have confirmed the content of toxic additives used in the production process to enhance tyre performance and stability. Examples include PAHs-containing highly aromatic (HA) oils used as softeners, and plasticizing phthalates or alkylphenols (APs) and their ethoxylates (AP/EOs) for aging protection (Ahlbom and Duus 1994, Källqvist 2005, Marcus 2006). Since 2010, European legislation restricts the use of HA oils in rubber processing, which may lead to future reductions in PAHs emissions (Andersson et al. 2006). Tyres containing HA-oils may still exist on Swedish roads, due both to a delay in tyre replacement and to rubber recycling and international transport (ETRMA 2010, 2011).

**Brake linings** of a vehicle are subjected to high friction heat during forced deceleration, which leads to lining wear. The wear, composed of particles containing various chemicals, is released into the environment (Bukowiecki et al. 2009, Warner et al. 2000). Approximately 35% of the brake component mass loss is emitted as airborne particulate matter (Garg et al. 2000). The most abundant organic compounds identified in brake lining dust are polyglycol ethers, used mainly in hydraulic fluids. Other compounds found in trace amounts in the lining dust include alkanes, alkanolic acids, PAHs, oxy-PAHs, benzaldehydes, benzoic acids, and oleic acids (Rogge et al. 1993).

External polymeric materials used in e.g. bumpers, mudguards or bodywork parts of vehicles are susceptible to extensive wear. Plastic elements of **vehicle body parts** may contain phthalates, phenols, PAHs or amines (Nielsen et al. 2000), and lacquers and paints may contain phthalates or phenols (Hoffmann 1996, Johansson et al. 2000). Emissions may increase in summer as the release of e.g. phthalates from plastic components strongly depends on temperature. Polymeric materials are widely used in the automobile industry to enhance appearance and increase cost effectiveness due to lower fuel consumption, and there has been a significant increase in their use over the past decades.

Car care products, used e.g. for car cleaning, polishing, and detailing, contain a cocktail of different chemicals. Products intended for protection and preservation of lacquered vehicle surfaces are sources of AP/EOs, an abundant group of **detergent chemicals**. In addition, cleaning agents, grease or wax are sources of substances such as phthalates, APs/EOs and naphtha residues (Andersson and Sörme 2004a, Björklund et al. 2007, Johansson et al. 2000).

**Fuel and exhausts emissions** make up a sizeable proportion of the on-road emissions of organic pollutants. In the US EPA studies on mobile exhaust and evaporative emissions, over 1,000 OPs were recorded (EPA 2006). Identified organic compounds in diesel and gasoline exhausts are e.g. (n-, branched, cyclo-) alkanes and alkenes; aromatic hydrocarbons including PAHs and oxy-PAHs; biomarkers such as steranes, hopanes, terpanes; aldehydes and ketones; and alkanolic, alkanedioic, aromatic and benzoic acids (Brewer et al. 2013, Fingas 2016, Rogge et al. 1993). In addition to petroleum hydrocarbons, oil and lubricant spills are also sources of phenols, e.g. bisphenol A (BPA) and AP/EOs used as fuel additives or in hydraulic fluids (Ahlbom and Duus 1992, Johansson et al. 2000). Antioxidants including 2,6- and 2,4-di-tert-butylphenols are used as lubricants in the petroleum industry or as additives in hydraulic oil (Remberger et al. 2003).

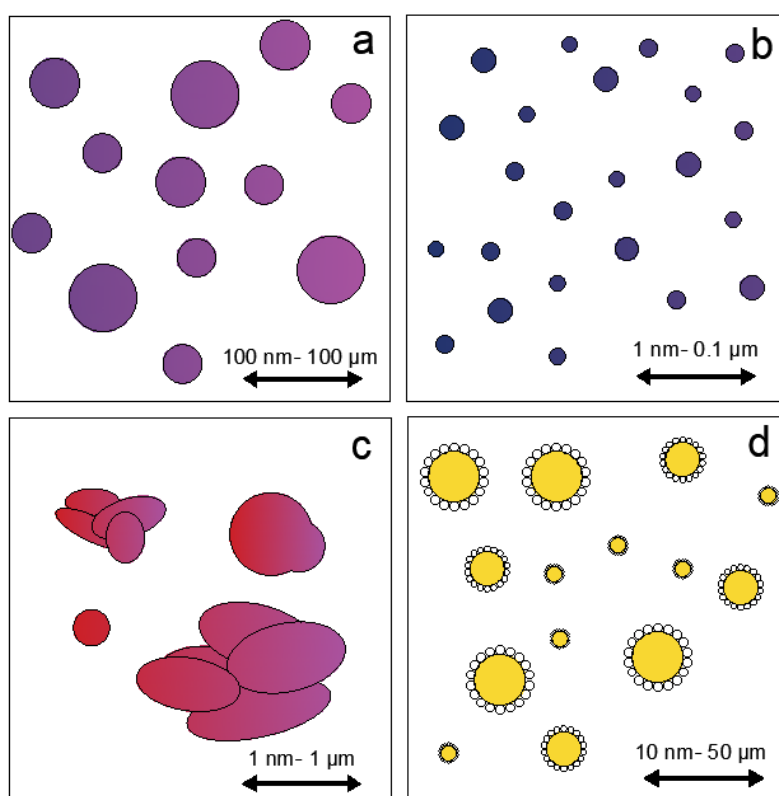
Abrasion of **road materials** is an important source of emissions of organic pollutants in road environments. Road wear depends strongly on factors such as traffic characteristics, use of studded tyres, the material's susceptibility to abrasion, and weather conditions (Andersson-Sköld 2020, Klint 2001b). The production of asphalt involves supplementation with additives; in recent years the proportion of these additives has increased, to meet higher demands for resistance and durability (Andersson et al. 2006). The most common additives include liquid and mineral adhesives, such as amines and amides; polymers like elastomers and plastomers; synthetic wax; and fibres (Huntsman 2007, Morgan et al. 2013, NVF 2006), but also recycled

tyre granules, which are a source of phthalates and PAHs (Burstyn et al. 2000, Chauhan et al. 2012, Klint 2001a, Källqvist 2005).

**Concrete pavement** materials contain various additives and admixtures such as water reducers and accelerators, air-entraining, water-proofing and de-foaming agents (Rixom and Mailvaganam 1986). Some of these admixtures are based on organic substances like sodium thiocyanate, resin acids and nonylphenol ethoxylate, of which all have been proven to be susceptible to leaching (Togerö 2006).

**Road paint** is heavily exposed to abrasion, why it needs to be renewed every 5–10 years. Road marking products consist of plastic polymers, pigments, fillers, and additives (Andersson-Sköld et al. 2020). Alkylphenol ethoxylates, phthalates, and alkyd resins are present in road paint components, such as emulsifiers, gradation agents and hardeners (Andersson and Sörme 2004b, Aznar et al. 1997, Babić et al. 2015). According to ECB (2002) typical paint mixtures can contain up to 3% of nonylphenol ethoxylates.

## 2.2 Partitioning, sorption and transport of organic pollutants and particles



**Fig. 3.** a) Microparticles 100 nm – 100 μm, b) nanoparticles 1 nm – 0.1 μm , c) colloids 1 nm – 100 μm, d) nano- and microemulsions 10 nm – 50 μm (water in oil (W/O)).

## Partitioning

In this research micro- and nanoparticles are in focus as well as organic pollutants (OPs) partitioning to particles, colloids, emulsions or dissolved phases, as these forms have shown to lower settling velocities and enhance transport of pollutants with stormwater into receiving waters (Paper II, Nielsen et al. 2015). Partitioning of environmental pollutants is a common chemical process occurring in aquatic environments and is defined as the distribution of chemical substances between two phases, as for example in stormwater between suspended particulate matter and the liquid phase (Zgheib et al. 2011).

## Sorption processes

Several field and laboratory studies have reported on the use of various filter materials for stormwater treatment. Studied filter materials originated from waste products, minerals and plant based materials, such as fly-ash-amended sand for phosphorus removal (Zhang et al. 2008a). The studies were also conducted on perlite-volcanic glass to reduce loads and concentrations of suspended solids (Gironás et al. 2008), charcoal, clay minerals, zeolites, coconut fiber, pine bark to remove persistent OPs (Björklund and Li 2015, Nageeb 2013) and /or biochar-plant based biomass effective in removing metals, hydrophobic nutrients, and pathogens from stormwater (Ashoori et al. 2019, Mohanty et al. 2018).

Sorption involves both physical and chemical processes where molecules are attached to the sorption material. Sorption includes several basic processes as absorption, adsorption and ion exchange. *Absorption* means that the pollutants, such as OPs in stormwater, are incorporated into the absorbent through partitioning, and later dissolves or permeates into it. Absorption involves the whole volume of the sorption material. *Adsorption* means that the adsorbate, such as OP molecules, are physically adhering or bonding to the surface of the adsorbent. Adsorption may be physisorption by weak van der Waals forces, chemisorption through covalent bonding to the surface material or electrostatic attractions. *Ion exchange* is a process where ions exchange between the ions in a solution and complexes on the adsorbent. Ion exchange is not a common process for sorption of OPs as these molecules are electrically neutral. For this reason, the focus in this thesis is on adsorption and absorption. Desorption means the reverse process, where OP molecules leave the material by reversed absorption, adsorption and ion-exchange.

Sorption processes can be studied through collection of equilibrium data for the amounts of contaminants in the water versus the amounts in filter media (Allen et al. 2004). Equilibrium refers to a balanced state achieved in sorption systems when sorption and desorption occur at the same rate (Chowdhury and Saha 2012, Kalmykova 2009). This means that at equilibrium, the sorption and desorption take place at the same rate and no further uptake of the OPs occur. When equilibrium is reached, the sorption process is optimal and complete. The adsorption of molecules is often described through isotherms, where the amount of adsorbate on the adsorbent are described as a function of the adsorbate concentration in water, and in the literature, it can be found a plethora of different isotherm models (Chowdhury and Saha 2012, Foo and Hameed 2010). To construct an isotherm, several equilibrium points must be acquired experimentally by conducting batch tests on the adsorbent where either the amount of adsorbent changes or the concentration of adsorbate in the water changes.

The sorption processes in filter columns are more complex compared to the processes in batch studies (Lamichhane et al. 2016, Patel 2019). Parameters such as initial adsorbate concentrations, flow rate of adsorbate in the column, bed height, pH of adsorbent and adsorbate, particle size distribution, temperature and breakthrough curves are relevant to study to understand column sorption and leaching. It is also of interest to study the adsorbent capacity, adsorbent lifetime, and regeneration time using adsorption dynamics acquaintance and modelling. The sorption processes of OPs become also very complex in real life stormwater samples as it also depends on among others on the composition of the cocktails of pollutants, occurrence of emulsions, nano- and microparticles and iron and humic acid colloids.

### **Particles**

Particles (Fig. 3a, b) arise from processes such as erosion, wear and tear of tyres, vehicle parts, road surfaces and other construction materials in the urban environment (Paper III, Andersson-Sköld 2020, Peikertova and Filip 2015, Wagner et al. 2018). Particles may act as carriers for many pollutants by attracting chemical compounds to their surface (Sansalone and Kim 2008). Several studies have focused on the characterization of particulate matter occurring in stormwater, and the partitioning of associated pollutants such as metal species, inorganic and organic compounds (Kalmykova et al. 2013, Nielsen 2015, Wei et al. 2013, Zgheib et al. 2011, Zhang et al. 2008b). Various sources of stormwater contamination contribute to a high level of heterogeneity of particulate matter, often ranging vastly in size from <100 nm (Nielsen 2015) to >10 mm (Grant et al. 2003, Sansalone and Kim 2008), as well in shape, composition (Enroth et al. 2016, Grant et al. 2003), specific surface area and surface charge (Marsalek 2014). In this research partitioning/sorption has been analysed to clarify whether pollutants emerge as dissolved or sorbed to colloidal and particulate phases, with the aim of determining their fate and suitability for removal through treatment techniques (Paper II – V).

### **Colloids**

The terms colloid (Fig. 3c) and emulsion are sometimes used interchangeably, but in this thesis the term emulsion is used when both the dispersed and the continuous phases are liquids. If one of the phases is solid, the particle is called colloid. Colloids are ubiquitous in the environment and are composed of for example clay minerals, oxyhydroxides of iron and organic matter, including humic and fulvic acids (Genç-Fuhrman et al. 2016, Kretzschmar and Sticher 1997). Partitioning of pollutants to iron and humic colloids, investigated in this research (Paper II), is most probably only one of many fate mechanisms occurring in stormwater.

### **Emulsions**

The principle of emulsion formation is the mixing of two immiscible liquids in the presence of energy input and/or surfactants, solid particles or other stabilising agents. Emulsions can be divided according to the size of the droplets: (1) macroemulsions, usually within the range 0.5–50 µm; (2) nanoemulsions or microemulsions, with droplet sizes in the range 10–500 nm (Burguera and Burguera 2012) (Fig. 3d). Unlike nanoemulsions, microemulsions are thermodynamically stable (Tong et al. 2016), and occur when the system is in its lowest energy state, or in chemical equilibrium with its environment. Mixtures of water and oil are usually not stable, as droplets of both phases tend to merge and are susceptible to several breakdown processes (Tadros 2013).

## 2.3 Organic pollutants and environmental quality guidelines

### **Organic pollutants**

In this thesis, the focus is on organic pollutants (OPs) that are released into the road and traffic environment. The reason for studying OPs is because these compounds may be persistent and resistant to degradation in the environment. The persistence is related to the water solubility of the compounds and the high persistent compounds are non-polar with high lipophilicity. These compounds, if bioavailable, can be taken up into living organisms and bioaccumulated in fatty tissues, thus resulting in higher concentrations in the living organism than in the surrounding environment. In this way, the pollutants in living organisms can increase in concentrations through a food change from prey to predator in a process called biomagnification. One way to predict accumulation in living organisms is to determine the pollutants octanol-water partition coefficient  $K_{OW}$  and bioconcentration factor (BCF). If the  $\log K_{OW}$  value is between 5 and 8, the compound has a high bioaccumulation potential (Amiard-Triquet et al. 2011, ECETOC 2000). If less than 5, the compound is mostly water-soluble and if higher than 8, the compound is nearly impossible to dissolve in water and probably also the molecule is too large to be transported through biological membranes of organisms. In this study, most of the OPs have a high  $\log K_{OW}$  value (Table 1) and can therefore be potential accumulated in living organisms. If these compounds are taken up in living organisms, they can cause very serious damage, i.e. they are toxic, and can cause, for example, hormone disrupting effects, adverse effects on the organism nervous systems and immune systems, be carcinogenic (Kalyoncu et al. 2009, UNECE 1998a, Wahlang et al. 2019).

### **Stormwater quality guidelines**

Industrialized countries often have developed environmental quality guidelines for protection of the natural environment. Guidelines focusing on the protection of aquatic life can be general and international such as EU law setting Environmental quality standards applicable to surface water in Europe or the US EPA for aquatic life ambient water quality criteria. Guideline values for pollution of stormwater is missing. However, there are also more specific recommendations for prevailing conditions in some countries, such as for example national guidelines e.g. Canadian water quality guidelines for the protection of aquatic life, Danish environmental quality guidelines for inland surface waters or Canadian and Swedish sediment and soil quality guidelines (Table 1). The international and national environmental standards are tools to achieve the long-term objectives for good status of natural resources, by establishing the maximum permissible concentration of a pollutant in air, soil or water below which the risk of adverse effects on living organisms and the environment is acceptable. Guidelines are generally determined by using ecotoxicological data such as e.g. Henry's law constant ( $K_H$ ), the soil or aquatic particle water partition coefficient normalized to organic carbon ( $K_{OC}$ ), degradation half-life ( $T_{1/2}$ ), bioaccumulations concentration factor (BCF) and toxicity parameters such as half maximal effective concentrations ( $EC_{50}$ ) or median lethal dose ( $LC_{50}$ ) (Paper I) derived from experiments with aquatic organisms (Nugegoda and Kibria 2013).

**Table 1.** Environmental quality guidelines for organic pollutants in water and sediment.

Compounds	Guidelines/ physicochemical parameters	Water quality guidelines for the protection of aquatic life – freshwater (µg/L) <sup>a</sup> (Canadian)	General environmental quality guidelines (EQS) for inland surface waters (µg/L) <sup>b</sup> (Danish)	General guidelines for contaminated soil with sensitive land use (mg/kg of dry weight) <sup>c</sup> (Swedish)	Sediment quality guidelines for the protection of aquatic life-freshwater mg/kg of dry weight <sup>a</sup> (Canadian)	Log K <sub>ow</sub> <sup>d</sup>	BCF <sup>d</sup>
<b>PAHs</b>							
Naphthalene		1.1	2.4	–	0.030	3.4	85
Acenaphthylene		–	1.3	–	0.0060	4.1	270
Acenaphthene		5.8	3.8	–	0.0070	4.0	760
Fluorene		2.3	–	–	0.020	4.2	520
Phenanthrene		0.40	1.3	–	0.040	4.5	2.5×10 <sup>3</sup>
Anthracene		0.012	0.10	–	0.050	4.5	1.8×10 <sup>3</sup>
Fluoranthene		0.10	–	–	0.10	5.0	3.6×10 <sup>3</sup>
Pyrene		0.025	0.0046	–	0.050	5.0	1.5×10 <sup>3</sup>
Benzo(a)anthracene		0.018	0.012	–	0.030	5.6	260
Chrysene		–	0.014	–	0.060	5.2	12
Benzo(b)fluoranthene		–	0.030	–	–	6.0	3000
Benzo(k)fluoranthene		–	0.030	–	–	6.1	3415–6465
Benzo(a)pyrene		0.015	0.050	–	0.030	6.1	5.0
Dibenz(a,h)anthracene		–	–	–	0.060	6.9	9000
PAH-L		–	–	3.0	–	–	–
PAH-M		–	–	3.0	–	–	–
PAH-H		–	–	1.0	–	–	–
<b>Phthalates</b>							
di-(2-ethylhexyl) phthalate (DEHP)		16	–	–	–	7.6	590
Dibutyl phthalate (DBP)		19	–	–	–	4.5	170
<b>BTEX</b>							
<u>Benzene</u>		370	–	0.012	–	2.1	4.3
<u>Ethylbenzene</u>		90	–	10	–	3.2	15
<u>Toluene</u>		2.0	–	10	–	2.7	8.3
<u>Xylene</u>		–	–	10	–	3.1	14
<b>Aliphatic hydrocarbons</b>							
>C <sub>5</sub> –C <sub>8</sub>		–	–	12	–	4.1 <sup>e</sup>	500 <sup>m</sup>
>C <sub>8</sub> –C <sub>10</sub>		–	–	20	–	6.0 <sup>f</sup>	–
>C <sub>10</sub> –C <sub>12</sub>		–	–	100	–	6.0 <sup>g</sup>	–
>C <sub>12</sub> –C <sub>16</sub>		–	–	100	–	8.6 <sup>h</sup>	40 <sup>n</sup>
>C <sub>16</sub> –C <sub>35</sub>		–	–	100	–	12 <sup>i</sup>	165 <sup>o</sup>
<b>Aromatic hydrocarbons</b>							
>C <sub>8</sub> –C <sub>10</sub>		–	–	10	–	3.9 <sup>j</sup>	205 <sup>p</sup>
>C <sub>10</sub> –C <sub>16</sub>		–	–	3	–	4.7 <sup>k</sup>	1028 <sup>r</sup>
>C <sub>16</sub> –C <sub>35</sub>		–	–	10	–	6.0 <sup>l</sup>	6462 <sup>s</sup>

<sup>a</sup>(CCME 2014); <sup>b</sup>(EU 2010); <sup>c</sup>(Naturvårdsverket 2009); <sup>d</sup>(NCBI); <sup>f</sup>>C<sub>9</sub>–C<sub>12</sub>; <sup>g</sup>>C<sub>13</sub>–C<sub>18</sub>; <sup>h</sup>>C<sub>19</sub>–C<sub>36</sub>; <sup>i</sup>>C<sub>19</sub>–C<sub>36</sub>; <sup>j</sup>>C<sub>9</sub>–C<sub>12</sub>; <sup>k</sup>>C<sub>13</sub>–C<sub>15</sub>; <sup>l</sup>>C<sub>16</sub>–C<sub>24</sub>; <sup>e-l</sup>(BATTELLE 2007); <sup>m</sup>value for hydrocarbons, C5-C6, n-alkanes, isoalkanes, <5% n-hexane (DHC 2006; <sup>n</sup> alkanes>C<sub>10</sub>–C<sub>14</sub>; <sup>o</sup>nonadecane; <sup>p</sup>biphenyl; <sup>r</sup>9-Methylanthracene; <sup>s</sup>coronene; <sup>n-s</sup>(USEPA 2013).

## 2.4 Approaches to reduce urban runoff pollution

Global development has caused an increase in impervious areas and consequently excessive surface runoff, flooding and deteriorated water quality in receiving waters. This in turn, has led to advancement within stormwater drainage management. The initial goals of stormwater management were to mitigate flooding and later to decrease water pollution and maintain aesthetic and recreational values of water resources. Recent focus has expanded to i.a. restoration of flow regimes, preserving the ecology of receiving water and acknowledging stormwater as an important resource (Fletcher et al. 2015, Whelans et al. 1994). Practices such as low impact development (LID), sustainable drainage systems (SuDS) and water sensitive urban design (WSUD) offers different alternatives to drainage of stormwater close to the source, taking advantage of processes like infiltration and evapotranspiration to maintain the natural hydrologic behavior of a site (Flanagan et al. 2017). These techniques represent a network of natural and close to natural areas with objectives to restore base flows in streams, groundwater recharge, and protection of biodiversity (Hamel et al. 2013, Stephens et al. 2012). Similarly, best management practices (BMPs) are focused on preventive measures at the source and also include structural and non-structural methods for reducing pollution from stormwater discharge in large drainage areas (Zhang and Chui 2018). Below are listed some of the most popular techniques used in stormwater management with emphasis on treatment of road runoff.

### **Low impact development (LID) and water sensitive urban design (WSUD)**

Both approaches are nearly the same, developed in different parts of the world, LID in North America and New Zealand and WSUD in Australia, and in slightly different times (the 1970s and 1990s, respectively). The most common examples of LID and WSUD are bioretention systems, vegetated filter strips at the edges of impervious surfaces, curbless streets with swales, and porous surfaces such as pavers, permeable concrete and asphalt (Eckart et al. 2017). Because of cost constraints and limited available space in highly urbanized areas, the best stormwater solutions focus on modification of existing infrastructure (Damodaram et al. 2010). As particles carry various pollutants, techniques effective for particle retention through sedimentation and filtration are widely researched. One promising example is biofiltration swales with check dams, which retain particulate pollutants through sedimentation and filtration and dissolved pollutants through sorption processes. These swales receive water pretreated by vegetative filter strips, which also reduce runoff volume and have an addition traffic safety role of creating a distance between the road and the swale (Flanagan et al. 2018, 2019).

### **Sustainable drainage systems (SuDS)**

SuDS are techniques similar to LID and WSUD but developed and practiced in Europe and with the aim to drain stormwater in a more sustainable way than early stormwater management approaches (Eckart et al. 2017). Idea with SuDS is to consider sustainability criteria regarding stormwater management parameters i.e. water quantity, quality and ecology. These criteria include technical, environmental, social and economic factors to yield drainage systems minimizing e.g. cost, maintenance and consumption of resources (Ellis et al. 2004). The SuDS often applied alongside roads and highways are filter strips, swales and bioretention areas

consisted of permeable natural materials like vegetation and soils and using treatment processes like infiltration and evapotranspiration (Kanso et al. 2018).

### **Best management practices (BMPs)**

The tools included in the term BMP are the same as for LID, WSUD and SuDS, e.g filter drains, porous surfaces, filter strips, infiltration trenches, retention ponds, and constructed wetlands, and are based on biological, chemical and physical removal processes (Scholes et al. 2008). Even if BMPs consist of the same stormwater management techniques and treatment processes as for LID, WSUD and SuDS, the overall goal of BMPs is to prevent pollution in the most effective way through single or a series of techniques linking both non-structural (prevention of stormwater and pollution generation) and structural (stormwater management facilities/infrastructure) methods prior discharge to receiving waters (Fletcher et al. 2015, Hwang et al. 2019).

Non-structural measures aim to reduce the amount of pollutants on impervious surfaces and generation of surface runoff, before it is wash off to the drains. This includes for example street sweeping or vehicle wash (for details on performance and efficiency of these techniques see Chapter 2.6.2), promoting a reduction of impervious surfaces, and management of building-materials (Björklund et al. 2008, German 2003). Example of structural BMP is filtration of surface runoff in gully pots (German 2003) implementing sorption as physical and chemical removal process (Paper V and for details on performance and efficiency of these technique see Chapter 2.6.1.).

## **2.5 Studied stormwater management techniques**

### **2.5.1 Street sweeping and washing of vehicles**

*Street sweeping* techniques have been investigated as potential methods for reducing stormwater pollution close to the emission source multiple times in the past decades (Calvillo et al. 2015). Gustafsson et al. (2019) showed that the load of road dust particles <180 µm varied between 15 g/m<sup>2</sup> in early autumn and late spring and 200 g/m<sup>2</sup> in winter and early spring in Stockholm, Sweden. Large amounts of road dust and anti-skid sand are collected every year; the collected amount in Sweden in 2008, estimated by Sweden's municipalities and county councils, was 750,000 tonnes. The collected material by street sweeping contains debris and particles of different sizes; the finest fractions are assumed to be the most polluted, and are composed of minerals, rubber, asphalt, other organic materials and emulsions, which are all efficient carriers of pollutants (Aryal et al. 2017). High concentrations of pollutants, including particles, microplastics, metals and a variety of OPs such as organochlorine pesticides polychlorinated biphenyls, flame retardants and PAHs are often found in road dust (Paper III; (Anh et al. 2019, Järllskog et al. 2020). A strong correlation between smaller particle sizes and high concentrations of metals and PAHs have been observed in street sweeping materials (Lloyd et al. 2018).

National regulations on disposal of road dust from street sweeping are currently missing in most countries, why the waste is often deposited on-site or in landfills, where sorbed pollutants

risk being released back into the environment. If these urban materials are treated to remove pollutants and reused, landfill deposition and extraction of natural gravel, a limited resource that is often used for anti-skid purposes, could be reduced. Street sweeping has the potential to be an effective and affordable way to reduce the occurrence of pollutants in road dust, thereby also reducing the spreading of pollutants with particles in road runoff (Paper III). Furthermore, street sweeping is an "at the source" practice that can limit contamination from traffic-related sources.

**Vehicle runoff** contains OPs, originating from the vehicle itself, but also collected on the vehicle surface through precipitation, road splashes and atmospheric deposition. Main sources of OPs from vehicles are exhaust gases, tire wear, lubricant oils, abrasive road surfaces, and brake linings (Paper I). Runoff from vehicle surfaces is a source for water pollution as it enters the receiving waters (Wada et al. 2015). Accordingly, there is a need to study vehicle washwater as an important source of OPs in urban runoff as not many studies can be found in the literature (Ganiyu et al. 2018, Hashim and Zayadi 2016). Washwater from *carwash* facilities contains many pollutants such as aliphatic and aromatic hydrocarbons (mainly BTEX and PAHs) originating from degreasing solvents and petroleum products, oil and grease, phthalates from plastic vehicle components, hydrofluoric acid, surfactants, paint residues, asphalt, and phosphates (Bhatti et al. 2011, Paxéus 1996). There is no general regulation for washing of private vehicles in Sweden. In Gothenburg, car washing on the street is only prohibited in the water protection areas, but the municipality strongly recommends using only certified car wash companies that use environmentally friendly washing detergents (Miljöförvaltningen 2013).

### 2.5.2 Alternative sorption filters

Preventive measures may be an effective way to reduce the amounts of contaminants being transported with urban runoff; for example, in-situ treatment techniques such as street sweeping and vehicle wash have been proven to be successful pollution control measures (Paper III and IV). Stormwater treatment is often based on sedimentation that is generally not designed for efficient removal of organic pollutants (OPs), metals, and inorganic substances, as the forms that attach to particles  $<1 \mu\text{m}$  do not settle (Haranas et al. 2012, Ilyas and Muthanna 2017). For this reason, there is an urgent need also to develop efficient treatment methods that can prevent further transport and spread of OPs into the environment. Filtration of stormwater through a sorption material is one of the most promising techniques for removal of colloidal and dissolved OPs. Sorption filters have the capability to remove OPs attached to micro- and nanoparticles and in emulsions and colloidal and truly dissolved forms from stormwater. To be able to understand the processes controlling the sorption of OPs in these filter columns (Paper IV) it is of importance to understand the basic principles of the sorption processes.

### **Alternative filter materials**

The efficiency of sorbents is characterised by physical-chemical properties such as polarity, aromaticity, surface area, pore size, and pore volume (Wenzhong et al. 2008, Xi and Chen 2014). When selecting materials to use in filters, their sorption selectivity, mechanical stability, environmental impact and toxicity, cost-effectiveness, and reusability potential must also be considered. One of the challenges of stormwater treatment using sorption filters is to find sustainable materials in which the OPs are effectively degraded, while sorbed metals can be recovered (Fedje et al. 2015, Fedje and Strömvall 2019), and un-degraded litter such as microplastics separated after use. Clogging is another challenge recognised as a key limiting factor of sorption filters for stormwater treatment (Kandra et al. 2015). Clogging is caused by physical, biological and chemical processes; clogging can for example be caused by fine-grained particles migrating into the pores of a coarser sorption material, biological growth on, or degradation of, the sorption material, or chemical precipitation of metal salts.

### **Granular Activated carbon (GAC)**

Although expensive compared to natural organic materials, activated carbon is one of the most used sorbents for water treatment worldwide owing to its efficiency in removing various pollutants, and low operating costs (Moona et al. 2018, Pamidimukkala and Soni 2018). The high adsorption capacity of activated carbon is related to its internal structure which consists of a broad range of pore sizes, from visible to molecular-sized cracks and crevices. Activated carbon can be both hydrophobic and hydrophilic in nature (Ania et al. 2007). Common organic functional groups present on activated carbon are carboxylic acids, phenols, aldehydes, ethers, amines, nitro compounds, and phosphates formed from heteroatoms such as oxygen, nitrogen, phosphorus, hydrogen, chlorine, and sulfur (Bansal and G. 2005). Surface functional groups determine the self-organization, chemical stability and reactivity in adsorptive and catalytic processes (Banosz and Ania 2006). GAC has mainly been used for sorption of aromatic hydrocarbons, dyes and pharmaceuticals.

### **Peat**

*Sphagnum* peat is a complex organic material containing minerals and partially decomposed organic matter, where organic compounds such as lignin, cellulose, fulvic, and humic acids are major components (Ahmaruzzaman 2008). Peat is good adsorbing material for organic species because of the content of polar functional groups such as e.g. aldehydes, acids, ketones and ethers and also contain hydrocarbons and aromatic parts able to adsorb non-polar petroleum compounds (Kalmykova 2009). The previous uses of peat indicated good removal of heavy metals, grease and oils, solvents, odours and pesticides in treatment of contaminated waters (Couillard 1994, Kalmykova et al. 2009). Peat has been shown to be an effective sorption material for metals but has not been studied to any great extent for sorption of OPs (Lamichhane et al. 2016). The exact sorption mechanisms of OPs in peat are unclear and important to consider in future studies. The sorption may be a linear absorption process in which pollutants in high concentrations are partitioned into the peat's humic and fulvic substances (Kalaitzidis et al. 2006). The sorption in peat may also occur as a non-linear process, where OPs in low

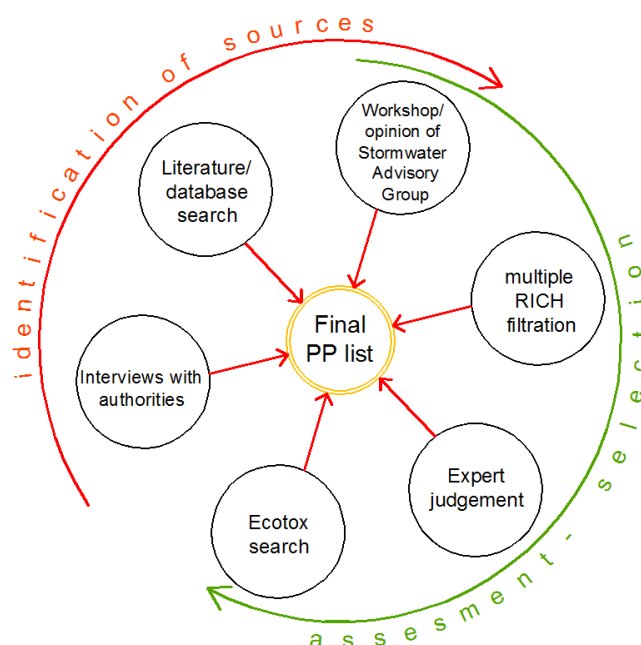
concentrations accumulate on parts of the peat with more condensed or oxidized organic matter, through adsorption, filling, and condensation within micropores.

### **Bark**

Bark from pine (*Pinus silvestris*) is a waste product from the forest industry and can be used, without any additives or chemical preparation, for absorption of liquids such as petroleum products, emulsions, cutting fluids, glycol, paint, varnish, urine, and blood (Larsson 2015). Pine bark is also effective in retaining hydrophobic OPs such as organochlorine pesticides (Ratola et al. 2003), pentachlorophenol (Brás et al. 2004), and PAHs (Björklund and Li 2015). The low porosity and specific surface area of pine bark do not affect its sorption capacity, as most of its removal efficiency has been attributed to its content of organic compounds, such as lignin, which is hydrophobic and has a high aromatic content (Huang et al. 2006, Li et al. 2010, Xi and Chen 2014). The chemical composition of bark is otherwise very complex and depends both on the tree species and on the morphology of the bark (Valentín et al. 2010). Pine bark consists mainly of lipophilic extractives, such as fats, waxes, terpenes, terpenoids, and higher aliphatic alcohols, and hydrophilic constituents, including condensed tannins (phenolic acids), but also contains insoluble compounds like polysaccharides, lignin, and suberin. All these compounds are likely to contribute to the OP sorption capacity of bark.

### 3. METHODS AND MATERIALS

#### 3.1 Selection of priority pollutants and substance flow analysis



**Fig. 4.** The iterative selection process used for identifying and selecting organic priority pollutants in urban road environments (**Paper I**).

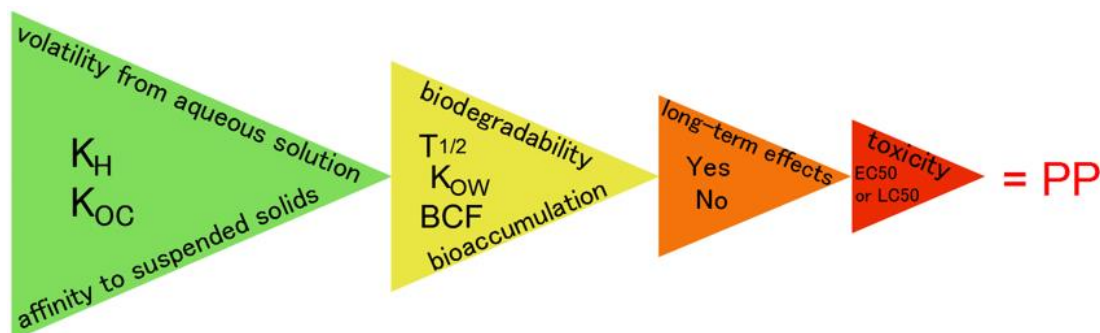
Data on OPs expected to occur in road environments and their sources were gathered through (Fig. 4):

- An extensive *literature search* in abstract and citation databases as well as common internet search engines, covering both international and national reports and scientific journals.
- *Research of the database* International Material Data System (IMDS) for substances present in polymeric vehicle components.
- *Interviews with experts* from car manufacturing companies and companies responsible for the production of road materials in Sweden.
- Regional and federal *reports of OP monitoring campaigns*.

Because the composition of various vehicle parts vary between the suppliers, searches in the IMDS database were performed with regard to suppliers to car manufacturers in Sweden and based on information on polymeric elements used in vehicles, gathered from Štrumberger et al. (2005).

In this study, RICH (Ranking and Identification of Chemical Hazards) was applied to classify the identified road-related OPs. The RICH method has been developed to provide transparent ranking for a wide range of substances in stormwater, using the substances' inherent physico-

chemical properties and biological effects (Baun et al., 2006). The tool is used for assessing environmental partitioning and chemical hazards and can help identify the most crucial pollutants for stormwater studies, i.e. priority pollutants (Fig. 5).



**Fig. 5.** The RICH (Ranking and Identification of Chemical Hazards) filtration process for ranking and identification of chemical hazards and priority pollutants (adopted from Baun et al. 2006) (**Paper I**).

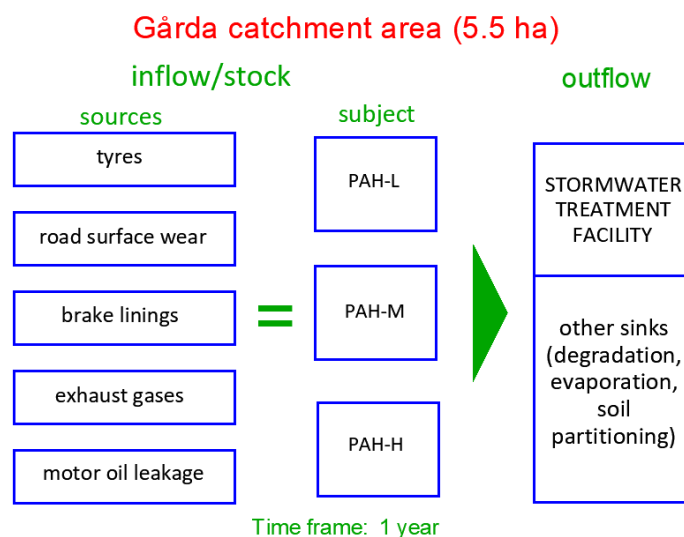
Data not available in RICH were collected using the ECOTOX database (EPA 1995), the Swedish chemical database KEMI, the online chemical database OCHEM, and the software Estimation Program Interface (EPI) Suite developed by the US EPA. Advanced Database Query was used to extract data, including e.g. BCF and the concentration based EC<sub>50</sub> or LC<sub>50</sub>.

The list of identified traffic-related OPs was reviewed by a Stormwater Advisory Group during a workshop with, among others, experts on stormwater quality and chemicals, as well as representatives from the transportation administration and local and regional environmental authorities. The specific objectives of the workshop were to discuss the overall concept of OPs present in road runoff and to identify substances whose priority is unlikely to be established by e.g. literature or database searches. Subsequent steps in the PP selection engaged the experts who, by applying expert knowledge and experience within the field, identified additional substances according to the following criteria:

- Risk of emission/leaching of pollutants from sources to stormwater systems.
- Specific (or groups of) substances emitted from more than one source in the road environment.
- Quantity of OPs present in vehicles, fuels, road construction materials and other sources in Sweden and in the EU.
- Hazardous effects on aquatic environments and human health, determined through physico-chemical properties available in RICH.
- Ability of commercial or research laboratories to analyse the chosen substances in sediment and water.
- No previous SFA study available for the particular pollutant or group of pollutants.

Based on the suggested PP list, and the expert judgement criteria described above, 16 specific PAHs prioritised by the US EPA and released from vehicles, road surfaces and other traffic-related sources, were selected for inclusion in the SFA study, see Figure 6.

To illustrate stocks and fluxes of PAHs in the road environment (Paper I), the substance flow analysis (SFA) method was chosen as it is an analytical tool developed for quantitative assessment of individual substances through a given system, specified in space and time (Björklund 2010, Bringezu 2006, Huang et al. 2012) (Fig. 6). This method allows evaluation of the amounts of OPs emitted to aquatic environments, as well as estimation of the scale of the potential contamination. In this study, the SFA covered substance flows during one year; the system space boundary was the urban catchment area Gårda. The substance flows in the studied area were calculated using emission factors (EFs) for each source and individual pollutant. The EFs were estimated from literature data on emission rates and substance content in various source materials. Vehicle exhaust-related emissions were based on data found in the air pollutant emission inventory guidebook, published by the European Environment Agency (EEA, 2013). Tyre, road material and break lining emissions were determined using data on wear per driven kilometre and content of substance in tread, asphalt and lining material, respectively. Emissions of motor oil and lubricants were calculated from the substance content in used oils/lubricants and the estimated loss of oil/lubricant by leakage per driven distance. The factors for vehicle-related emissions were expressed in the format [ $\mu\text{g}/\text{vkm}$ ]; mass of substance emitted per travelled vehicle-kilometre. The total substance flows were subsequently calculated using data on the length of the road and the total number of vehicles traveling through the area in one year. For more details of how the SFA was performed see Paper I.



**Fig. 6.** Flow chart of the substance flow analysis for the Gårda catchment area, with main sources of inflow, outflow to the stormwater facility and other sinks of polycyclic aromatic hydrocarbons divided into PAH-L, PAH-M and PAH-H (**Paper I**).

## 3.2 Case study areas

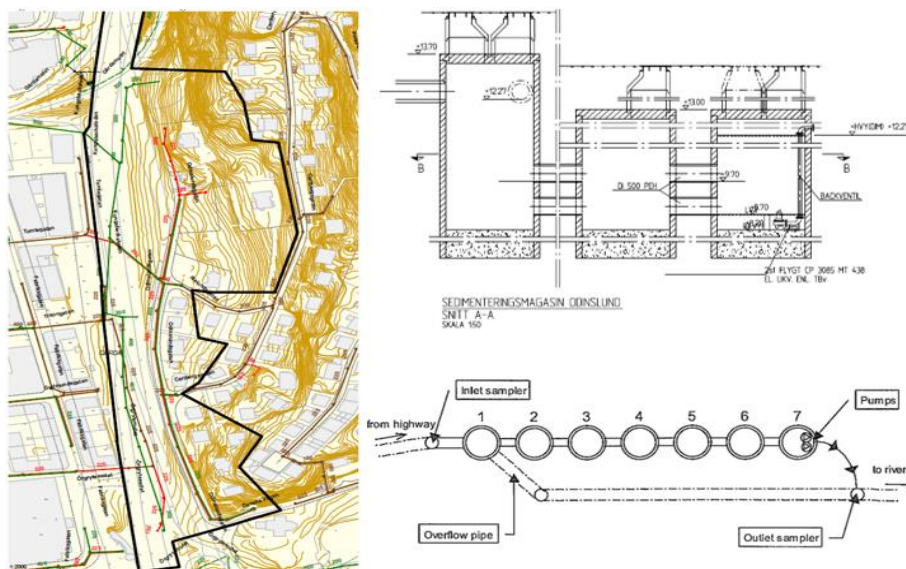
### Järnbrott areas



**Fig 7.** Location of the Järnbrott catchment area and stormwater pond, Gothenburg Sweden (**Papers II and III**).

The Järnbrott stormwater sedimentation pond (Fig. 7) collects runoff from a highway (annual average daily traffic is approximately 40,000 vehicles) as well as from industrial, commercial and residential areas, with a total surface area of 480 ha, of which impermeable surfaces make up 160 ha. The pond is located 5 km outside Gothenburg, Sweden, with a surface area of 6200 m<sup>2</sup>, and can retain approximately 6000 m<sup>3</sup> of water, with a maximum inflow of 1100 L/s (Pettersson 1998). Inlet water to the Järnbrott stormwater sedimentation pond was used in the studies reported in Paper II and III. In Paper II samples were grab-sampled from the inlet of the pond and used as a comparison with the laboratory made emulsions for determination of the particles size distributions. In Paper III the pilot sorption filter plant was located at the inlet of the pond.

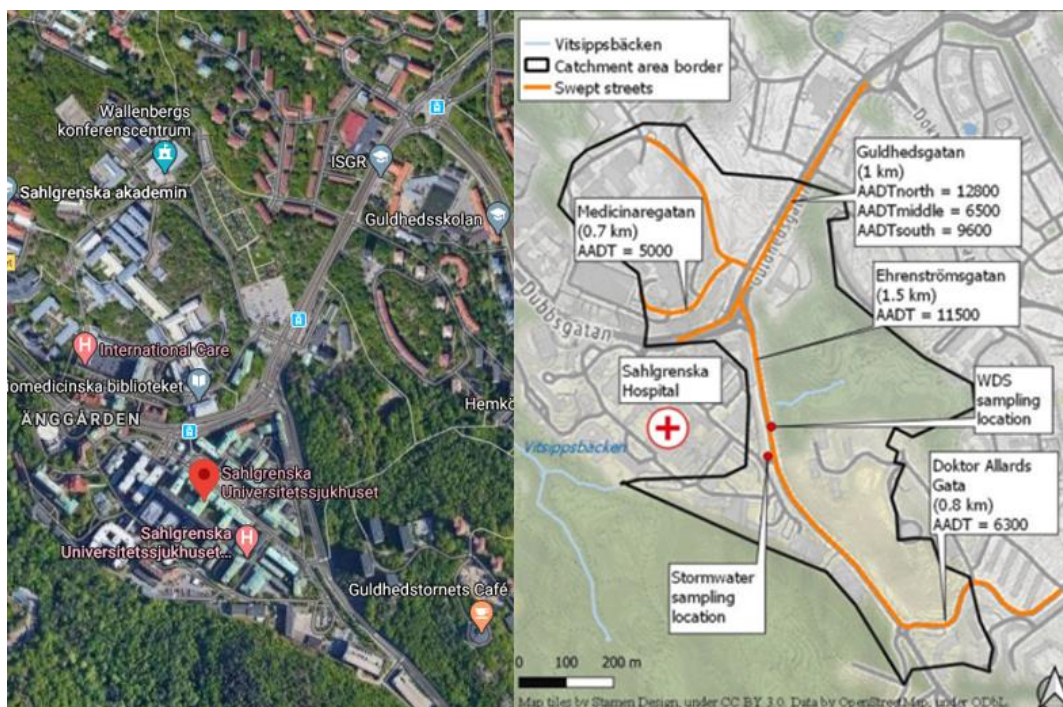
### Gårda area



**Fig. 8.** Location and design of the Gårda underground highway runoff sedimentation treatment facility Gothenburg Sweden (**Papers I and II**).

The Gårda stormwater treatment system (Fig. 8) is composed of seven sedimentation chambers with a total volume of 122 m<sup>3</sup>, collecting runoff from a catchment area of 5.5 ha, of which impervious surfaces constitute 64% (Pettersson et al. 2005). After treatment (40 h hydraulic retention time), the water is pumped via a draining pipe to a nearby stream. The facility receives runoff from the E6/E20 highway crossing the central parts of Gothenburg, with a daily traffic intensity of approximately 100,000 vehicles; it is assumed that 100% of the OPs reaching the chambers originate from traffic-related activities. The Gårda catchment area and stormwater treatment facility were used for the case studies presented in Paper I and II. In Paper I Gårda served as a case for the substance flow analysis (SFA) and OPs loads in the stormwater sediment were analyzed to verify the SFA results. Sediment samples were collected by grab sampling from the sedimentation chambers 1, 3, 5 and 7. In Paper II stormwater samples were grab-sampled from the inlet chamber of the sedimentation facility.

### Sahlgrenska area



**Fig. 9.** The studied urban area and catchment area of the small stream Vitsippsbäcken, located in Gothenburg, Sweden (**Paper IV**).

An area at Sahlgrenska was the case study area for investigating the effects of street sweeping on the spread of OP and small particles to stormwater, presented in Paper IV. The study area is a mixed catchment adjacent to the Sahlgrenska Hospital in central Gothenburg and includes hospital and university buildings with large copper roofs, parks, forest, parking lots and roads with annual average daily traffic volumes of between 2,000 and 24,000 (Fig. 9). The total area of the drained catchment is around 50 ha, made up of 10% parking lots and roads, 13% buildings, 17% other paved areas, and 60% pervious areas. Runoff from impervious surfaces is drained via separate storm sewers, without any treatment, to a natural stream, Vitsippsbäcken.

### 3.3 Experimental set-ups

#### **Street sweeping**

The sweeping (Paper III) was performed in the morning on streets that were not closed off for traffic while the sweeping took place, which resulted in slight variations in the sweeping performance and covered distances (Fig. 9). In most cases, the right lane of the road, nearest the kerb, was swept. The sweeping machine used is a vacuum type produced by Johnston Beam. To suspend the finest particles during sweeping, the pipe that sucks up the road particles is moisturized with water. In dry weather conditions, the machine also sprays water onto the road to prevent fine dust from being emitted into the air. The total water storage volume in the machine was approximately 1.3 m<sup>3</sup>. The amount of water sprayed during the sweeping events varied depending on weather conditions, which is in line with regular sweeping routines. As the width of the machine is approximately  $\frac{3}{4}$  of the width of a lane, the entire road surface was not swept on every occasion. For more details of the sampling see paper III.

To evaluate the efficiency of the street sweeping, road dust was also sampled before and after sweeping, using the Wet Dust Sampler II (WDSII) technique (Paper III), designed and operated by the Swedish National Road and Transport Research Institute (VTI) (Gustafsson et al. 2019, Jonsson et al. 2008, Lundberg et al. 2019). Samples were collected both before and after street sweeping at two occasions. At both occasions, the samples were collected randomly on the kerb, in wheel tracks, and between wheel tracks across the left lane along 5 m of the street, and 10 subsamples were pooled to a composite sample of approximately 10 L, to represent the road pollution level before street sweeping. The procedure was repeated on an adjacent road surface area after street sweeping was performed.

#### **Flow proportional stormwater sampling**

In parallel with the weekly street sweeping in Paper III, stormwater was collected during rain events. An automatic sampler (type ISCO 6712) and an area velocity flow meter (Type Triton + ) were installed in a stormwater manhole located close to the outlet to Vitsippsbäcken (Fig. 9), allowing flow-weighted sampling of stormwater. One representative composite sample comprising of flow-weighted subsamples collected during entire rain events was sampled for each rain event. Close to the sampling point, a tipping bucket rain gauge (type MJK) was installed on one of the hospital buildings to monitor rainfall. Precipitation amounts and intensity for sampled storm events were registered

#### **Carwash and rain simulations**

The carwash and rain simulations were performed in an experimental carwash test using different cars, which were initially washed in a professional carwash facility and driven for four weeks in the winter prior the experimental car wash. For each simulation, the vehicles subjected to the washing were of different brand and fuel type (Paper V). Design of the washing experiment considered: 1) washing materials and chemicals with known content to minimize background contamination of OPs, nanoparticles and microplastics to the washwater 2) a washwater collection basin made of 100% polyethylene sheet that was changed to a new one before each simulation 3) simulation of professional manual car wash using conventional and

environmentally friendly detergents and 4) simulation of rain events with low and high intensity.

The simulations were conducted in late March after two consecutive dry days. The first car was rinsed with a high-pressure washer (Kärcher™) twice, before and after cleaning, with soft brushes and sponges soaked in the conventional detergent. The procedure involved washing the vehicle body and tires with water saving mode, a procedure commonly used in professional manual washing facilities. The cleaning process was repeated for the second car, but instead using eco-labelled detergent. In the rain simulation, the third car was sprayed with a garden hose sprinkler on the top, sides and from beneath, with the intensity 1.1 l/min and duration 15 min. For the fourth car the simulation procedure was repeated but with a higher intensity 1.3 l/min during 30 min. For more details about the simulation experiments see Paper IV.

### **Sorption filters pilot plant**

Stormwater was pumped to the sorption filter pilot plant located at the inlet of the stormwater sedimentation pond in Järnbrott (Paper V) from a concrete basin containing standing stormwater mixed with groundwater (baseflow <10 L/s). The pilot plant was designed to minimise maintenance and operational needs, why self-regulating gravity filtration was used. By pumping the stormwater from the concrete basin to an elevated level above the columns, the columns were fed with water through gravity flow. The stormwater was first filtered through a sand column, then diverted into three parallel lines and divided between the GAC, peat, and bark columns. All columns were modified pipes of rigid PVC (h 2200 mm, Ø 300 mm), with a 450 mm drainage layer of graded gravel at the bottom. The graded gravel underdrain was made up of different layers of sand and gravel in sizes, from bottom, of 64–32 mm, 32–16 mm, 25–10 mm, 10–5.0 mm, 5.0–3.0 mm, 3.0–2.0 mm, and 1.2–0.8 mm. The sand filter consisted of a 300 mm deep sand bed of particles in the size range 0.6–0.8 mm, and the bed height of the sorption filters was 600 mm. The height of the bed was calculated to achieve a flow of 2 L/min and a contact time of 20 min, using the empty bed contact time equation (Tchobanoglous et al. 2014). All four columns were designed to allow backwashing, to avoid clogging of the bed. The backwashing pressure was empirically determined to obtain a filter bed expansion of approximately 30%. During winter, the temperatures in the columns were kept above 0°C.

### **Chemical analysis**

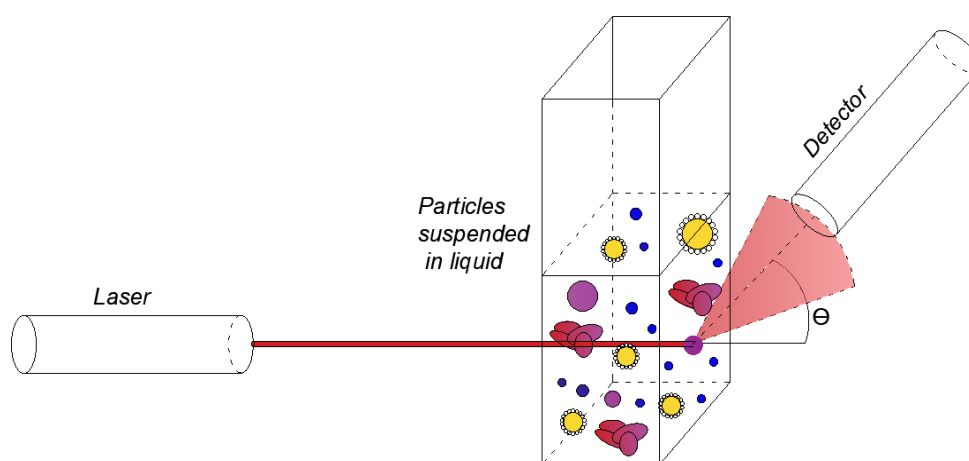
The samples in Papers 1 – V were analysed following standardised analytical methods for: pH, total and dissolved organic carbon, total suspended solids, loss of ignition, 16 specific US EPA PAHs (PAH-16), nine oxy-PAHs, 13 phthalates, five aldehydes, five fractions of aromatic hydrocarbons C<sub>8</sub>–C<sub>35</sub> (aromates), BTEX (benzene, toluene, ethylbenzenes and xylenes) and six fractions of aliphatic hydrocarbons (aliphates/alkanes) C<sub>5</sub>–C<sub>35</sub>. toxic trace metals, particle size distribution, particle concentrations and zeta potential. A non-standardised GC-MS screening method for OPs, based on spectral deconvolution for GC/MS (Du and Zeisel 2013), was also used in Paper V for analysis on the used filter materials.

### 3.4 Particle measuring techniques

Particle Size Distributions (PSDs) were analysed in Papers II, III, IV and V using following techniques:

#### Dynamic Light Scattering (DLS)

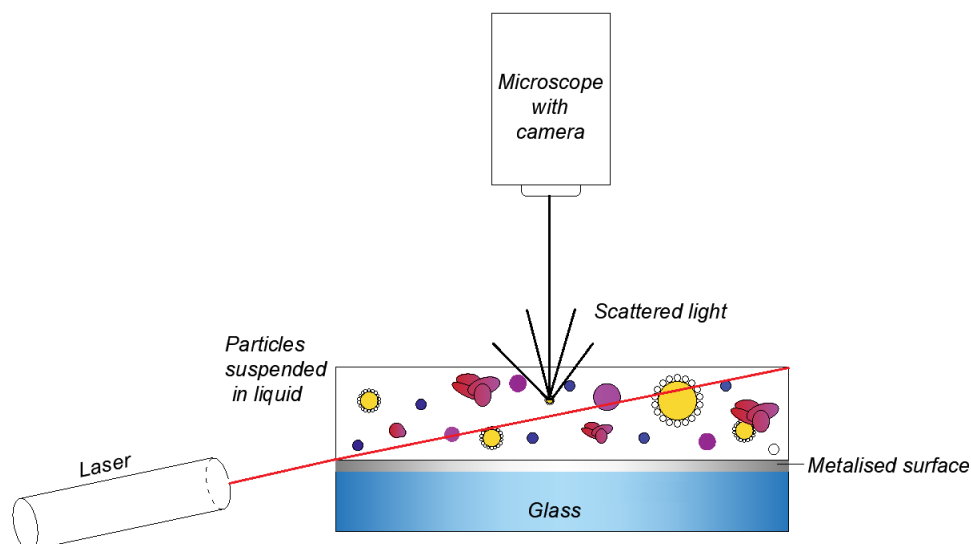
The DLS technique measures the random molecular motion of particles, i.e. the Brownian motion, via fluctuations in scattering intensity, which depend on the time difference between each scatter (Dudkiewicz et al. 2011) (Fig. 10). Size parameters are yielded by measuring average intensities of the scattered light at the angle that is most preferable for detection, i.e. back ( $175^\circ$ ), side ( $90^\circ$ ) or forward ( $15^\circ$ ). Particles of different sizes scatter light with different intensities, which can be related to particle speed and average particle size. The collected data is used to calculate the size distribution of the particles, in intensity weight, which can then be converted to volume or number weight.



**Fig. 10.** The principle of dynamic light scattering measurement.

#### Nanoparticle Tracking Analysis (NTA)

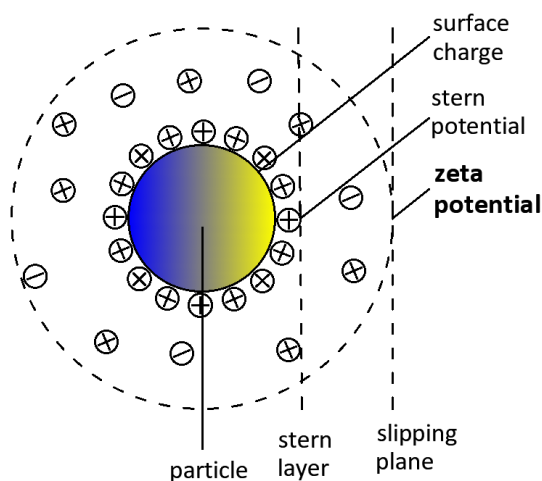
The Nanoparticle Tracking Analysis method visualizes and measures the diffusion of nanoparticles in suspension and provides information about particle count and concentration for particles in the size range  $0.01\text{--}2\ \mu\text{m}$ , in samples with particle concentrations ranging from  $10^7$  to  $10^9$  particles/mL. With this technique, the Brownian motion of the particles is tracked using a beam laser of wavelength selected among 405 nm (violet), 488 nm (blue), 532 nm (green) or 642 nm (red) on approximately 0.3 mL of the sample, which has been injected into a viewing chamber (Fig. 11). The scattered light is then recorded with a charge-coupled device camera. Videos are recorded and used to calculate particle sizes and concentrations with the NTA3.2 Nanosight Dev Build 3.2.16 software.



**Fig. 11.** The principle of nanoparticle tracking analysis measurement.

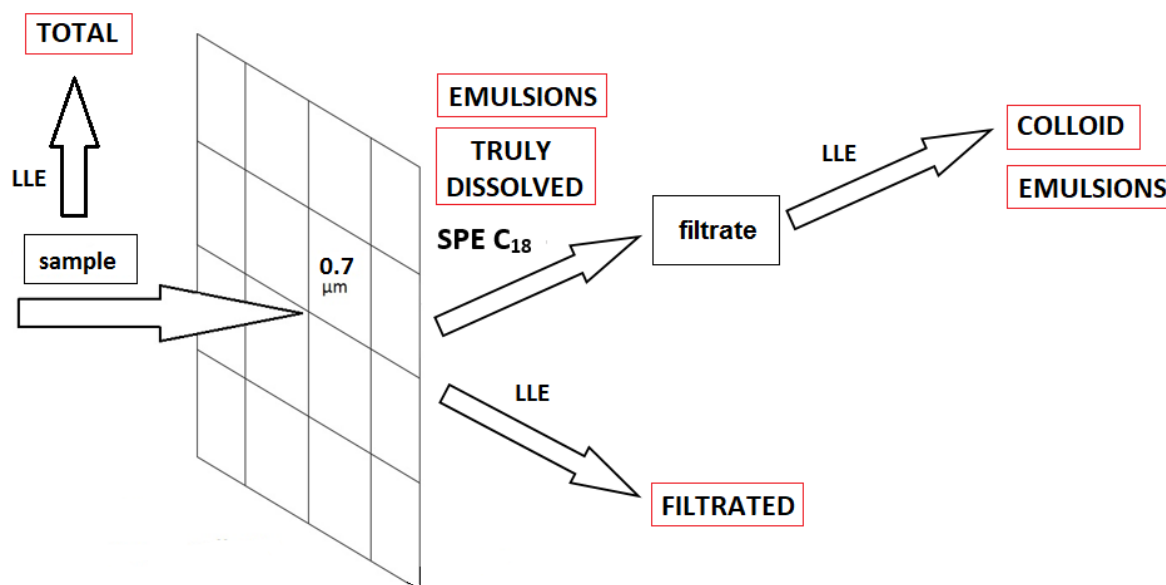
### Zeta Potential (ZP)- particle charge

Zeta potential (ZP) of the particles (Fig. 12) was analysed in Paper II, IV and V. ZP was measured in the range  $> \pm 500$  mV, to verify the surface charge of particles in prepared dispersions, using a Malvern Zetasizer Nano ZS instrument (Malvern Instruments Ltd, Malvern, UK) in Paper II and in the range  $> \pm 600$  mV, using Litesizer™ 500 (Anton Paar) in Paper IV and V. The instrument uses a laser Doppler electrophoresis technique in combination with an M3-PALS method to determine frequency shifts of the scattered light from moving particles in an applied electric field. Zeta potential (Fig.12) is the electrical potential of the electric double layer (i.e. the structure near a surface of a particle in a liquid medium) measured from the velocity of the charged particles moving towards an electrode when an external electric field is applied (Sapsford et al. 2011). The Stern layer is a layer of oppositely charged ions covering the surface of a charged particle, after which the diffuse layer of loose negative and positive ions begins and ends at the slipping plane (i.e. the interface between mobile fluid and fluid attached to the particle (Öberg and Rippe 2013)).



**Fig. 12.** A negatively surface charged particle and location of zeta potential measured.

### 3.5 Phase separation of organic pollutants



**Fig. 13.** Separation of the phases for chemical analysis of polycyclic aromatic hydrocarbons (Papers III, IV and V).

Separation of the phases (Fig. 13) was performed on the samples containing OPs in Paper III, IV and V. The total, particle bound, colloid bound and truly dissolved concentrations were determined for all compounds, following a procedure further developed from Kalmykova et al. 2013 and Nielsen et al. 2015 as follows:

- 1) First total concentrations of OPs were determined on unfiltered samples using solvent liquid extraction (LLE)
- 2) In the next step the sample was filtrated through 0.7  $\mu\text{m}$  glass fiber filter and the filtrate was extracted LLE to determine OPs in the filtrated fraction.
- 3) Part of this filtrate was extracted through a solid-phase extraction (SPE)  $\text{C}_{18}$  disk and to the filtrate from the SPE disc was LLE to determine the occurrence of OPs in the colloidal fraction.
- 4) Truly dissolved concentrations of OPs were determined by subtracting colloid concentrations from filtrated phase.

In Paper II it was found that the truly dissolved and colloidal fractions can contain emulsions. Note that in this study, the colloidal fraction concentrations were analysed and the truly dissolved calculated compared to the previous studies where the truly dissolved were analysed and the colloidal concentrations calculated (Kalmykova et al. 2013, Nielsen et al. 2015). The differences in the methodology may explain some differences in the results found.

## 4. RESULTS AND DISCUSSION

### 4.1 Priority pollutants, substance flows and routes of transport

Sources, transport routes and selection criteria scoring for priority pollutants (PP) are presented in Table 2. The different groups of organic pollutants (OPs) were prioritised using developed selection criteria (Paper I). From the literature review, as many as 1100 specific OPs were identified that could potentially be released into the road environment. However, Table 2 shows only the tip of an iceberg, as thousands of chemicals are used in the production of vehicles, fuels and engine oils, and used in car care products. Many OPs are also released from vehicles exhausts and body, brake and tyre wear.

Transport routes for the OPs (Table 2) were investigated through studies of emulsions in a laboratory scale (Paper II), and the colloidal transport was studied in sorption filters in a pilot scale (Paper V). The occurrence of nanoparticles in road materials, road surface water, runoff and stormwater and that may be correlated with transport of OPs was also investigated in Papers III, IV and V and will be discussed later in this chapter.

**Table 2.** Score of the selection criteria ranking, sources and routes of transport for priority pollutants (PPs).

PP group/compound	Score according to the selection criteria <sup>a</sup>	Sources	Routes of transport	Paper <sup>c</sup>
Priority order from the highest to the lowest				
<b>PAH-16</b>	7	tyre wear, brake lining, undercoating, lubricant oil, exhaust gases, bitumen/asphalt	particulate, dissolved, colloidal	(Paper I, II, III, IV, V)
<b>Alkanes C<sub>20</sub>–C<sub>40</sub></b>	7	tyre wear, brake lining, exhaust gases	Emulsions	(Paper I, II, III, IV, V)
<b>APs (alkylphenols)</b>	6	tyre wear, plastic vehicle components, vehicle paint/lacquer, car care products, lubricant oil, bitumen/asphalt, concrete, road paint	emulsions dissolved colloidal	(Paper I, II)
<b>Phthalates</b>	6	tyre wear, undercoating, plastic vehicle components, vehicle paint/lacquer, car care products, lubricant oil, bitumen/asphalt, road paint	emulsions dissolved colloidal	(Paper I, II)
<b>Aldehydes C<sub>1</sub>–C<sub>40</sub></b>	6	brake lining, exhaust gases	n.a. <sup>b</sup>	(Paper I)
<b>Phenolic antioxidants</b>	5	lubricant oil, exhaust gases, bitumen/asphalt	emulsion, dissolved colloidal	(Paper I, II)
<b>BPA (bisphenol A)</b>	5	plastic vehicle components, lubricant oil, bitumen/asphalt, road paint	emulsions dissolved colloidal	(Paper I, II, V)
<b>Oxy–PAHs</b>	5	brake lining, exhaust gases	particulate, dissolved, colloidal	(Paper I)
<b>Naphtha C<sub>5</sub>–C<sub>12</sub> (petroleum)</b>	5	car care products, lubricant oil, undercoating	emulsions, colloidal	(Paper I, II)
<b>Amides</b>	4	bitumen/asphalt	n.a.	(Paper I)
<b>Amines</b>	3	plastic vehicle components, bitumen/asphalt	n.a.	(Paper I)

<sup>a</sup> Risk of transport from source to stormwater, higher risk = higher score; Emission from more than one source; Significant amounts in the sources estimated by the Expert group; Hazardous effects according to RICH; Chemical analysis available; SFA available for road environment; High concentrations in the sediment in the Gårda case study area.. <sup>b</sup>n.a. – not analysed.

<sup>c</sup>Priority Pollutant score and routes of transport analysed in the papers.

### **Sources of organic pollutants**

Possible sources of OPs in the road environment are summarized in Table 2, which contains information collected through literature reviews, national Swedish screening reports and interviews with experts (Paper I). The results clearly show that most OPs are released from vehicles, as opposed to the road itself, and is the main source of emissions that should be addressed with powerful measures. Solving the problems of OP emissions close to the source of pollution is the best, simplest and most sustainable way. When the OPs enter the road runoff and are further spread into the stormwater, the pollution problem becomes more complicated to solve with technical solutions due to large amounts of water and sediment containing OPs that need to be treated. Therefore, it is extremely important that the automotive and oil industry develop vehicles that no longer contain OPs or need fuels, tyres and other products that contain OPs or create OPs during use. Furthermore, as investigated in this research, vehicle wash can be an effective source-control measure to prevent OPs spread into the stormwater (Chapter 4.2.2 and Paper IV).

### **Score according to the selection criteria**

From the RICH evaluation, a list of 109 compounds with high impact on the environment and/or humans was identified in Paper I. This list was further evaluated at an expert meeting with four researchers and experts in OPs. After the expert meeting, ten groups of compounds were chosen to be on the PP list of OPs emitted from the road and traffic environment. In Table 2, the compounds are presented in order from the highest priority to the lowest. Except for phenolic antioxidants, amides and amines (analytical methods not available), all of the compounds were measured in high concentrations compared to results from other studies and water quality guidelines in sediment from Gårda (Paper I). This list was also in line with the outcomes of the Stormwater Advisory Group workshop, where compounds were deemed high priority depending on their sources and potentially high emitted loads. The following groups of compounds met all the selection criteria: PAHs, alkanes, APs, phthalates and aldehydes. For APs and phthalates, an SFA has already been performed for the Gårda area (Björklund 2010), and the results showed that as much as 2.1 kg of total phthalates and 200 g of NPs and NPEOs may be emitted per hectare and year. In Paper I, the SFA of PAHs is presented. The PAHs were selected for the SFA because they are often the most frequently detected OPs in road environments (Eriksson et al. 2007, Gasperi et al. 2008), and several of the PAHs are included in the priority pollutant list from the European Water Framework Directive.

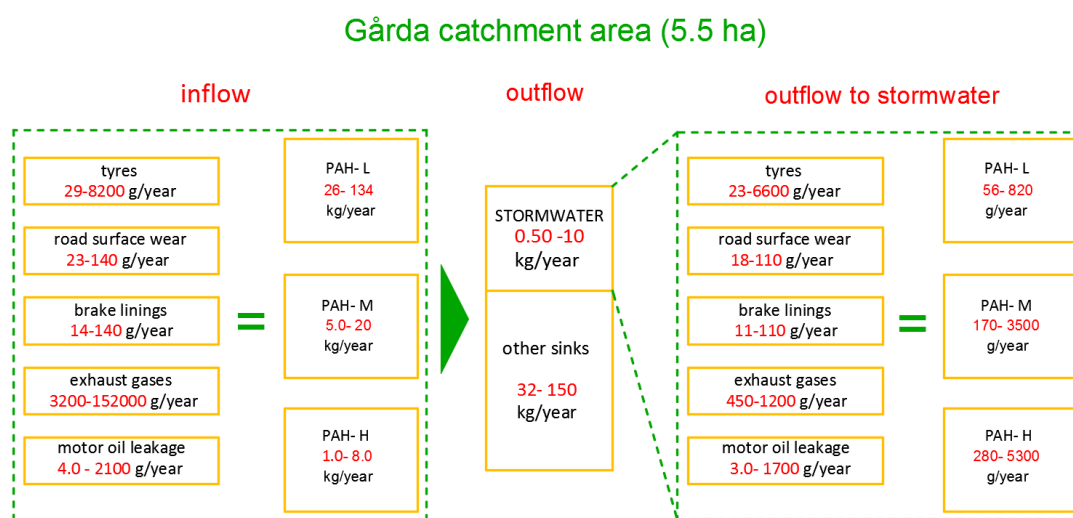
### **Routes of transport**

The main routes of transport for the PPs are presented in Table 2. Studies on the partitioning of OPs have shown that selected APs, phthalates and PAHs were predominantly attached to colloids and/or truly dissolved, hence may be transported over large distances in contrast to their expected strong sorption to particulate matter and subsequent sedimentation (Kalmykova et al. 2013, Nielsen et al. 2015). In Paper II it was found that some of the OPs that were previously identified as truly dissolved and/or colloidal phases could be emulsions. Based on our findings, it is more correct to separate compounds in a road runoff sample into four phases: solids > 0.7 µm, colloids (solids < 0.7 µm), truly dissolved, and emulsions (liquid ‘particles’ <

0.7  $\mu\text{m}$ ). For further reading, see Chapter 4.3 Organic pollutants in colloidal and emulsion phases.

This research found that the samples identified as potential emulsions were mixtures containing: diesel (aliphates), APs and APEOs; phthalates; and all OPs together, both with and without HA + Fe colloids (Paper II). The diesel used in this study is a potential emulsifier, due to the addition of rapeseed oil methyl ester by 5–7%, as well as other additives (OKQ8 2017). Alkylphenols and their ethoxylates are well known emulsifiers used in asphalt, concrete, tyre rubber, plastics, agricultural agents, and household products (Björklund 2010, 2011, Boza Troncoso and Acosta 2015). This result indicates that in road runoff, with relatively low concentrations of HA and Fe colloids (Nielsen et al. 2015), the formation of emulsions may be a possible transport route for OPs, in addition to colloidal transport. The samples with all OPs and HA + Fe colloids showed high repulsive forces between particles ( $ZP=71$  and  $80$  mV), hence it was assumed that the HA and Fe colloids may be emulsion facilitators under favourable conditions (pH, conductivity, contact angle, etc.) (Hiraide et al. 2002, Pensini et al. 2018, Zhou et al. 2012). These findings are of interest for further studies.

### Substance Flow Analysis



**Fig. 14.** Estimated fluxes of polycyclic aromatic hydrocarbons in the Gårda case study area (Paper I).

The results of the SFA (Fig. 14) of the Gårda catchment suggest an annual PAH emission load of 5.8–29 kg/ha. These results also indicate that only 2–6% of the total amount of PAHs emitted in Gårda end up in the stormwater treatment facility. Most of the PAHs are distributed to other sinks, through emissions to air, and immobilized in surrounding soils and on urban surfaces. Unaccountable losses of water and PAHs, e.g. through degradation, in the underground pipe system is also a possible sink. The results are surprising, as chemical analysis of PAHs in sediments show substantially lower emissions to the stormwater in Gårda than the loads calculated using emission factors. Possible uncertainties in the load estimations, sediment sampling and analysis have been discussed in detail in Paper I.

The largest sources of PAHs in the Gårda catchment area calculated from emission factors, i.e. the inflow (Fig. 14), are exhaust gases >> tyres > motor oil leakage > road surface wear = brake linings. The PAHs that dominate are PAH-L and PAH-M, naphthalene >> phenanthrene > fluoranthene = pyrene, all deriving from emissions from vehicles run on diesel, gasoline, E85 or CNG, and from both cars and LCVs (Paper I). Results of Paper I contribute with important information that PAHs present in the stormwater are found in much smaller amounts compared to the total loads of PAHs emitted to the catchment area, but contain much more of the hazardous PAHs, for example chrysene and indeno[1,2,3-c,d]pyrene that are classified as probable human carcinogen agents (ATSDR 2009).

## 4.2 Sustainable and effective solutions to protect stormwater from organic pollutants

Table 3 presents a comparison of water quality resulting from the investigated stormwater pollution mitigation techniques. Both source control measures, i.e. street sweeping and car washing, and end-of-pipe sand and sorption filters were investigated. Among the studied PPs aliphates C<sub>5</sub>–C<sub>35</sub>, followed by phthalates and PAH-16, occurred most frequently in the water samples. The highest concentrations of aliphates C<sub>5</sub>–C<sub>35</sub> and PAH-16 were analysed in the street sweeping washwater, and the highest concentrations of phthalates were found in the car washwater. Table 3 clearly shows that a combination of sand and sorption filters such as GAC, peat and bark effectively remove OPs from polluted stormwater (Paper V). It is also seen that the street sweeping machine collects large amounts of OPs in the washwater, thus preventing further spread of OPs with road runoff (Paper III). The results show that with car washing, large amounts of OPs are removed and protected from further spread to the road environment (Paper IV).

Oxygenated PAHs (oxy-PAHs) were only analysed in street sweeping washwater and simulations of carwash and rain (Papers III and IV). The total concentration of the nine analysed specific oxy-PAH were 0.11 µg/l in the street sweeping washwater. Oxygenated PAHs may be directly emitted from vehicle exhausts (Bandowe et al. 2014, Keyte et al. 2016) or found as a degradation product of PAHs (Lundstedt et al. 2007, Zhu et al. 2018). The calculated ratio of quantified oxy-PAH/PAH-16 in this study was very high (Paper III) compared to previous results from contaminated soil (Lundstedt et al. 2007), which indicates that oxy-PAH concentrations in water samples may be high even where the concentrations of PAH-16 are low. No other study analysing oxy-PAHs in urban surface runoff has been found in the literature. The occurrence of oxy-PAHs in street sweeping washwater is alarming, as the toxicity of oxy-PAHs is much higher than that of corresponding PAHs; oxy-PAHs also have a higher water solubility, and thereby a higher mobility in the environment (Lundstedt et al. 2007). As only a few samples were analysed for oxy-PAHs in this study, more studies are needed on their occurrence in road dust and runoff.

In the street sweeping washwater also methylated PAHs were analysed in concentrations up to 63 µg/L (Paper III). Of the OPs on the PP list (Table 2), and possible to analyse in water

samples, alkylphenols and their ethoxylates were below the limit of quantification. The aldehydes on the PP list were not analysed in the water samples. In all investigations (Paper III – IV), benzene, toluene, ethylbenzenes, xylenes (BTEX) were quantified only in the stress test where the sorption filter influent was spiked with petrol. This suggests that BTEX, although relatively water soluble, are emitted to air in traffic and road environments. Phenolic antioxidants, bisphenol A (BPA) and amides and amines, all on the top ten PP list (Table 2) were not analysed in the water samples as no analytical methods were available.

**Table 3.** Minimum to maximum (median) concentrations of organic pollutants measured in influents to and effluents from sorption filters, washwater from street sweeping machine, road surface water (WDS<sup>b</sup>), car wash and rain simulation (**Paper III – V**). Where no median is given, the value is <q.l. or the results are average values.

Compounds	Matrix analysed Unit	Sorption filters					Street sweeping			Car wash		Rain simulation	
		Sand filter influent <sup>a</sup>	Sand filter effluent = influent sorption filter	GAC effluent	Peat effluent	Bark effluent	Street sweeper	WDS <sup>b</sup> ≈ road surface water	Stormwater EMC <sup>c</sup>	Conventional detergent	Eco-labelled detergent	Light rain	Heavy rain
		Stormwater					Washwater	Washwater	Stormwater EMC	Washwater	Washwater	Vehicle runoff	Vehicle runoff
								Before SS <sup>d</sup> After SS	With SS Without SS				
<b>PAH-16</b>	[µg/L]	<q.l. <sup>e</sup> -3.6	<q.l.-0.10	<q.l.-0.080	<q.l.-0.030	<q.l.-0.080	0.30-120 (7.3)	1.5-3.0 (2.3) 2.4-1.3 (1.9)	0.33-0.80 (0.50) <q.l.-2.9 (1.4)	1.5	0.90	1.0	0.40
<b>PAH-L</b>	[µg/L]	<q.l.-3.6	<q.l.-3.6	<q.l.-0.080	<q.l.-0.030	<q.l.-0.080	<q.l.-1.0 (0.070)	<q.l.- 0.020 <q.l.	<q.l.-0.050 <q.l.-0.040	0.030	0.070	0.035	0.020
<b>PAH-M</b>	[µg/L]	<q.l.-0.80	<q.l.-0.10	<q.l.	<q.l.	<q.l.	0.20-55 (3.3)	0.80-1.5 (1.1) 1.1-0.60 (0.80)	0.20-0.41 (0.20) 0.050-1.7 (0.50)	0.85	0.50	0.50	0.20
<b>PAH-H</b>	[µg/L]	<q.l.-0.90	<q.l.	<q.l.	<q.l.	<q.l.	0.10-61 (4.0)	0.80-1.5 (1.1) 0.70-1.2 (0.95)	0.17-0.40 (0.20) <q.l.-1.2 (0.80)	0.60	0.40	0.40	0.20
<b>Oxy-PAHs 9 compounds</b>	[µg/L]	n.a. <sup>f</sup>	n.a	n.a	n.a	n.a	0.10-0.30	n.a	n.a.	<q.l.	<q.l.	<q.l.	<q.l.
<b>Phthalates 13 compounds</b>	[µg/L]	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	1.2-150	3.6-4.1 (3.9) 2.8-4.2 (3.5)	n.a	220	170	640	370
<b>Aliphates C<sub>5</sub>-C<sub>35</sub> 6 fractions</b>	[µg/L]	<q.l.-480,000	<q.l.-37,000	<q.l.-2700	<q.l.-5500	<q.l.-9400	12-53,000 (73)	630-1100 (870) 460-920 (690)	n.a	400	760	720	380
<b>Aromatics C<sub>8</sub>-C<sub>35</sub> 5 fractions</b>	[µg/L]	<q.l.-1.8	<q.l.-2.9	<q.l.	<q.l.-0.13	<q.l.-0.060	0.060-82 (2.0)	<q.l.-1.2 (0.70) <q.l.-1.1 (0.60)	n.a	<q.l.	<q.l.	<q.l.	<q.l.
<b>BTEX<sup>c</sup></b>	[µg/L]	<q.l.-2.1	<q.l.-2.1	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	n.a	<q.l.	<q.l.	<q.l.	<q.l.
<b>Methylated PAHs 4 groups</b>		<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.-63	<q.l.-1.2 <q.l.-1.1	n.a	<q.l.	<q.l.	<q.l.	<q.l.

<sup>a</sup> Samples with very high concentrations at the inlet were spiked with polluted stormwater sediment, diesel or petrol; <sup>b</sup>WDS = wet dust sampler; <sup>c</sup> EMC = event mean concentrations <sup>d</sup> SS = street sweeping; <sup>e</sup> <q.l. = below the limit of quantification; <sup>f</sup> n.a.=not analysed; <sup>g</sup>BTEX =benzene, toluene, ethylbenzenes and xylene

#### 4.2.1 Reduction of organic pollutants using street sweeping

Data on the OPs analysed in washwater from the street sweeping machine are presented in Table 3, and concentrations of all the approximately 70 specific compounds are found in Paper III. The washwater collected by the street sweeping machine had extremely high concentrations of OPs in comparison to results from other studies and water quality guidelines. Aliphates C<sub>5</sub>–C<sub>35</sub>  $\leq$  53 000  $\mu\text{g/L}$  and PAH-16  $\leq$  120  $\mu\text{g/L}$  were quantified in the highest concentrations after a period of more than three months when no street sweeping was carried out. In the wet dust sampler (WDS) samples from the same sweeping event, the concentrations of PAH-16 were much lower and varied between 1.3–3.0  $\mu\text{g/L}$ . These lower PAH concentrations may be explained by the smaller amount of road dust collected with the WDS than with the sweeping machine. The street sweeping machine provides an average value, i.e. a representative composite sample, from all the streets in the entire catchment area of approximately 55 ha, while the WDS samples were taken as a composite samples on a small surface (approximately 10 m<sup>2</sup>) within the area. The lowest quantification frequency and concentrations of OPs were detected in the two washwater samples collected midway through the sweeping campaign in September and October. The event mean concentrations (EMCs) of PAH-16 analysed in stormwater during the street sweeping campaign were 0.33–0.77  $\mu\text{g/L}$  (Table 3), and in the same order of magnitude as EMCs reported for stormwater in other studies (Hou and Li 2018, Pettersson et al. 2005, Zgheib et al. 2012).

It was evident that higher concentrations of PAH-16 and aliphatic and aromatic petroleum hydrocarbons were quantified in washwater samples from the first sweeping event in the spring March 2018, compared to the first sampling occasion of the study in August 2017 (Paper III). However, it was not evident which factor(s) that would have the largest effect on pollutant abundance in collected samples. Time between sweeping events (one month for August 2017, three months for March 2018) is only one of the factors affecting the build-up of particles and pollutants on road surfaces. Other factors are precipitation, winter road maintenance actions including snow removal, de-icing and sanding, and seasonal emission variations. Increased emissions of vehicle-related pollutants during winter conditions could be due to increased road wear (including bitumen) caused by studded tyres (Gustafsson et al. 2019) or lower ambient air temperatures and cold-start conditions, which have been shown to cause higher PAH emissions for diesel vehicles (Alves et al. 2015), as well as higher PAH and oxy-PAH emissions for ethanol/gasoline fuelled vehicles (Ahmed et al. 2018).

#### 4.2.2 Reduction of organic pollutants through car wash

Diethylphthalate (DEP), di-(2-ethylhexyl) phthalate (DEHP) and di-iso-nonylphthalate (DINP) were found in high concentrations, in comparison to results from other studies and water quality guidelines, in the carwash and rain simulation waters (Paper IV). Of the phthalates, DINP was quantified in the highest concentrations of 640  $\mu\text{g/L}$  and was 2–4 times higher in the light rain simulation compared to the other studied events. The car exposed to light rain simulation was the only petrol driven car and had the longest driving distance during the experimental period,

which could be correlated with high concentrations of DINP. It has been found that tire wear, PVC, undercoating and paints may all contain phthalates released from vehicles to runoff (Björklund 2010). The low concentrations of DINP in the car washwater compared to water from the rain simulations may be due to the use of detergents. DINP has replaced DEHP in many applications due to EU regulations, which has led to its increased use. In a study of polluted snow in Gothenburg from 2009, the most abundant occurring phthalates were in relative concentration percentage DINP (62%) > DIDP (21%) > DEHP (15%) (Björklund et al. 2011). The results from the car wash and rain simulations showed the following relative concentration percentages: DINP (90%) > DEHP with (9%) > DEP (1%). This is an increase in the relative concentration of DINP over the past eight years and may be due to the previously mentioned EU regulations for the use of DEHP. The results also showed that as much as 0.10–0.40 µg per driven km were emitted from the cars in the simulation study (Paper IV).

Aliphatic hydrocarbons C<sub>5</sub>–C<sub>35</sub> were measured in high concentrations (compared to results from other studies and water quality guidelines) of up to 760 µg/L in car wash water and up to 720 µg/L in simulated rain (Table 3). This suggests that carwash and rain can remove OPs collected on vehicle surfaces during driving. The long-chain aliphates may be derived from diesel with C<sub>9</sub>–C<sub>23</sub> aliphatic hydrocarbons (Brewer et al. 2013, Fingas 2016). Only the car from the light rain simulation had a petrol engine, whereas the others had diesel engines. However, high concentrations of long-chained aliphates were also detected in washwater from the petrol car. The results indicate atmospheric deposition of diesel exhaust on this vehicle's surface. In the snow from Gothenburg, the most frequently detected aliphates were in relative concentration percentage C<sub>16</sub>–C<sub>35</sub> (96%) > C<sub>5</sub>–C<sub>16</sub> (2%) = C<sub>12</sub>–C<sub>16</sub> (2%) (Björklund et al. 2011). The distribution in the carwash and rain simulations samples was similar with aliphates C<sub>16</sub>–C<sub>35</sub> (83%) > C<sub>5</sub>–C<sub>16</sub> (8%) > C<sub>10</sub>–C<sub>12</sub> (5%) ≈ C<sub>12</sub>–C<sub>16</sub> (4%). Among PAHs, the PAH-M were quantified in the highest concentrations 0.21–0.85 µg/l (Table 3). High PAH-M concentrations from the conventional carwash scenario may possibly be due to the conventional detergents are better than eco-labelled detergents at removing hydrophobic pollutants from the vehicle surface. In a snow analysis from Gothenburg in 2009, the most frequent PAHs were in relative concentration percentage pyrene (26%) > phenanthrene (22%) > fluoranthene (18%) (Björklund 2011). Pyrene (22%) ≈ fluoranthene (20%) > phenanthrene (11%) also belonged to the most abundant PAHs found in the car washwater (Paper IV). The results also showed that aliphates were emitted 0.020–0.60 µg per driven km and PAH-16 2.5×10<sup>-4</sup>–2.5×10<sup>-3</sup> µg per driven km from the cars in the simulation study.

The results show the effectiveness of vehicle washing regarding the removal of OPs, but also that high concentrations and amounts of OPs are emitted from vehicles during rain events. Consequently, these results confirm that vehicles are an important source of OPs to urban road runoff. Because vehicle washing has shown effective OP removal, a solution could be to install a car washing system in a controlled and regulated environment, for example at toll or petrol stations.

### 4.2.3 Reduction of OPs in sorption filters

The occurrence of PAHs, aliphates, and aromates in the influent to the pilot filter facility may be due to their frequent occurrence in urban runoff (Kayhanian et al., 2007; Paper I) and their occurrence in polluted pond sediment (Strömvall et al. 2007), although the main source is assumed to be diesel and petrol fuels, which were spiked to the influent water to the pilot plant during stress tests (Paper V). In the sorption filter facility, the extremely high concentrations in the influent of aliphates  $>C_5-C_{16}$  up to 480,000  $\mu\text{g/L}$  (Table 3) is due to the spiking of diesel. Diesel contains approximately 80% aliphatic compounds, mainly  $C_9-C_{23}$ , and 20% aromates, of which  $<1\%$  are BTEX compounds (Brewer et al. 2013, Fingas 2016). Further, diesel contains mainly PAH-L and -M, but lower levels of PAH-H (de Souza and Corrêa 2016). Petrol contains mainly aliphates  $C_3-C_{13}$  and BTEX. Among the aliphates and aromates, the highest concentrations quantified were also related to petrol and diesel aliphates  $>C_5-C_{16}$  in the effluent from most of the sorption filters during all events (i.e. weekly, heavy rain, and stress tests) (Table 3). Concentrations of aromates  $>C_8-C_{16}$  were low (0.06–2.9  $\mu\text{g/L}$ ) and close to quantification limits in water samples from all events.

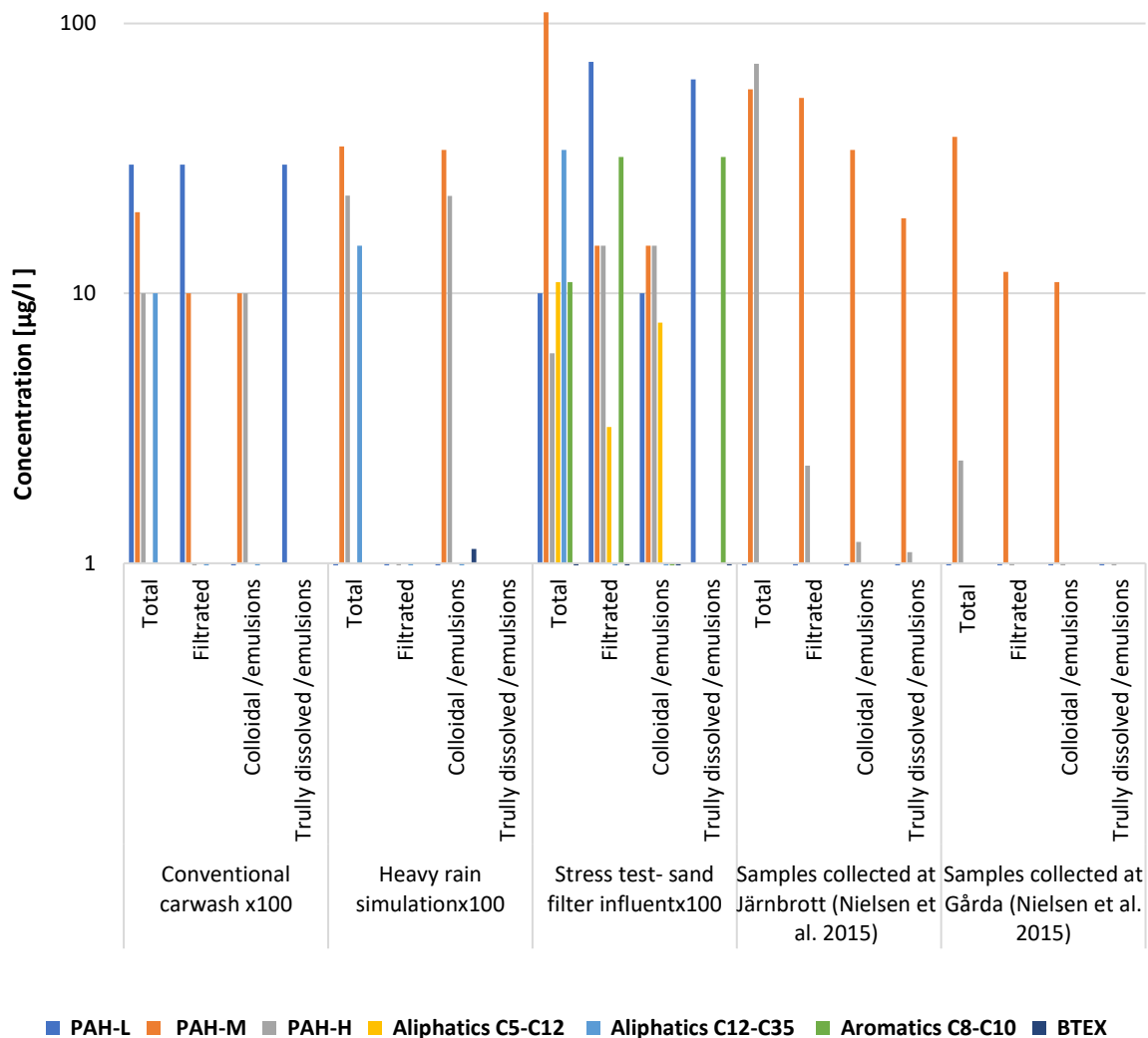
Samples collected during heavy rain events and stress tests showed high enough pollutant concentrations in the influent to allow calculation of the removal efficiency (Paper V). Naphthalene was the only specific compound quantified frequently enough in the influent stormwater to the filter facility during the *weekly sampling* to calculate the removal efficiencies. Naphthalene leached from the GAC filter (100% release), was not removed in the peat filter (0%) but was efficiently removed by 100% in the sand and bark filters. The results from the *heavy rain events* with relatively higher concentrations of OPs showed excellent (100%) removal efficiencies by all filters for aliphates  $>C_{16}-C_{35}$ , benzene, phenanthrene, fluoranthene, and pyrene. The high PAH removal rate for bark was confirmed in a batch test in which approximately 80% PAH-M was removed within 30 min (Björklund and Li 2015), and for activated carbon with a removal rate of 73–95% of PAHs (Lamichhane et al. 2016). Batch tests however are not entirely representative of the conditions in the filter column. However, during rain events the removal rate for naphthalene was only 32% by the sand filter and 80% by the bark filter and the compound was more efficiently sorbed in the peat and GAC filters. During rain events, concentrations of aliphates  $>C_5-C_{16}$  increased after passing the sorption filters, and concentrations of aromatics  $>C_{10}-C_{16}$  increased after passing the peat filter, indicating release of these pollutants from the filters. This may be caused by the competition for active sites in the sorbents, where relatively lower molecular-weight and more water-soluble compounds are released first. During the *stress tests*, the detection frequencies were high for many of the OPs, and the removal efficiency was 100% for all filters, except in the case of naphthalene, which was less efficiently sorbed in the sand filter. The recommendation is to use a combination of sand pre-filtration and all the studied sorption materials in stormwater filters in series, to achieve effective removal of different types of OPs.

## 4.3 Organic pollutants in colloidal and emulsion phases

### 4.3.1 Distribution of PAHs among phases in vehicle runoff and stormwater

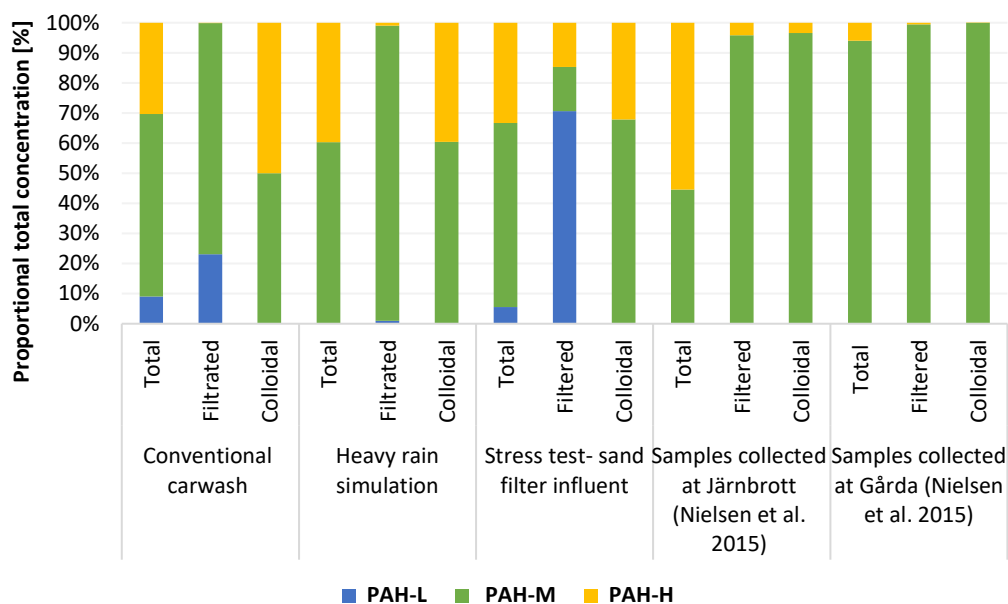
Given the current knowledge, it is assumed that PAHs are both truly dissolved and sorbed to solid colloids, but PAHs in mixtures with other hydrophobic OPs could possibly agglomerate into emulsions (Paper II), knowing their ubiquitous occurrence and high hydrophobicity (Abdel-Shafy and Mansour 2016). If emulsions occurred, they would have been identified as truly dissolved and/or colloidal phases in the previous studies, because it was believed that OPs occurred in two phases: a solid phase  $>0.7 \mu\text{m}$  and a dissolved phase composed of all that passed through the filters. Based on the findings in this thesis work (Papers II, IV and V), it is more correct to separate compounds in a road runoff sample into four phases: solids  $>0.7 \mu\text{m}$ , colloids (solids  $<0.7 \mu\text{m}$ ), truly dissolved, and emulsions (liquid ‘particles’  $<0.7 \mu\text{m}$ ).

The distribution of PAHs, aliphates  $>C_{16}-C_{35}$ , aromates  $>C_8-C_{10}$  and BTEX among the total, filtrated and colloidal/emulsion fractions is presented in Figures 12 and 13 (Paper IV and V). The truly dissolved fractions, which may also include some of the emulsions, were calculated from the results to be very low in most samples. The results are from carwash, heavy rain simulations and sorption filter testing, and are compared with stormwater samples from Nielsen (2015), which were collected through grab sampling from two stormwater sedimentation facilities in Gothenburg during the wet weather period. The results clearly show that all fractions of PAH-16, aliphates  $C_5-C_{12}$  and BTEX occur in the colloidal fractions and confirm that OPs in road runoff may occur in the colloidal fraction that also include emulsions. Overall, the PAH concentrations in this study are much lower compared to the concentrations found by Nielsen (2015), with the highest concentration found for PAH-H of  $71 \mu\text{g/L}$  in the total fraction and  $53 \mu\text{g/L}$  and  $34 \mu\text{g/L}$  for PAH-M in filtrated and colloidal fractions, respectively (Nielsen et al., 2015). The most polluted samples from this study were from the sorption filter stress tests with spiked influent; the highest value for PAH-M ( $1.1 \mu\text{g/L}$ ) was found in the total fraction, and PAH-L ( $0.72 \mu\text{g/L}$ ) in the filtrated fraction (Fig 15).



**Fig 15.** The concentrations in µg/l of organic pollutants in the total, filtered and colloidal fractions found in this project and compared to results from Nielsen 2015. Note that the y-axis has a logarithmic scale.

Similarly, the highest concentrations of aliphates  $>C_5-C_{35}$  and aromates  $>C_8-C_{10}$  were quantified in the total and filtrated fractions of samples from the sorption filter stress tests (Paper V). In one of these samples the concentrations of several OPs were high enough to be quantified also in the emulsion/colloidal fraction. The relatively high concentrations of BTEX and PAH-L may be because these compounds are more water soluble than the other groups of analysed OPs. PAHs were present in the total, filtrated and colloidal fractions in the car wash and simulated rain experiments (Paper IV).



**Fig. 16.** The relative composition of polycyclic aromatic hydrocarbons in different fractions found in Paper IV and V compared to earlier studies by Nielsen et al. 2015.

In Fig. 16, the relative composition of PAHs in different fractions was compared for this study (Paper III and IV) with earlier results (Nielsen et al. 2015). In stormwater from the filter treatment facilities, PAH- M and PAH-H dominated in the total and colloidal fractions, but the filtered fraction were dominated by the more water-soluble PAH-L. In the car washwater, the colloidal fractions had a high relative amount of PAH-H, which shows that even if these compounds are not that water soluble, they may be transported by emulsions and colloids.

#### 4.3.2 Organic pollutants may form emulsions

In this study three hypotheses for OP emulsion formation were tested and proven in Paper II:

i) Simulated stormwater samples containing diesel and/or hydrophobic OPs with or without HA and Fe colloids could produce emulsions with small particles measurable at the nano- and micro-scale using dynamic light scattering (DLS) and nanoparticle tracking analysis techniques (NTA). Measurements with both the Zetasizer (DLS) and Nanosight (NTA) instruments imply that emulsions in the samples were found in the nano-range 60–580 nm and 30–660 nm, respectively, and a smaller portion of the emulsion particles <28%, were found to be micro-sized.

ii) The particle sizes and concentrations were different for samples mixed shortly before measurements and those samples with short and long-term stabilisation. These differences are possible to explain by the coalescence or Ostwald ripening process, i.e. smaller droplets dissolve in larger droplets over time, and also by the fact that with the longer stabilisation time, the samples became less polydisperse.

iii) Addition of HA and Fe colloids increased the size and reduced the number of particles in the emulsions because of formation of Pickering emulsions, i.e. emulsions stabilised by solid particles, occurring when micelles emerge as stabilised by colloids, and/or due to Fe colloids co-precipitation with HA colloids. In the mixture containing colloidal HA and Fe, as well as all the studied OPs, the number of ‘the larger’ micro-scale particles decreased after mixing due to agglomeration, whilst the number of ‘the smaller’ nano-scale particles increased significantly when the sample was left stagnant and stabilised due to the break down and dispersion of the agglomerated larger particles. In addition, the mixture of HA and Fe colloids reduced in the number of particles by 1.3–3.5 times after energy input.

This study suggests that emulsion formation could be an important transport route for OPs in road runoff and urban stormwater. Research on actual stormwater samples from different environments, seasons, temperatures and rain events may clarify the importance of emulsion formation for the transportation of OPs in stormwater sewers and treatment systems.

## 4.4 Sustainable and effective solutions to protect stormwater from nanoparticles

### 4.4.1 Removal of nanoparticles from stormwater, vehicles and streets

Removal of nanoparticles from stormwater has been studied in sorption filters, street sweeping and car wash experiments (Table 4).

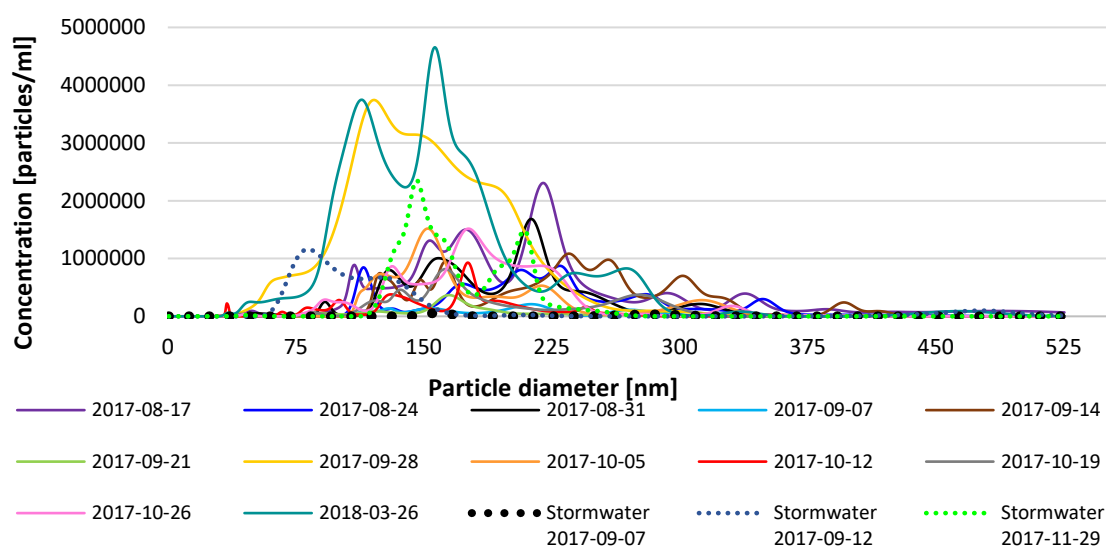
**Table 4.** Minimum to maximum (median) values of TSS<sup>a</sup>, TOC<sup>b</sup>, DOC<sup>c</sup>, ZP<sup>d</sup>, PSD<sup>e</sup> and MD<sup>f</sup> measured in effluents from sorption filters, washwater from street sweeping machine, car wash simulation and runoff from vehicles. Where no median is given the results are average values.

Compounds	Matrix analysed Unit	Sorption filters					Street sweeping			Car wash		Rain simulation	
		Sand filter influent	Sand filter effluent	GAC effluent	Peat effluent	Bark effluent	Street sweeper	WDS <sup>g</sup>	Stormwater	Conventional detergent	Eco-labelled detergent	Light rain	Heavy rain
		Storm-water	Storm-water	Storm-water	Storm-water	Storm-water	Washwater	Washwater	Stormwater	Wash-water	Washwater	Vehicle runoff	Vehicle runoff
								Before SS <sup>h</sup> After SS	With SS Without SS				
TSS	[mg/L]	0.40–1100 (17)	0.40–66 (4.8)	<q.l.*–20 (1.4)	<q.l.–33 (2.4)	<q.l.–15 (1.6)	270–52000 (2400)	600–760 (680)	160 n.a	670	870	770	1000
Particle average total concentration (ATC <sup>i</sup> )	[particle/ml]	2.1×10 <sup>8</sup>	3.3×10 <sup>7</sup>	1.6×10 <sup>7</sup>	2.5×10 <sup>7</sup>	1.8×10 <sup>7</sup>	2.0×10 <sup>8</sup>	6.2×10 <sup>8</sup> 3.5×10 <sup>7</sup>	4.9 x10 <sup>6</sup>	1.8×10 <sup>8</sup>	2.3×10 <sup>8</sup>	6.2×10 <sup>7</sup>	3.1×10 <sup>7</sup>
Particle mean diameter	[nm]	190	240	150	210	290	160	220 185	170	130	160	190	170
Particle ATC < 100 nm	[particle/ml]	1.05×10 <sup>7</sup>	2.9 x10 <sup>7</sup>	4.3 x10 <sup>6</sup>	9.9 x10 <sup>4</sup>	0	1.6×10 <sup>7</sup>	4.4×10 <sup>6</sup> 1.2×10 <sup>6</sup>	1.7 x10 <sup>7</sup>	2.4×10 <sup>7</sup>	1.5×10 <sup>7</sup>	2.0×10 <sup>6</sup>	2.4×10 <sup>6</sup>
TOC	[mg/L]	7.8–830 (230)	6.5–890 (170)	1.3–810 (230)	7.1–710 (120)	9.5–930 (240)	n.a	<0.50 <0.50	n.a	14	13	8.2	7.1
DOC	[mg/L]	6.8–890 (190)	6.0–720 (92)	1.6–800 (240)	7.2–790 (140)	8.9–920 (240)	47–640 (270)	<0.50 <0.50		9.9	12	8.1	6.6
Zeta potential	[mV]	n.a	n.a	n.a	n.a	n.a	-10	-7.0 -23	n.a	-19	-2.3	-10	-3.5

<q.l. - below the limit of quantification; n.a. – not analysed; <sup>a</sup>TSS – Total suspended solids; <sup>b</sup>TOC – Total organic carbon; <sup>c</sup>DOC – Dissolved organic carbon; <sup>d</sup>ZP – Zeta potential; <sup>e</sup>PSD – Particle size distribution; <sup>f</sup>MD – Mean diameter; <sup>g</sup>WDS – Wet dust sampler; <sup>h</sup>SS – Street sweeping; <sup>i</sup>ATC – Average total concentration.

### Reduction of nanoparticles through street sweeping

The finest fractions of the particles found in the washwater after collection by the street sweeping machine were in the same size range as those found in the sampled stormwater, and mainly in the size range of 100–300 nm (Fig. 16, Paper III). Similar PSD have been observed in other traffic-related matrices, e.g. stormwater (Nielsen et al. 2015) and water from car washing (Paper IV), tyre and pavement wear (Grigoratos et al. 2018, Gustafsson and Eriksson 2015, Mathissen et al. 2011), and brake wear (Puisney et al., 2018, Kukutschová et al., 2011, Wahlström et al., 2010). Many of the samples (Fig. 16) contained relatively large percentages of nanoparticles smaller than 30 nm, and in further research studies it will be of high interest to try to identify the content of these extremely small particles. This will be a challenge for analytical chemists and may be possible by combining very advanced analysis techniques and methods (Mourdikoudis al. 2018).



**Fig. 17.** Particle size distribution in washwater sampled by the street sweeping machine on 14 occasions, and in stormwater sampled on two occasions in the sweeping case study area. Analysed by dynamic light scattering (Litesizer<sup>TM</sup>500). Notice that the x-axis has a logarithmic scale.

Several studies have investigated in detail the effect of precipitation on transport of particles of different sizes from road surfaces (Egodawatta et al. 2007, Murakami et al. 2004, Zhao and Li 2013). The general conclusion is that more intense rain events have a greater ability to mobilize coarser road dust particles than less intense rain. However, Egodawatta et al. (2007) suggested that mobilization of fine particles also increases with more intense rainfall because less intense rain events cannot mobilize high-density fine particles. In this study too few stormwater samples were studied to confirm this tendency, however Fig. 17 shows that low intensity precipitation of 14.3 L/(s×ha) on 2017-09-07 resulted in a low concentration of particles in the stormwater sample. A few days later, on 2017-09-12 an intense rainfall of 160 L/(s×ha) resulted in a considerable increase in the particle concentration. Moreover, Fig. 14 shows occurrence of slightly smaller particles down to approximately 70 nm after the intense precipitation on 2017-09-12 than after the light rain on 2017-09-07 down to approximately 110 nm, which suggest higher mobilization of fine particles of high density.

### **Emissions of nanoparticles from carwash and rain simulation**

Rain simulations showed that the total amount of nanoparticles in the water was twice as high for the light rain than for the heavy rain simulation,  $62 \times 10^6$  and  $31 \times 10^6$  particles /ml respectively (Table 4). In general, the car wash simulations show a considerably higher number of nanoparticles up to  $255 \times 10^6$  per driven kilometer sized 2.5–400 nm measured with Nanosight (Paper IV). Results from the Litesizer instrument, illustrate no difference in relative composition of the particles between rain simulations and conventional car wash samples. Nanoparticles in the size range 90–260 nm were quantified in all samples. However, smaller nanoparticles 30–70 nm were quantified in the washwater with eco-labelled detergent.

### **Removal of nanoparticles by sorption filters**

Only the sand filter was able to remove TOC and DOC, whereas GAC, peat and bark filters appeared to release DOC, and therefore the median removal efficiency of DOC for the entire plant was negative (Table 4, Paper V). This is alarming, because a loss of organic colloids could mean a loss of OPs, which bind to the colloids. This transport process was demonstrated in the leaching of metals from peat filters, where the presence of humic material and iron colloids led to colloid-facilitated transport of metals from peat filters (Kalmykova et al. 2010). Loss of DOC from peat and bark filters in the treatment of contaminated waters in laboratory tests has been reported in other studies, which also showed that leaching of DOC decreased over time (Kalmykova 2009, Ribé et al. 2009). The continuous leaching of DOC in the current study may be caused by the decomposition of the peat and bark materials into smaller constituents, which is promoted by oxidation, higher temperatures, and a neutral to basic pH (Kalmykova 2009).

The results from the Nanosight showed that the stormwater influent to the filter facility contained a substantial number of nanoparticles in the size range 50–400 nm, with a mean diameter of 190 nm and average concentration of  $2.1 \times 10^8$  particles/mL (Table 4). The concentration of nanoparticles was reduced by one order of magnitude after passing the sand filter, to  $3.3 \times 10^7$  particles/mL. All sorption filters removed nanoparticles: GAC by 51% > bark by 46% > peat by 22%. The peat filter was least effective, suggesting the possible co-release of attached OPs, as the release of some aliphates also increased after passing the peat filter after the rain event. Results from the Litesizer showed that peat and bark filters released larger nanoparticles than those present in the effluent from the sand filter, which shows a possible escape of the coarser fraction of the materials from these filters. Contrarily, the results for the GAC filter show that very small nanoparticles were released from the filter component. The effluent samples from one stress test in the pilot filter facility (May 2017, 20 L sediment and 1 L diesel added to pilot plant influent) were also subjected to partitioning studies and PSD analysis, see Paper V. All the investigated filters released nanoparticles in high concentrations and most of the nanoparticles with particle average total concentration < 100 nm (Table 4); therefore, it is important to investigate in which phases the particles are likely to emerge. Particles in the filtered samples were 0.1–10  $\mu\text{m}$  in size, except in the GAC effluent where 82% of the particles were smaller than 0.7  $\mu\text{m}$ . Particles in the colloidal fraction of the influent, and in the effluents of the sand and bark filters, were 0.2–5  $\mu\text{m}$  and for the GAC and peat filter effluents 0.2–1.4  $\mu\text{m}$ . In the phase separation, emulsions of OPs that may occur as particles in

nm (Paper II) were trapped in the C<sub>18</sub> sorbent used. Left in the filtrate from the C<sub>18</sub> was the colloidal fraction extracted from the filtered phase. The results also show relatively high concentrations of BTEX, aliphates C<sub>5</sub>–C<sub>12</sub>, aromates C<sub>8</sub>–C<sub>10</sub>, and PAH-L in the truly dissolved and emulsion fraction, which may be due to the fact that these compounds are relatively more water soluble than the other groups of OPs analysed, see Table S1 in Supplementary material, Paper V.

## 4.5 Organic pollutants in solid materials

The concentrations of OPs were analysed in solid materials, including used sorption filter materials (Paper V), street sweeping sand and particles < 0.7 µm in street sweeping washwater (Paper III), and are presented in Table 5.

### 4.5.1 Organic pollutants in sorption filters materials

Like for the influent water samples, the quantified concentrations of PAH, aliphates, and aromates in the filter materials (Table 5) reflect the abundance of these compound groups in diesel (Brewer et al. 2013, Fingas 2016). It can be assumed that the highly hydrophobic compounds (aliphates, larger aromates, PAH-M and -H) partition to particles in the influent stormwater, and/or are easily sorbed to the filter media, hence are removed in the top layer of the filter bed (Table 5). The BTEX and lighter aromatic compounds, on the other hand, are dissolved and tend to migrate through the column beds, as seen in Table 5.

Generally, higher concentrations of BTEX, aromates, and PAH-16 were quantified in the GAC than in the bark and peat. Although GAC is generally hydrophobic (Gonçalves et al. 2010, Mohammad-Khah and Ansari 2009) the material exhibits higher concentrations of hydrophilic BTEX compounds, and lower concentrations of the hydrophobic aliphatic and aromatic hydrocarbons than peat and bark. In a previous study, where GAC and peat filters were used for treatment of landfill leachate, similar results were found: the more volatile and water-soluble OPs were effectively sorbed by GAC and the more hydrophobic pollutants were more effectively sorbed by peat (Kalmykova et al. 2014). The lignin of pine bark is full of aromatic groups that may attract hydrophobic compounds, but bark also contains hydrophilic surface groups that may attract hydrophilic compounds (Valentín et al. 2010). Peat also contains both hydrophilic and hydrophobic surface groups (Rezanezhad et al. 2016). The recommendation is therefore to use a combination of the studied sorption materials in stormwater filters connected in series to achieve effective removal of OPs with different molecular size, volatility, and water solubility, where GAC would sorb the small and relatively more water soluble compounds, peat the more high-molecular weight and lipophilic OPs, and bark the compounds in between. The suggestion is to place the sorption filters in a series, starting with prefiltration using a sand filter to remove TSS, DOC and nanoparticles, followed by a GAC filter that removes the most volatile hydrocarbons, then bark and finally peat for removal of the high-molecular weight OPs.

**Table 5.** Loss on ignition (%) and quantified concentrations (mg/kg dry substance) of organic pollutants in the upper 0–10 cm and centre 10–35 cm of the bed of used sorption filter materials and filtered particles (>0.7 µm) in washwater, and in road dust collected by the street sweeping machine. Where no median is given, the value is <q.l.

Compounds	Fraction analysed Unit	Sorption filters materials						Street sweeping machine	
		GAC top	GAC centre	Bark top	Bark centre	Peat top	Peat centre	Road dust	Particles in washwater retained on 0.7 µm filter
Loss on ignition	[%]	68	82	78	75	79	80	1.1–5.5 (2.6)	13
PAH-16	[µg/L]	1.6	0.70	1.3	0.44	0.56	0.38	<q.l.–0.73	3.1
PAH-L	[µg/L]	0.80	0.57	0.74	0.15	0.14	0.092	<q.l.	0.10
PAH-M	[µg/L]	0.85	0.15	0.52	0.29	0.35	0.29	<q.l.–0.65	1.8
PAH-H	[µg/L]	<q.l.	<q.l.	0.074	<q.l.	0.085	<q.l.	<q.l.–0.59	1.3
Oxygenated-PAHs 9 compounds	[µg/L]	<q.l.	n.a	<q.l.	n.a	<q.l.	n.a	<q.l.	n.a
Phthalates 13 compounds	[µg/L]	<q.l.– 0.69	n.a	<q.l.– 0.89	n.a	<q.l.– 1.4	n.a	<q.l.–12	<q.l.
Aliphates C <sub>5</sub> –C <sub>35</sub> 6 fractions	[µg/L]	<q.l.–180 (36)	<q.l.–260 (38)	<q.l.– 6600	<q.l.–250	<q.l.– 1100	<q.l.– 1200	<q.l.–780	950
Aromates C <sub>8</sub> –C <sub>35</sub> 5 fractions	[µg/L]	<q.l.–31 (1.1)	<q.l.–53	<q.l.– 190 (2.0)	<q.l.–10	<q.l.– 2.7	<q.l.– 4.0	<q.l.	<q.l.–1.8 (1.5)
BTEX	[µg/L]	<q.l.– 0.056	0.10–0.80 (0.22)	<q.l.	<q.l.–0.13 (0.060)	<q.l.	<q.l.– 0.085	<q.l.	<q.l.
Aldehydes C <sub>1</sub> –C <sub>5</sub> 5 compounds	[µg/L]	n.a	n.a	n.a	n.a	n.a	n.a	<q.l.–7.6 (1.2)	n.a
Nonylphenols, octylphenols and –(mono- tri)ethoxylates 8 compounds	[µg/L]	n.a	n.a	n.a	n.a	n.a	n.a	<q.l.–0.15	n.a
Methylated PAHs 4 groups	[µg/L]	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	n.a	1.3

<q.l – below the limit of quantification

n.a – not analysed

#### 4.5.2 Organic pollutants in street sweeping sand and dust

Data on the OPs analysed in road dust samples and particles in the washwater >0.7 µm are presented in Table 5, and concentrations of all the approximately 70 specific compounds are available in Paper III. The compound groups generally found in the highest concentrations were aliphates C<sub>5</sub>–C<sub>35</sub> > aromates C<sub>8</sub>–C<sub>35</sub> > phthalates > PAH-16 > aldehydes C<sub>1</sub>–C<sub>5</sub>. Alkylphenols and their mono-triethoxylates were only quantified in a few samples. The highest quantification frequency, as well as the highest concentrations of PAHs, aliphatic and aromatic petroleum hydrocarbons in road dust and washwater particles, were found in the samples collected in March and April 2018, after a period of more than three months when no street sweeping was carried out. In these samples, the concentrations of OPs were at least one magnitude higher than in the other samples. From the results found in Paper III, it is not evident which factor(s) that would have the largest effect on pollutant abundance in the collected solid matrices.

In general, more aliphatic and aromatic petroleum hydrocarbons and PAHs were quantified in street sweeping washwater than in road dust samples (Tables 1 and 5). Phthalates (DnBP, DnOP, DCHP and DINP) were sporadically quantified in sieved road dust samples (Paper III). In the non-sieved road dust samples, only aliphates  $>C_{16}-C_{35}$  and DEHP were quantified. The only alkylphenol quantified, i.e. 4-*tert*-octylphenol, was found in one of the road dust samples. The OPs analysed in the road dust samples did not show a strong time trend, unlike in the washwater samples, where OP concentrations were exceptionally high after the winter sweeping break.

The particles ( $>0.7 \mu\text{m}$ ) in washwater contained 13% organic matter (OM); more than the corresponding sieved road dust sample with size 63–125  $\mu\text{m}$  and 3.3% OM (Paper III). In addition, concentrations of total PAHs were almost three times higher in the particles in washwater than in the corresponding road dust particles. These findings were expected, as hydrophobic organic compounds are preferentially sorbed to particles with organic content, and smaller particles can sorb more pollutants per weight unit than large particles (Dong and Lee 2009, Hengren et al. 2010, Sansalone and Buchberger 1997).

The Swedish guidelines for less sensitive land-use (e.g. offices, roads, industries) were exceeded for aliphates  $C_{16}-C_{35}$  in all road dust samples (Naturvårdsverket 2009). In addition, the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life were exceeded for several PAHs (e.g. fluoranthene and pyrene) in three of the road dust samples. The findings call for proper management of street sweeping waste. For regions where sweeping cannot be performed during winter, which may result in highly polluted street sweeping dust and washwater in spring, the road administrations could prioritize treatment of washwater from the first sweeping events in spring. As the larger dust fractions contained lower concentrations of OPs, these may be most suitable for reuse. It is imperative to develop innovative and sustainable methods to treat the polluted waste from the street sweeping machine, as further research has shown that these materials besides OPs also contain metals and microplastics (Järnskog et al. 2020).

## 5. CONCLUSIONS

This thesis contributes to increased knowledge about colloidal organic pollutants in road and traffic environments by tracking emissions and sources, prioritizing pollutants, calculating loads, studying transport routes and formation of emulsion, and determining the effectiveness of treatment alternatives. The knowledge from this thesis can inspire and contribute to further studies of organic pollutants (OPs) transport routes and development of innovative and sustainable treatment options.

The following recommendations are suggested to prevent further spread of OPs and nanoparticles to the urban environment:

- Frequent street sweeping of the most polluted streets in urban areas should be introduced as soon as possible.
- Frequent washing of vehicles in urban areas should be mandatory, especially during winter when emissions of exhaust gases and vehicle wear are greatest.
- The final step for treating highly polluted stormwater must contain sorption filters to effectively remove OPs and especially OPs in colloidal forms.

The most important conclusions from this PhD thesis are as follows:

- 1100 OPs were identified as potentially emitted to the environment from traffic- and road-related sources. This comprehensive list of OPs was further systematically reduced to a priority pollutant (PP) list using literature and database searches, advice from practitioners and experts, as well as the RICH method. Through the iterative selection processes developed in this thesis the following list of PPs was obtained: PAH-16 > alkanes C<sub>20</sub>–C<sub>40</sub> > alkylphenols > phthalates > aldehydes > phenolic antioxidants > bisphenol A > oxy-PAHs > naphtha C<sub>5</sub>–C<sub>12</sub> > amides > amines.
- A substance flow analysis was performed for PAH-16 in a highway case study area, and the total amounts of PAHs emitted from traffic and roads were calculated to 990–3900 µg per driven vehicle kilometre. Although only 2–6% of the total amount of PAHs are transported to stormwater in the catchment area, this load contains a higher proportion of the hazardous PAHs, originating mainly from tyres, motor oil leakage and exhaust gases.
- Simulated stormwater samples containing diesel and/or hydrophobic OPs with or without HA and Fe colloids could produce emulsions with small particles measurable at the nano- and micro-scale using dynamic light scattering and nanoparticle tracking analysis techniques. Measurements implied that most emulsions in the samples were found in the nano-range 30–660 nm, and a smaller portion of particles <28%, were found to be microsized.
- Addition of HA and Fe colloids to the simulated stormwater samples increased the size and reduced the number of particles in the emulsions because of formation of Pickering

emulsions, i.e. emulsions stabilised by solid particles, occurring when micelles emerge as stabilised by colloids, and/or due to Fe colloids co-precipitation with HA colloids.

- The results from the studies of OPs in different fractions clearly show that PAH-16, aliphatic hydrocarbons C<sub>5</sub>–C<sub>12</sub> and BTEX occur in the colloidal fractions and confirm that OPs in road runoff may occur in the colloidal fraction that also include emulsions.
- This is the first study where nanoparticles in sizes down to 1 nm have been identified in washwater from street sweeping. The washwater contained nanoparticles, with the highest presence in the size range 25–300 nm. This indicates that nano- and microparticles are collected effectively by the street sweeping machine.
- The highest concentrations of OPs were found in streets sweeping sand and washwater after a 3-month long break in sweeping during winter, and concentrations of aliphates > phthalates > aromatics > PAH-16. The concentrations of long chain >C<sub>16</sub>–C<sub>35</sub> aliphates and PAH-16 in washwater were extremely high, ≤ 53 000 µg/L and ≤ 120 µg/L respectively, compared to results from other studies and water quality guidelines. Phthalates, such as DBP, DEHP and DINP, were detected in both washwater and road dust, and toxic oxy-PAHs were identified in one washwater sample.
- The waste material collected inside the street sweeping machine contains high concentrations of nano- and microparticles and OPs, hence the material requires treatment before it is disposed or reused.
- The design of the pilot filter plant was appropriate for assessing the ability of sorption materials to remove non-particulate OPs. The results show that all three sorption filters were removing OPs to a high degree, especially during the stress tests with high pollutant loads when the removal efficiency was 100% for all three sorption filters.
- All filters also effectively removed total suspended solids (particles >1.2 µm). Total organic carbon was removed by the sand and peat filters, but all filters leached dissolved organic carbon (<0.45 µm). All sorption filters sorbed some size fractions of nanoparticles while releasing nanoparticles in other size fractions. The loss of nanoparticles correlates well with the loss of dissolved organic carbon; this is concerning as loss of OPs and other contaminants can bind to nanoparticles, or form nanoparticles in the form of emulsions, if they occur in high concentrations.
- The results from the car wash and rain simulations showed that emissions of phthalates were 0.10–0.40 µg per driven km, aliphatic hydrocarbons 0.020–0.60 µg per driven km and PAH-16  $2.5 \times 10^{-4}$ – $2.5 \times 10^{-3}$  µg per driven km. The concentrations of DEHP was up to 50 µg/L and DINP of up to 640 µg/L in the simulation waters. Nanoparticles in the size range 10–450 nm were also released in large amounts and the rain simulation and car washwater contained  $3.0 \times 10^5$ – $3.3 \times 10^6$  of nanoparticles per litre.

- Mandatory and frequent carwash, especially in winter, is an important measure that can be introduced in urban areas and which effectively would reduce pollution of stormwater in our cities. A solution could be to install a car washing system in controlled and regulated environments, as for example at toll or petrol stations.

## 6. FUTURE WORK

Recommendations and suggestions for future work based on the result in this PhD study are as follows:

- The suggested list of PPs provides guidance for how to select pollutants that should be subjected to further study, either by the means of an SFA or by monitoring. The SFA results can complement or substitute empirical monitoring of pollutant emissions. The procedure and results of this study can be used for predicting the load of OPs in road environments and to propose ways to prevent their emission into the aquatic environment.
- This study suggests that emulsion formation could be an important transport route for OPs in road runoff and urban stormwater. Research on actual stormwater samples from different environments, seasons, temperatures and rain events may clarify the importance of emulsion formation for the transportation of OPs in stormwater sewers and treatment systems. Further studies should investigate the formation of oil-in-water emulsions that cause synergistic effects on the water solubility of the OPs, as explained by the compounds' hydrophobicity, and that may cause an increased transport of OPs in stormwater.
- Treatment of contaminated materials is a complex issue as washwater from street sweeping may contain extreme concentrations of OPs and fine particles, and the pollutant abundance in the solid waste is often dependent on particle size. It is currently not well investigated how these materials can be decontaminated and prepared for reuse. Treatment methods of the polluted washwater require additional research, that was beyond the scope of this study.
- For the sorption filter facility, it was not possible to achieve the desired waterflow through the filters. It is suggested that future research should focus on improving the hydraulic characteristics of the filter beds.
- For the car washing and rain simulation research, further studies on a larger scale is recommended with larger sample size, similar driving patterns and distances travelled. Washing of different parts of vehicles are of interest, and heavy-duty vehicles should be included in the studies.
- Finally, a multi-criteria decision analysis (MCDA) would be interesting to perform to compare the treatment options studied in this research, together with other options, to find the most sustainable solutions for real-life case study areas. The MCDA is a decision support tool which aims to evaluate several criteria for multiple alternatives and provide a ranking of these alternatives.

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