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Generation of nano- and micro-sized organic pollutant emulsions in simulated road runoff

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ABSTRACT

A wide range of organic pollutants (OPs) are emitted from the road and traffic environment and transported with road runoff to receiving waters. To provide an understanding of the transport routes of OPs in the environment, an investigation was carried out with the aim to determine whether OPs are transported with nano- and microparticles in the form of emulsions. Tests were performed on simulated road runoff, using laboratory prepared mixtures of ultrapure water and specific polycyclic aromatic hydrocarbons (PAHs), alkylphenols (APs) and their ethoxylates (APEOs), phthalates, diesel oil (aliphatic hydrocarbons), with and without addition of humic acid (HA) and iron (Fe) colloids. The samples were analysed directly after mixing and after a few days of stabilisation for particle size distribution (PSD) and concentrations of particles in the size range 10 nm–100 µm, and zeta potential $> \pm 500$ mV. Further, after long-term storage to achieve stabilisation, selected samples were investigated for the PSD and particle concentrations in the ranges 10 nm–2 µm, to determine whether stable emulsions had formed. The following simulation mixtures, both mixed and stabilised, were identified as potential emulsions: diesel, APs and APEOs, diesel with APs and APEOS, phthalates, and a mixture of all OPs with and without colloids. Measurements with the Zetasizer and Nanosight instruments imply that the majority of particles in the samples were found in the nano-range of 30–660 nm respectively, and a smaller portion of particles $<$ 28% also measured with Coulter Counter were found to be micro-sized. Higher concentrations of the smallest nanoparticles were found in the mixture of all OPs without colloids added, than in the OP mixture with colloids added. The results indicate that the addition of colloids favours the formation of larger micro-sized emulsions that may break down with time into nano-sized particles. In the mixed samples, the number of micro-sized particles decreased, while the number of nanoparticles increased; this process may also occur in road runoff transportation systems during heavy rain events. This is the first study to indicate that emulsions of OPs may be formed in road runoff, and that emulsions may act as carriers of OPs in urban stormwater.

1. Introduction

Stormwater and receiving waters are sinks for pollutant loads transported with runoff over impermeable surfaces. Rapid population growth, climate change and urbanization have intensified pollution discharge into the environment, and consequently resulted in the deterioration of stormwater and receiving water quality (Bruen et al., 2006; Crabtree et al., 2008; Gnecco and Lanza, 2013). This has influenced the decision to introduce preventive actions and reduce the impact of human activities on water bodies by implementation of e.g. the European Water Framework Directive (European Commission, 2000) and Environmental Quality Standards (EU, 2008). Consequently, recent research has focused on the selection of priority pollutants and understanding transport routes and mechanisms of these substances from their sources to their endpoints (Markiewicz et al., 2017; Nowack and Bucheli, 2007; Zgheib et al., 2012).

Particles arising from processes such as erosion, wear and tear of tyres, road surfaces and building materials are of major concern as these particles may contain substances subject to leaching, for example phthalates from PVC, alkylphenols from e.g. concrete and plastics (Lamprea et al., 2018; Björklund, 2010), or PAHs and other organic chemicals leaching from tyre and road wear particles (Kalbe et al., 2013; Unice et al., 2015), but also because many dissolved stormwater contaminants have an affinity for particles. 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

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et al., 2013; Nielsen et al., 2015a; Wei et al., 2013; Zgheib et al., 2011; Zhang et al., 2008). Partitioning has been analysed to clarify whether pollutants present in the water phase emerge as dissolved or adsorbed to colloidal and particulate phases, with the aim of determining their fate and suitability for removal through treatment techniques. Several studies have shown that hydrophobic organic compounds that are assumed to occur as attached to particles, are in fact also found as truly dissolved or bound to colloids in urban runoff (Flanagan et al., 2019; Nielsen et al., 2015a; Kalmykova et al., 2013; Zgheib et al., 2011). Stormwater containing organic pollutants (OPs) is of special concern, since these substances may be persistent, bioaccumulate, hormone disruptive, carcinogenic, toxic, and of high risk to human health and the environment (The United Nations Economic Commission for Europe (UN-ECE), 1998). Traffic has been identified as the source of many OPs in stormwater (Björklund, 2010; Jonsson et al., 2008; Månsson et al., 2008). Through literature and database searches, up to 1100 different organic substances were identified as potentially emitted from the road environment (Markiewicz et al., 2017), and the following OPs as having highest priority for removal: polycyclic aromatic hydrocarbons (PAHs) > alkanes C_{20}–C_{40} > alkylphenols > phthalates > aldehydes > phenolic antioxidants > bisphenol A > oxygenated-PAHs > naphtha C_5–C_{12} > amides > amines. Facilities using sedimentation processes for treatment are inefficient for colloidal bound pollutants; as colloids do not settle and remain dispersed in the liquid phase, thereby enabling transport of attached pollutants in aquatic media (Hofmann and von der Kammer, 2009; Kalmykova et al., 2013; Nowack and Bucheli, 2007; Roy and Dzombak, 1998; Schijf and Zoll, 2011). Sorption to filter media could be effective for removing dissolved and colloidal stormwater pollutants. However, Flanagan et al. (2019) and Kalmykova et al. (2014) showed that removal of dissolved and colloidal contaminants in soil, peat and activated carbon filters is less effective than removal of particulate compounds. Currently, there are no effective technologies to treat OPs in nano-and micro-sized phases, i.e. OPs occurring as emulsions, or bound to colloids or other nano- and microparticles.

Studies on the partitioning behaviour of OPs have shown that selected alkylphenols, phthalates and PAHs were predominantly attached to colloids and/or truly dissolved in contrast to their expected strong sorption to particulate matter, and it was suggested that the higher organic content in the colloids decreases the compounds' partition to larger particles (Kalmykova et al., 2013). Surprisingly high concentrations of PAHs were also found in the dissolved fractions of synthetic solutions (Nielsen et al., 2015a), and approximately 45% of the PAHs in the stormwater samples were present in the colloidal and dissolved fractions. The highest concentrations of the PAHs were found in samples with occurrence of nano-sized particles, 10–100 nm. 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, 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 μm and a dissolved phase composed of all that passed through the filters. From the current state of knowledge, 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 μm). An emulsion is defined as a mixture of two or more liquids that are normally immiscible. The terms colloid and emulsion are sometimes used interchangeably, but in this paper 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 is most probably only one of many fate mechanisms occurring in stormwater. It is hypothesised that under appropriate conditions, such as heavy rainfall and high turbidity, the mixing of water and oily substances may create emulsions of droplets due to the hydrophobic nature of many organic molecules. These hypothetically formed emulsions containing mixtures of OPs may act similar to colloidal particles and could be an alternative transport route for OPs in stormwater. So far, the process of emulsion formation in stormwater has not been studied and this paper aims to fill this gap. Whether OPs occur in the form of emulsions, as sorbed to colloids or are truly dissolved needs to be taken into consideration when designing stormwater treatment measures, because these forms of nano- and microparticles will behave differently in the treatment processes. For example, if stormwater is treated in a sorption filter, truly dissolved PAHs may be more efficiently sorbed to the filter material than the PAHs trapped in emulsions or sorbed to the surface of colloids. If emulsions are formed by OPs in road runoff, then the environmental risks may increase because higher amounts of OPs occur in the dissolved phase than theoretically possible. As a consequence, OPs are transported longer distances with stormwater, and do not settled with sediment particles close to the sources of emission.

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). 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): *creaming and sedimentation*, *flocculation*, *coalescence* and *Ostwald ripening*. Occurrence of nanoparticles in the ranges 1–200 nm has recently been identified in wash water generated during street sweeping, road runoff and car-wash water (Polukarova et al., 2019; Nielsen, 2015; Markiewicz et al., 2019).

The aim of this study is to determine whether selected groups or specific OPs form stable emulsions in stormwater, using laboratory made mixtures of specific PAHs, alkylphenols (APs) and their ethoxylates (APEOs), phthalates, diesel oil, humic acids (HA) and iron (Fe) colloids as test samples. The OPs included in the study were selected from the list of priority pollutants indicated in previous research as compounds of high interest regarding their extended emission to, and detrimental effects on, stormwater and receiving waters (Markiewicz et al., 2017). Different techniques based on dynamic light scattering were used to analyse the mixtures and stormwater samples for micro- and nanoparticle concentrations, sizes and size distribution, including zeta potential measures to identify stable emulsions. The results from the laboratory experiments were used to prove the following hypotheses:

i) The mixtures of OPs in stormwater form emulsions of small particles, measurable in the nano- and microscales using dynamic light scattering and nanoparticle tracking analysis techniques.
ii) There is a difference in particle size and concentration between samples left stagnant for a given time and samples mixed shortly before measurement, due to coalescence, which is manifested by thinning and rupture of a film separating the droplets and results in merging into larger droplets, or Ostwald ripening processes, which may occur in polydisperse samples (i.e. samples with particles of varied sizes in the dispersed phase). The latter occurs when there is a difference in solubility between droplets of different sizes, wherein smaller droplets usually have higher solubility and will, over time, dissolve in the larger droplets (Pichot, 2010).
iii) HA and Fe colloids increase the size and reduce the number of particles in the emulsions because of formation of Pickering emulsions, i.e. an emulsion that is stabilised by solid particles which adsorb onto the interface between the two phases (Akartuna et al., 2008; De Paolis and Kukkonen, 1997; Kraft et al., 2010), and/or due to co-preciptiation of Fe with HA colloids (Angelico et al., 2014; Ngai and Bon, 2015).

Research on nano- and microparticles transport processes and their environmental impact is extensive. However, research concerning road environment mainly focuses on atmospheric pollution, exhaust emissions and metals in road dust, but also wear and tear of tyres as the main source of microplastic emissions to the environment (Leads and Weinstein, 2019; Unice et al., 2019; Wagner et al., 2018; Kole et al., 2017). Therefore, this study focuses entirely on the organic pollutants emitted in the road environment and research on the possibility for these compounds to generate nano- and micro-sized emulsions in simulated road runoff, which has not been studied before.

2. Experimental set up

2.1. Materials

Laboratory mixtures of different concentrations of specific PAHs, APs and APEOs, phthalates, diesel oil, with and without HA and Fe colloids in ultrapure water were used as test samples to simulate highly polluted road runoff. Urban stormwater is a complex matrix composed of a mixture of a large number of natural occurring materials and chemical compounds, as well as chemicals and materials caused by human activities, most notably traffic activities (Markiewicz et al., 2017). Hence, to achieve repeatable sample conditions and eliminate some of the unknown factors affecting natural stormwater quality, artificial mixtures of simulated stormwater with OPs and colloids were used in this study. Humic acid and Fe colloids are commercially available and are often used in synthetic stormwater, to simulate naturally occurring colloids (Massoudieh and Ginn, 2008; Nielsen et al., 2015a).

The US EPA PAH 16 861291 Supelco PAH Mix 3, purchased from Sigma-Aldrich, was used and contained acenaphthene 1000 μg/ml, acenaphthylene 2000 μg/ml, anthracene 100 μg/ml, benz[*a*]anthracene 100 μg/ml, benzo[*b*]fluoranthene 100 μg/ml, benzo[*k*]fluoranthene 100 μg/ml, benzo[*g,h,i*]perylene 200 μg/ml, benzo[*a*]pyrene 100 μg/ml, chrysene 100 μg/ml, dibenz[*a,h*]anthracene 200 μg/ml, fluoranthene 100 μg/ml, fluorene 200 μg/ml, indeno[1,2,3-*cd*]pyrene 100 μg/ml, 1-methylnaphthalene 1000 μg/ml, 2-methylnaphthalene 1000 μg/ml, naphthalene 1000 μg/ml, phenanthrene 100 μg/ml, and pyrene 100 μg/ml.

A fossil fuel-based diesel with 5–7 vol% of RME (rapeseed oil methyl esters) was purchased from OK/Q8, containing mainly alkanes and cycloalkanes with C_{10}–C_{17}. The stock solutions for the samples containing PAHs and diesel were diluted in acetone in a 1:25 ratio.

Sigma-Aldrich 33623 alkylphenol/ethoxylate target analyte mix solution, containing 4-*tert*-octylphenol 1 μg/ml, 4-*tert*-octylphenol monoethoxylate 1 μg/ml, 4-*tert*-octylphenol-di-ethoxylate 1 μg/ml, technical grade isononylphenol 5 μg/ml, technical grade isononylphenol monoethoxylate 5 μg/ml, technical grade isononylphenol diethoxylate 5 μg/ml, and bisphenol A 1 μg/ml was purchased from Sigma-Aldrich. For the phthalates 36,735 Sigma-Aldrich analytical standard bis(2-ethylhexyl) phthalate Pestanal®, 80,135 Sigma-Aldrich diisodecyl phthalate (Selectophore™), and 376,663 Aldrich technical grade diisononyl phthalate were used. The HA and Fe technical standards were purchased from Sigma-Aldrich Chemical Company Inc.

2.2. Preparation of laboratory mixtures

Samples with mixtures of 500 ml ultra-pure Milli-Q water and acetone, diesel, selected groups of OPs, Fe and HA colloids were prepared in concentrations according to Table 1. A laboratory-scale blender (Waring commercial) was used to homogenize all the samples at a speed of 3600 rpm for 120 s at room temperature (20 ± 2 °C). This process is defined as a high-energy emulsification and is considered the simplest method for mixing two immiscible phases in the presence of a surfactant (Kulawik-Pióro and Tal-Figiel, 2017). The samples were left to settle for a short time (5–10 days) or were stored long-term (approximately 2 years) for stabilisation before further monitoring was performed. Laboratory refrigerator was used to keep the samples in dark and at +4 °C. The samples stored short-time were analysed without and with mixing a few minutes before the analysis. The samples stored long-term were analysed without mixing. Mixing directly before the analysis simulates turbulent conditions that may occur during high flows under intense rain, or when tyres run over water on road surfaces. Stabilisation (i.e. long-time storage) simulates conditions that may occur during retention of stormwater, e.g. in ponds, or stagnant conditions in pipes and wells.

Concentrations of OPs in the solutions exceeded the guideline values for stormwater discharges according to the City of Gothenburg Environmental Administration, to simulate conditions occurring in road runoff during high pollutant loads (Miljöförvaltningen, 2013; Polukarova et al., 2019). Stock solutions of HA and Fe colloids were prepared to serve as a model colloidal phase following the procedure in Florence (1982), and the concentrations were selected to be comparable with the results in Kalmykova et al. (2013) and Nielsen et al. (2015a). Colloids of the HA were expected to be mainly in the micro-size range (approximately 150 nm), and the Fe colloids in the much smaller nano-size range (6–30 nm) (Nielsen, 2015). The HA colloids are slightly negatively charged in solutions at low pH and the negatively charge on the surface decrease with increasing pH and at pH above 9 the zeta potential were measured to less than −30 mV. Fe colloids are positively charged at low pH and negatively charged under basic condition. The selection of OPs, diesel oil and colloids, and the concentration of each constituent were determined from earlier studies of OPs and colloids occurring in road runoff (Table 1).

2.3. Urban stormwater samples

In addition to the laboratory mixtures made for simulation of highly polluted road runoff, urban stormwater was grab-sampled in March 2015 from two stormwater facilities in Gothenburg (Sweden), using a Ruttner water sampler. The samples were collected from the inlet of the Gårda sedimentation facility, and from the Järnbrott stormwater treatment pond. There had been a one-week dry period, i.e. stagnant water, prior to sampling. The Gårda stormwater treatment system is composed of seven sedimentation chambers collecting runoff from a catchment area of 5.5 ha, of which impervious surfaces constitute 64% (Pettersson et al., 2005). The facility receives runoff from the E6/E20 highway, with a daily traffic intensity of 80,000 vehicles; it is assumed that 100% of the OPs reaching the chambers originate from traffic-related activities (Markiewicz et al., 2017). The Järnbrott stormwater pond collects runoff from a highway (daily traffic intensity 20,000 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.

2.4. Characterization of laboratory mixtures and urban stormwater samples

The 15 samples (Table 1), as well as two urban stormwater samples, were analysed for particle concentrations, size and size distribution. The samples were also tested for stability by measuring the zeta potential of the dispersion, to investigate whether the mixtures produced stable emulsions. All samples were analysed a few days after preparation without mixing and after mixing just before the analysis. The samples were analysed for micro-sized particles using a Coulter Counter, for nano-sized particles and zeta potential with a Zetasizer, and for nano-sized particles using Nanosight. After long-term storage and stabilisation, the samples were analysed for nano-sized particles again, without mixing, using the Nanosight instrument.

2.4.1. Quantification of micro-sized particles by Coulter Counter

To quantify the number and number concentration of micro-sized particles in each sample and assess particle size ranges, a Z2™ Coulter Counter® Analyzer was used, with a 100 μm aperture and the electrical sensing method (ESM) as counting principle. This instrument counts

Table 1
Laboratory mixtures of selected OPs, HA and Fe colloids and their concentrations in ultrapure water used to simulate road runoff under controlled conditions.

Sample no.	Concentrations of OPs and colloids in ultrapure water in the laboratory mixture	References for the selection of concentrations
1	Acetone 10%	Used as a solvent for dilution of the chemicals, control sample
2	Diesel 14 mg/l	Polukarova et al., *2019*; Markiewicz et al., *2017*; Björklund et al., *2011*; Strömvall et al., *2007*
3	Diesel 105 mg/l	
4	Diesel 116 mg/l + acetone 5%	
5	Diesel 34 mg/l + APs[a] + APEOs[b] 1–5 µg/l	Polukarova et al., *2019*; Markiewicz et al., *2017*; Kalmykova et al., *2013*; Miljöförvaltningen, 2013; Björklund et al., 2011; Björklund et al., *2011*; Björklund et al., *2009*; Strömvall et al., *2007*
6	Diesel 114 mg/l + APs + APEOs 5–25 µg/l	
7	APs + APEOs 1–5 µg/l	
8	DEHP[c] ≈ 50 µg/l + DIDP[d] ≈ 50 µg/l + DINP[e] ≈ 50 µg/l	
9	DEHP ≈ 500 µg/l + DIDP ≈ 500 µg/l + DINP ≈ 500 µg/l	
10	HA[f] ≈ 15 mg/l	Nielsen, 2015; Nielsen et al., *2015a*; Kalmykova et al., *2013*; Badin et al., *2008*; Herngren et al., 2006
11	HA ≈ 15 mg/l + Fe ≈ 60 mg/l	
12	Fe ≈ 60 mg/l	
13	HA ≈ 15 mg/l + Fe ≈ 60 mg/l + diesel 115 mg/l + PAHs[g] 16 mix (10–100 µg/l of each PAH) + DEHP ≈ 500 µg/l + DIDP ≈ 500 µg/l + DINP ≈ 500 µg/l + APs + APEOs 5–25 µg/l	Polukarova et al., *2019*; Markiewicz et al., *2017*; Nielsen, 2015; Nielsen et al., *2015a*; Kalmykova et al., *2013*; Miljöförvaltningen, 2013; Björklund et al., 2011; Björklund et al., *2011*; Björklund et al., *2009*; Badin et al., *2008*; Strömvall et al., *2007*; Herngren et al., 2006
14	PAHs 16 mix (10–100 µg/l of each PAH) + DEHP ≈ 500 µg/l + DIDP ≈ 500 µg/l + DINP ≈ 500 µg/l + diesel 116 mg/l + APs + APEOs 5–25 µg/l	
15	PAHs 16 mix (10–100 µg/l of each PAH)	

[a] Akylphenols.
[b] Alkylphenol ethoxylates.
[c] Diethylhexyl phthalate.
[d] Diisodecyl phthalate.
[e] Diisononyl phthalate.
[f] Humic acid.
[g] Polycyclic aromatic hydrocarbons.

particles using the resistance difference between a particle passing through the orifice between two electrodes, and a weak electrolyte in which the electrodes are submerged (Beckman Coulter, 2012). For the measurement, low concentrations of the particles were used so that they could be counted one at a time. The size ranges in which particles were measured are 2–6, 6–10, 10–50, and 50–100 µm. In the method, 0.2 ml of each sample was dissolved in 20 ml of a low concentration electrolyte (Isoton® II Diluent) and measured in three replicates. Analysis of the data was performed with the Beckman Coulter Windows-based AccuComp® software.

2.4.2. Dynamic Light Scattering (DLS) and Nanoparticle Tracking Analysis (NTA)

The size and size distribution of colloids and particles in the range of 10 nm–10 µm were measured using a Malvern Zetasizer Nano ZS instrument (Malvern Instruments Ltd., Malvern, UK). The instrument uses a dynamic light scattering (DLS) technique, which measures the Brownian motion of the particles by analysing variations in scattered intensity depending on time and relates it to their hydrodynamic diameter (Brar and Verma, 2011). Each of the mixtures presented in Table 1 was analysed in duplicate, one after short-time (days) stabilisation and the other one after mixing minutes before the measurements. Approximately 2.5 ml of each sample was placed into quartz cuvettes and measured three times; the results are presented as average values. The stormwater samples were measured in triplicate. Data analysis was performed using Zetasizer 7.11 software. The acceptable quality of the measurement from the Zetasizer instrument is provided in the quality report produced for each measurement. Often, a high PDI together with factors such as presence of aggregates, dust, settling particles and/or inadequate sample concentration will cause the measurement to be defined as poor.

Nanosight NS300 (Malvern Instruments Ltd., Malvern, UK) uses a nanoparticle tracking analysis (NTA) method to measure the particle size, size distribution and particle number concentration at the nano- and micro-scales (10 nm–2 µm). The method combines actual time visualization for identifying and tracking the core of each particle using a charge-coupled device camera, with laser light scattering microscopy. The technique is suitable for polydisperse samples, as it allows simultaneous measurement of particle size and scattering intensity. Seven of the mixtures (Table 1), selected via pre-scanning by laser pointer showing distraction of light, were measured after a few days of settling, and 11 of the mixtures were stored in the dark at +4 °C and measured after long-term stabilisation.

The measurement was carried out by injecting approximately 0.3 ml of the sample into a small viewing chamber on a laser illumination module, where the laser beam refraction took place. For accurate analysis, the concentration of the particles should be within the range of 10^7 to 10^9 particles/ml. Particle sizes and concentrations were calculated from three captures of 60 s videos. Data analysis was performed using NTA3.2 Nanosight software.

2.4.3. Zeta potential measurements

Zeta potential (ZP) was measured in the range > ± 500 mV, to verify the surface charge of particles in prepared dispersions, using a Malvern Zetasizer Nano ZS instrument (Malvern Instruments Ltd., Malvern, UK). 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. The measurement of each sample was repeated three times, and the results obtained are given as average values.

2.4.4. Statistical test

A statistical comparison of the results from the Coulter Counter instrument was performed using a Wilcoxon signed-rank test, where a p-value < 0.05 indicates that the mean difference between two sets of observations is significant. Analyses were performed using the IBM SPSS statistics software.

3. Results and discussion

3.1. Analysis of micro-sized particles with the Coulter Counter

For all 15 mixtures with OPs and the two urban stormwater samples in both stabilised and mixed conditions, the results show that the main number fraction of the larger particles occurred in the range 2–6 µm (Table 2), with no or very few particles detected in the upper ranges.

Table 2
Number and number concentration of microparticles 2–100 µm detected in each sample and each size range with the Coulter Counter instrument. The value for the blank is subtracted from the values for the samples. Font in bold indicates potential emulsions (see Table 3).

Sample no.	OP and colloid mixtures with Milli-Q water and urban stormwater samples	Short-time stabilisation before measurement						Mixed directly before measurement					
		2–6 (µm)	6–10 (µm)	10–16 (µm)	Total particle count	Total particle count (ml^{-1})	Total size-range (µm)	2–6 (µm)	6–10 (µm)	10–16 (µm)	Total particle count	Total particle count (ml^{-1})	Total size -range (µm)
0	Isotonic water (IW)[a]	150	2	0	150	750	2–11						
1	Acetone	240	4	0	240	1200	2–11	< IW	0	0	< IW	< IW	2–7
2	**Diesel low**	**540**	**7**	**1**	**550**	**2800**	**2–12**	**120**	**< IW**	**0**	**120**	**590**	**2–11**
3	**Diesel high**	**4000**	**5**	**3**	**4000**	**20,000**	**2–11**	**3000**	**5**	**1**	**3000**	**15,000**	**2–19**
4	**Diesel high + acetone**	**6600**	**67**	**5**	**6600**	**3300**	**2–19**	**4500**	**50**	**14**	**4600**	**23,000**	**2–12**
5	**Diesel low + APs + APEOs**	**1000**	**2**	**0**	**1000**	**5200**	**2–11**	**560**	**1**	**1**	**560**	**2800**	**2–19**
6	**Diesel high + APs + APEOs**	**3500**	**22**	**2**	**3500**	**18,000**	**2–14**	**2600**	**6**	**5**	**2700**	**13,000**	**2–22**
7	**APs + APEOs**	**290**	**9**	**3**	**300**	**1500**	**2–19**	**1100**	**0**	**0**	**1100**	**5600**	**2–11**
8	Phthalates low	85	2	1	88	440	2–19	61	1	0	62	310	2–11
9	**Phthalates high**	**< IW**	**< IW**	**0**	**< IW**	**< IW**	**2–11**	**560**	**0**	**0**	**560**	**2800**	**2–11**
10	HA-colloids	320	< IW	0	320	1600	2–8	370	< IW	0	370	1900	2–11
11	HA + Fe-colloids	100	0	1	110	530	2–15	720	2	0	720	3600	2–11
12	Fe-colloids	44	1	2	47	240	2–15	550	1	0	560	2800	2–9
13	**All OPs with HA + Fe colloids**	**26,000**	**160**	**2**	**26,000**	**130,000**	**2–15**	**13,000**	**1**	**0**	**13,000**	**63,000**	**2–11**
14	**All OPs (without HA + Fe colloids)**	**6700**	**30**	**5**	**6700**	**34,000**	**2–19**	**4100**	**1**	**0**	**4100**	**20,000**	**2–11**
15	PAHs mix	< IW	2	0	< IW	< IW	2–11	460	6	0	470	2300	2–11
16	Järnbrott urban stormwater	1300	25	6	1330	6700	2–14	520	1	0	520	2600	2–9
17	Gårda urban stormwater	630	62	6	700	3500	2–21	360	1	0	360	1800	2–11

[a] Low concentration electrolyte (Isoton® II Diluent).

The highest number concentration of particles was found in sample 13, which had all OPs added in addition to the HA and Fe colloids. This combination of OPs and colloids appears to have a synergistic effect on the formation of micro-sized particles, which may be explained by the fact that HA colloids increase the size and reduce the number of particles in emulsions, due to hydrophobic interactions affecting the binding capacity of the molecules and promoting formation of Pickering emulsion (Akartuna et al., 2008; De Paolis and Kukkonen, 1997; Kraft et al., 2010). Moreover, metal ions can bind to functional groups of the HA by a ligand exchange mechanism as a result of induced attraction of metal cations to anionic groups of HA, when in close contact. These conditions may cause side electrostatic repulsion around metal-HA complexes to be decreased and promoting additional agglomeration (Vermeer et al., 1998; Shaker et al., 2012). The zeta potential of the sample with both HA and Fe colloids added (sample 11 in Table 3) indicated weak to no stability meaning low repulsive forces among the particles. This hypothesis is strengthened by the results from sample 14, which included all the OPs but without colloids, where the number of micro-sized particles is much lower. The mechanism for this will be the focus of clarification in further studies.

After mixing the pure solutions with HA and Fe colloids into one sample (sample number 11), the number of particles decreased substantially for both the stabilised (3.5 times lower) and mixed samples (1.3 times lower), see Table 2. This suggests that in the absence of OPs, colloids may agglomerate creating fewer and larger particles, likely through Fe-colloids coprecipitated with HA-colloids (Angelico et al., 2014; Nielsen, 2015). The comparatively high concentration of particles in the diesel samples (samples 3 and 4), indicates that the diesel used in this study may contain emulsifying additives. Several of the samples indicated in Section 3.2 as containing emulsions, i.e. samples 2–7 and 9, exhibited relatively high amounts of particles in the lower micro-range. The lowest concentrations of micro-sized particles were found in the samples not identified as potential emulsion, particularly sample 8 with phthalates, sample 15 with the PAH mix, and sample 12 which included only Fe colloids.

The concentrations of micro-sized particles in the stormwater samples from Järnbrott and Gårda (March 2015) were much lower than in samples measured in a previous study (spring 2013) but confirm the results from 30 stormwater samples collected at five sites around Europe, where most particles were < 10 μm (Nielsen, 2015). The lower concentrations of particles measured in the current study, are explained by the fact that the samples were collected from a stormwater pond and underground sedimentation chamber with stagnant water after a one-week period of dry weather; agglomeration into fewer and larger particles and/or sedimentation of particles with low settling velocity may occur during that time frame. Differences in particle concentrations between samples can also be explained by the inherent variability of stormwater quality.

The total particle counts in the samples with ‘indicated potential emulsions’ and marked as bold in Table 2 was lower for several of the samples mixed directly before measurement. Additionally, there is a trend towards a smaller number of micro-sized particles of 2–6 μm in the mixed samples. A Wilcoxon signed-rank test was performed, to clarify whether there was a significant difference in particle counts between the stabilised and mixed samples: the analysis did not present strong evidence that there is a difference in mean values ($Z = -1.396$; $p = 0.163$). However, it is reasonable to assume that with the right speed and duration, mixing will cause larger particles in the micro-size to break down into smaller nano-sized particles (Kulawik-Pióro and Tal-Figiel, 2017; Solans et al., 2005), which are not measurable using the Coulter Counter.

3.2. Selection of samples for physical characterization

To determine whether a given mixture contains a potential emulsion, data from the DLS analysis with the Zetasizer, including the polydispersity index (PDI) and ZP values, are presented (Table 3). For a sample to be indicated as a stable emulsion, at least two of the following criteria should be fulfilled: (i) the DLS analysis results should reach an acceptable quality for the measurement; (ii) the PDI should be between

Table 3

Polydispersity index (PDI) and zeta potential (ZP), measured with the Zetasizer to determine possible formation of emulsions. Font in bold indicates stronger potential for emulsion formation; bold/italic indicates weaker potential for emulsions formation as not all three criteria were fulfilled; and italic indicates no formation of emulsions.

Sample No.	OPs and colloid mixtures[a] with Milli-Q water and urban stormwater	Short-time stabilisation before measurement[d]			Mixed directly before measurement[e]		
		High quality run	PDI[b]	ZP[c] (mV)	High quality run	PDI[b]	ZP[c] (mV)
1	*Acetone*	*No*	*0.8*	*-17*[f]	*No*	*0.9*	*−25*
2	***Diesel low***	***Yes***	***0.2***	***0.0***	***Yes***	***0.2***	***−33***
3	**Diesel high**	**Yes**	**0.3**	**−30**	**Yes**	**0.4**	**−47**
4	***Diesel high + acetone***	***No***	***0.3***	***−32***	***No***	***0.4***	***0.0***
5	**Diesel low + APs + APEOs**	**Yes**	**0.2**	**−38**	**Yes**	**0.2**	**−37**
6	**Diesel high + APs + APEOs**	**Yes**	**0.4**	**−37**	**Yes**	**0.4**	**−45**
7	**APs + APEOs**	**Yes**	**0.5**	**−35**	**Yes**	**0.3**	**−31**
8	*Phthalates low*	*No*	*0.3*	*0.0*	*Yes*	*0.3*	*−25*
9	***Phthalates high***	***Yes***	***0.3***	***−30***	***Yes***	***0.2***	***−27***
10	*HA colloids*	*No*	*0.6*	*0.0*	*No*	*0.5*	*0.0*
11	*HA + Fe colloids*	*No*	*0.3*	*41*[f]	*No*	*0.4*	-[g]
12	*Fe colloids*	*No*	*0.4*	*0.0*	*No*	*0.5*	*0.0*
13	***all OPs with HA + Fe colloids***	***No***	***0.7***	***71***	***No***	***0.9***	***80***
14	***all OPs*** (***without HA + Fe colloids***)	**Yes**	**0.4**	**−38**	**Yes**	**0.4**	***0.0***
15	*PAHs mix*	*Yes*	*0.4*	*−29*	*No*	*0.7*	*−23*
16	*Järnbrott stormwater*	*No*	*0.6*	*−19*	*No*	*0.7*	*−21*
17	*Gårda stormwater*	*No*	*0.5*	*0.0*	*No*	*0.4*	*−32*

[a] For concentrations, see Table 1.

[b] Polydispersity index.

[c] Zeta potential.

[d] Stabilised by being kept stagnant a few days before DLS analysis.

[e] Stabilised samples mixed shortly before DLS analysis.

[f] Standard deviation > 15.

[g] Not measured.

0.05 and 0.7; and (iii) the ZP should be < -30 mV or > 30 mV.

The polydispersity index is a dimensionless value quantifying the ratio between standard deviation of particle size distribution (PSD) and average particle diameter and is applied to evaluate homogeneity of particle solutions (Clayton et al., 2016). It indicates the width of the Gaussian PSD and the particle composition in the samples should be between 0.05 and 0.7, for the measurement to be deemed acceptable for further evaluation using the Zetasizer DLS instrument (International Organization for Standardization ISO, 2017). The PDI values for the samples in this study were 0.2–0.9 showing low to medium polydispersity in most of the samples and high polydispersity in sample 1 with acetone and 13 with all OPs and HA + Fe colloids (Table 3).

The zeta potential measurements resulted in zero value for a few samples (Table 3), indicating point-of-zero charge, or that the analysis did not meet the high-quality criteria for the measurement because of inappropriate sample concentration. Results within the ranges −20 mV to −30 mV and +20 mV to +30 mV indicate weak stability, whereas those below −30 mV or above +30 mV have good repulsing forces between particles, indicating a high stability of the particles in the sample (Bhattacharjee, 2016). Samples 3, 5–7 and 13 (i.e. diesel high; diesel low + APs/APEOs; diesel high + APs/APEOs; APs/APEOs; and all OPs with HA + Fe colloids), were found to have particles with good stability (Table 3). Samples 4, 9, and 14 (i.e. diesel high + acetone; phthalates high; and all OPs without HA + Fe colloids) had particles that were stable after short-time stabilisation but were unstable directly after mixing.

The composition of the mixtures and measurement control samples 1, 4, 10–13, 16 and 17 obtained low quality results for the PSD analysis, and samples 8 and 15 obtained high-quality results for only one of the conditions, stabilised or mixed (Table 3). However, the ZP of the particles in sample 13 with all OPs and HA + Fe colloids, was very high in both the stabilised and mixed sample, ZP = 71 and 80 mV respectively. Although sample 13 did not meet all the criteria, it will be considered as containing potential emulsions, because colloids combined with an oily substance can promote Pickering emulsions (Akartuna et al., 2008; Kraft et al., 2010), stabilised by the colloids which adsorb at the oil-water interface. Samples 9 with phthalates and 14 with all OPs (no colloids) met all the quality criteria with the exception for ZP in the mixed samples, however these samples could also be considered as containing potential emulsions due to high stability in the stable sample and relatively low PSD. The particles in sample 11, containing a mixture of the colloids, also had a high ZP in the stable state, but the standard deviation (resulting from error in the measurement due to poor quality of the run) for the ZP value of the three measured replicates was high (21), therefore this sample will not be regarded as potentially containing emulsions.

The samples identified as potential emulsions were mixtures containing: diesel (samples 2–4), APs and APEOs (sample 7), diesel + APs + APEOs (samples 5 and 6), phthalates in high concentrations (sample 9) and the mixtures with all OPs both with and without HA + Fe colloids (samples 13 and 14). 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, tyres, plastics, agricultural agents, and household products (Björklund, 2010, 2011; Boza Troncoso and Acosta, 2015). It is of high interest to find that samples with all the OPs added, but without the HA and Fe colloids (sample 14, Table 3), contained emulsions. This result indicates that in road runoff, even with relatively low concentrations of HA and Fe colloids (Nielsen et al., 2015b), the formation of emulsions may be a possible transport route for OPs. The samples with all OPs + HA and Fe colloids showed high repulsive forces between particles (ZP = 71 and 80 mV), and it was therefore assumed that the HA and Fe colloids may be emulsion facilitators under suitable 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.

3.3. Analysis of nanoparticle distributions with Zetasizer

Data from the analysis with the Zetasizer instrument were evaluated further for most samples with the criteria parameters approved in Table 3. To compare, two samples not identified as emulsions were also evaluated: phthalates with low concentrations and the sample with the PAH mix. The samples were evaluated for PSDs in the range 10–10,000 nm. The results are presented in distribution by volume, where each bin size represents a certain percentage of the total volume of the particles.

In the sample with low diesel concentration, smaller particles were found in the mixed than in the stabilised sample, indicating decomposition of large particles into smaller ones under high shear forces (Solans et al., 2005). However, the samples with a higher concentration of diesel were bimodal (Fig. 1b) and had larger particle sizes. This could be explained by the different solubility of diesel constituents in higher concentrations, and by the Ostwald ripening process which may partially occur after mixing. The zeta potential of the high concentration diesel sample was elevated after mixing (Table 3), possibly due to reactions reaching thermodynamic equilibrium and good dispersion of components in the mixture (Mo et al., 2016). In the high phthalate concentration samples, the particle size occurred in a narrower monomodal distribution after mixing than in the stabilised sample, and a larger number of particles appeared in the 120–140 nm size range (Fig. 1b). For the low phthalate concentration samples, only data from the mixed sample are available, but it can be seen that the PSD is similar to the high concentration and stabilised sample. For the PAH mix, data from the short-time stabilisation is showing occurrence of nanoparticles of approximately 150 nm.

Overall, the widths of the PSD for the stabilised and mixed samples were not very different, but according to the PDI, the stabilised samples were slightly more polydispersed than the mixed samples. This may be explained by an agglomeration process during stabilisation or breakdown of the particles into more homogenous nanoparticles when the samples are mixed (Table 3). This is also shown on peaks in the bimodal curves, especially the second peak with larger particles, are more distinct in the mixed samples (Fig. 1b) compared to the corresponding short-time stabilised samples (Fig. 1a). The average particle size in the sample with all the OPs, but no HA and Fe colloids, varied from approximately 800 nm in the stabilised sample, to approximately 400 nm in the mixed (Fig. 1a and b). For most of both the stabilised and mixed samples, the PSDs were monomodal for particle sizes between 70 and 400 nm. In the samples with diesel high, diesel high + APs/APEOs and all OPs without any colloids, the PSD was bimodal in the size ranges 70–2300 nm and 4000–6500 nm. The data implies that the compounds in the mixed samples have different properties, such as different charges, densities and solubility, which is also suggested by the fact that ZP resulted in the zero charge (Table 2).

The PSD of the samples with APs and APEOs, and the sample with high concentration phthalates showed a tendency to contain more nano-sized particles after mixing (Fig. 1). This was also indicated by the Coulter Counter, as the number of particles in the 2–6 μm range increased after mixing. Alkylphenol ethoxylates are strong surfactants, and therefor stable emulsions are assumed to be formed, and the input of energy does not significantly affect the size of the nanoparticles, leaving most of the particles with a size of < 1 μm.

When the results in Figs. 1 and 2 were compared with earlier measurements of PSD by DLS (Zetasizer) of 18 stormwater samples collected from five different sites around Europe (Nielsen, 2015), the mixtures produced in this study contained a greater proportion of larger nanoparticles (100–800 nm) than the stormwater samples, which mainly contained nanoparticles of around 10–100 nm. In a more recent study of the effect of street sweeping, stormwater collected during rain events in the swept area showed the same pattern as the potential emulsion mixtures in the current study, with a greater proportion of nanoparticles and bimodal PSD curves in the size ranges 50–2000 nm (Polukarova et al., 2019). The washwater collected in the street

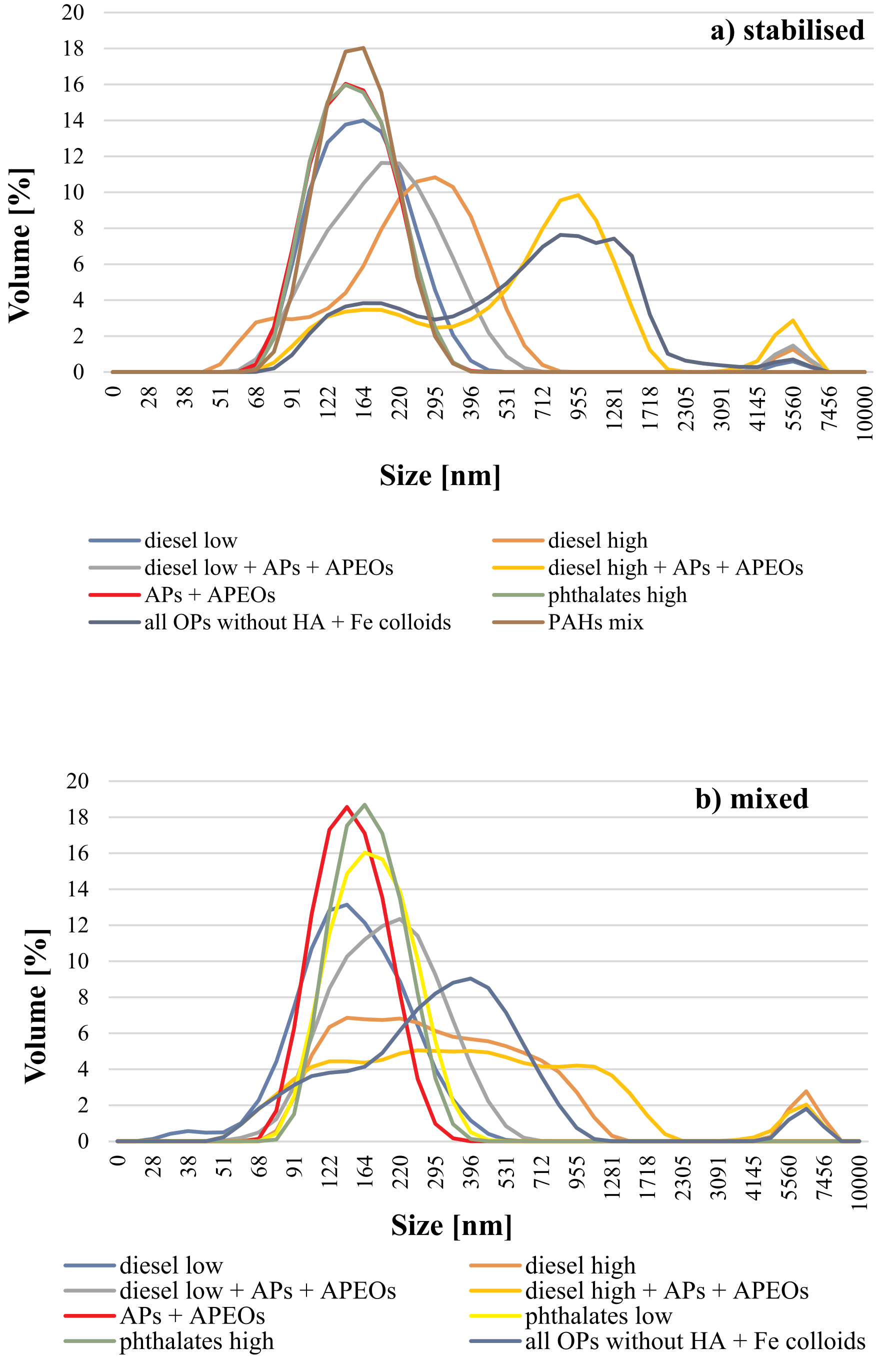

Fig. 1. Nanoparticle size distributions by volume percent (10–10,000 nm) in samples (a) short-time stabilised before measurement and the same samples (b) mixed just before analysis, measured by DLS (Zetasizer). The values on the x-axis are on a logarithmic scale.

sweeping machine, on the other hand, contained much more of the smaller nanoparticles in the range 1–50 nm. However, in Polukarova et al. (2019), a Litesizer™500 with a lower detection limit of 0.3 nm was used for the PSD analysis than in the current study. In washwater samples with high concentrations of diesel (aliphatics) and PAHs, the PSD curves exhibited the same shape as the potential emulsions in the short-time stabilised samples in the current study.

3.4. Number concentration of particles measured with nanosight

Among the samples stabilised for short time, the sample with all OPs and no HA and Fe colloids contained a substantially higher concentration of nanoparticles in the size range 10–500 nm than the sample with colloids added (Fig. 2a). However, after long-term storage for stabilisation, the relation of the nano-sized particles was the opposite, with higher concentrations in the sample with colloids (Figs. 2b and 3). In samples without colloids, the nano-sized particle content decreased one order of magnitude over time (Fig. 3). The results from the Coulter Counter analysis of samples stored short term showed that particles in the sample with OPs and added colloids (sample 13, Table 2) were much more likely to fall within a larger size-range of 2–6 µm, as it had a much higher (nearly four times) concentration of these micro-sized particles than the sample without colloids (sample 14, Table 2). The decrease in particle concentrations illustrated in Figs. 2b and 3 indicate that when the stabilisation period is longer, stable emulsions are not formed, but other particle types are, in particular when colloids are

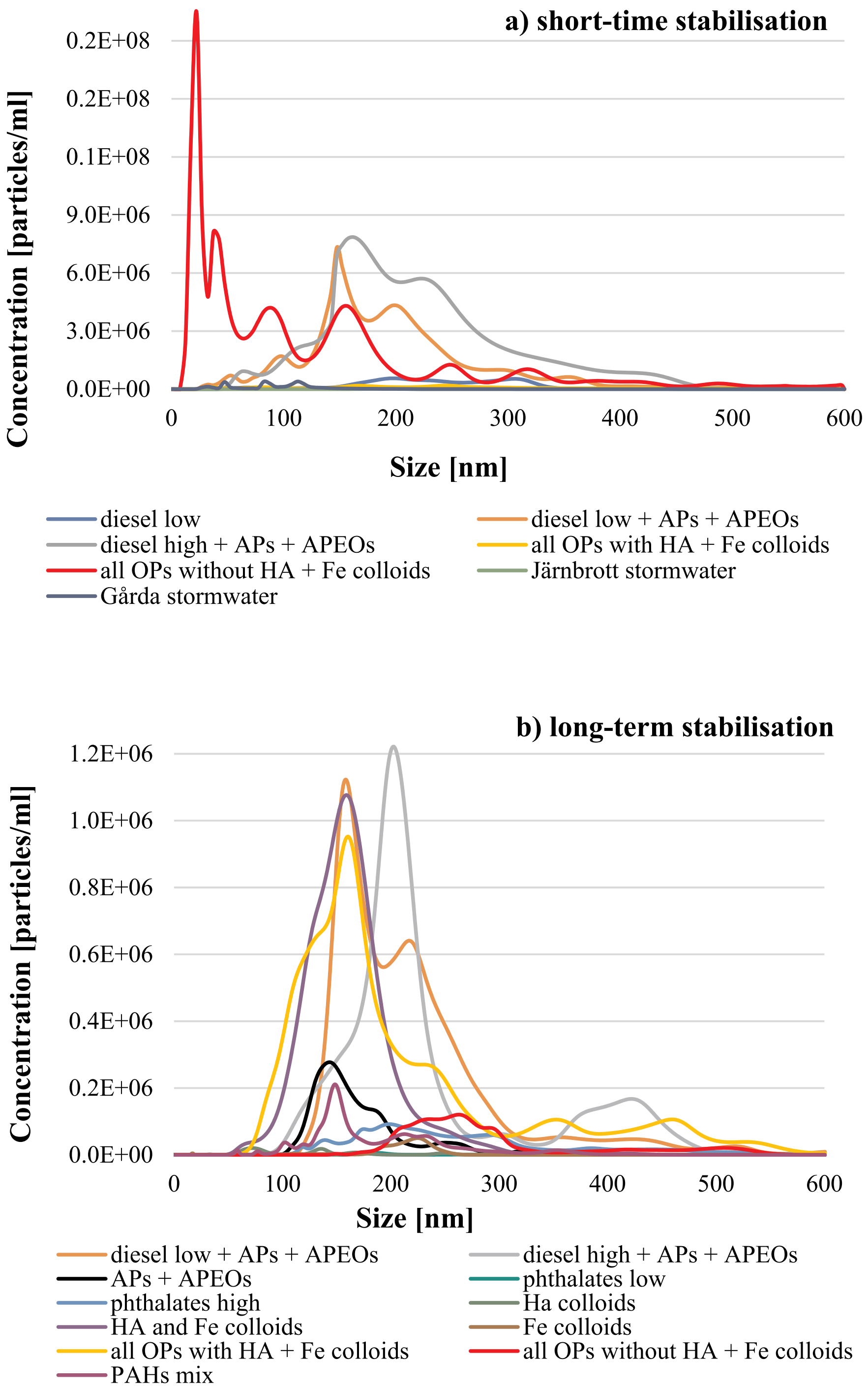

Fig. 2. Nanoparticle size distributions 10–2000 nm and particle number concentrations measured by NTA (Nanosight) (a) after short-time storage for stabilisation, with He—Ne laser wavelength of 633 nm, and (b) long-term stabilisation, with an Ar laser wavelength of 488. Note the differences in scale on the y-axes.

added, which may be the result of breakdown processes and separation of HA-Fe complexes (Hiraide et al., 2002). This knowledge indicates that close to the sources of emission, the road runoff may contain emulsions in the nano-size. Further downstream in the stormwater system, however, these emulsions may degrade, and the nanoparticles found consists of the degradation products from the colloids and is then more in a solid form.

The stormwater samples (Fig. 2a) generally showed low particle concentrations in comparison with other samples, and nanosize did not appear to be dominant among the particles in these samples, even though stormwater samples have often been shown to contain many nanoparticles between 10 and 100 nm (Nielsen, 2015; Polukarova et al., 2019). In this study, the stormwater samples were not collected during a rain event and therefore contained low concentrations of pollutants due to stagnant water in the pond (Järnbrott) and the sedimentation chamber (Gårda). However, when measured using the Coulter Counter, particles in the size range 2–6 µm occurred in relatively high concentrations in the stormwater samples (Table 2). Particles in stormwater generally have a negative surface charge, indicating the presence of organic acids and/or clay (Nielsen et al., 2015b). By comparing the Nanosight measurements of potential emulsion mixtures in this study with the corresponding measurements of road-dust washwater and stormwater in the street sweeping study of Polukarova et al. (2019), the same patterns appear with peaks in the range between 50 and 300 nm.

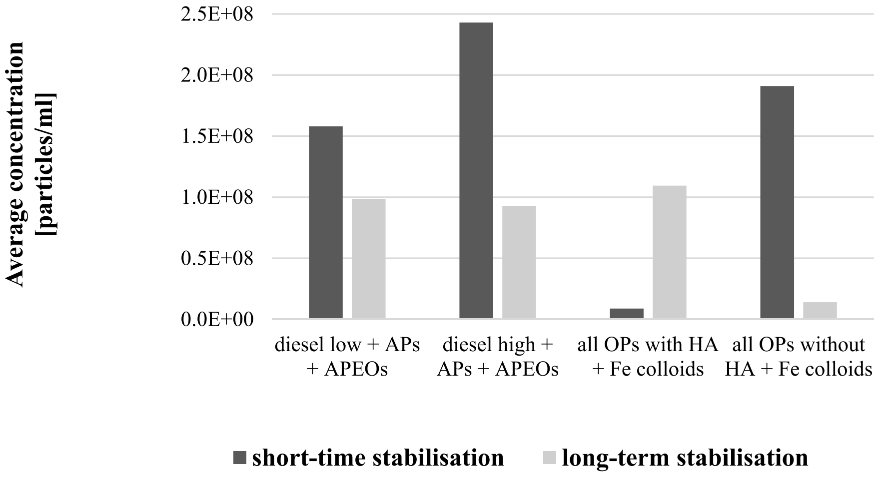

Fig. 3. Comparison of nano-sized (10–2000 nm) particle number concentrations in samples measured by nanotracking analysis (Nanosight) after short-time storage for stabilisation and long-term stabilisation.

The results from the Nanosight could not be correlated with those from the Zetasizer, as the latter indicates particles of a given size per unknown total volume of the sample, and the results from the Nanosight are shown as number of particles per given volume. However, the results from both instruments (Figs. 1 and 2) have shown that the particles in most of the samples occurred in sizes 30–660 nm, irrespective of sample volume. It is known that particles of these sizes are resistant to sedimentation as occurring in traditional sedimentation facilities (Hofmann and von der Kammer, 2009; Kalmykova et al., 2013; Nowack and Bucheli, 2007; Roy and Dzombak, 1998; Schijf and Zoll, 2011).

4. Conclusions

Three hypotheses were tested and proven:

i) This study shows that 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 the majority of emulsions in the samples were found in the nano-range 60–580 nm and 30–660 nm, respectively, and a smaller portion of particles < 28%, also measured by the Coulter Counter (ESM), 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-preciptation 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.

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, needs to be studied further.

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.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Abdel-Shafy, H.I., Mansour, M.S.M., 2016. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egypt. J. Pet. 25 (1), 107–123. https://doi.org/10.1016/j.ejpe.2015.03.011.
Akartuna, I., Studart, A.R., Tervoort, E., Gonzenbach, U.T., Gauckler, L.J., 2008. Stabilization of oil-in-water emulsions by colloidal particles modified with short Amphiphiles. Langmuir 24 (14), 7161–7168. https://doi.org/10.1021/la800478g.
Angelico, R., Ceglie, A., He, J.Z., Liu, Y.R., Palumbo, G., Colombo, C., 2014. Particle size, charge and colloidal stability of humic acids coprecipitated with ferrihydrite. Chemosphere 99, 239–247. https://doi.org/10.1016/j.chemosphere.2013.10.092.
Badin, A.L., Faure, P., Bedell, J.P., Delolme, C., 2008. Distribution of organic pollutants and natural organic matter in urban storm water sediments as a function of grain size. Sci. Total Environ. 403 (1–3), 178–187. https://doi.org/10.1016/j.scitotenv.2008.05.022.
Beckman Coulter Inc, 2012. The Coulter Principle for Particle Size Analysis. *Electronic Article.* Available from. https://www.azom.com/article.aspx?ArticleID=6020.
Bhattacharjee, S., 2016. DLS and zeta potential – what they are and what they are not? J. Control. Release 235, 337–351. https://doi.org/10.1016/j.jconrel.2016.06.017.

Björklund, K., 2010. Substance flow analyses of phthalates and nonylphenols in stormwater. Water Science & Technology 62 (5), 1154–1160. https://doi.org/10.2166/wst.2010.923.

Björklund, K., 2011. Sources and Fluxes of Organic Contaminants in Urban Runoff. Doctoral Thesis. Chalmers University of Technology, pp. 140. http://publications.lib.chalmers.se/records/fulltext/134241.pdf.

Björklund, K., Cousins, A.P., Strömvall, A.-M., Malmqvist, P.-A., 2009. Phthalates and nonylphenols in urban runoff: occurrence, distribution and area emission factors. Sci. Total Environ. 407, 4665–4672. https://doi.org/10.1016/j.scitotenv.2009.04.040.

Björklund, K., Malmqvist, P.A., Strömvall, A.M., 2011. Screening of organic contaminants in urban snow. Water Sci. Technol. 64 (1), 206–213. http://wst.iwaponline.com/content/ppiwawst/64/1/206.full.pdf.

Boza Troncoso, A., Acosta, E., 2015. The UNIFAC model and the partition of alkyl and alkylphenol ethoxylate surfactants in the excess phases of middle phase microemulsions. Fluid Phase Equilib. 397, 117–125. https://doi.org/10.1016/j.fluid.2015.03.035.

Brar, S.K., Verma, M., 2011. Measurement of nanoparticles by light-scattering techniques. TrAC Trends Anal. Chem. 30 (1), 4–17. https://doi.org/10.1016/j.trac.2010.08.008.

Bruen, M., Johnston, P., Quinn, M.K., Desta, M., Higgins, N., Bradley, C., Burns, S., 2006. Impact Assessment of Highway Drainage on Surface Water Quality. EPA, pp. 272. https://www.epa.ie/pubs/reports/research/water/EPA_highway_drainage_on_surface_water_quality_ERTDI49_final.pdf.

Burguera, J.L., Burguera, M., 2012. Analytical applications of emulsions and microemulsions. Talanta 96, 11–20. https://doi.org/10.1016/j.talanta.2012.01.030.

Clayton, K.N., Salameh, J.W., Wereley, S.T., Kinzer-Ursem, T.L., 2016. Physical characterization of nanoparticle size and surface modification using particle scattering diffusometry. Biomicrofluidics 10 (5), 54107. https://doi.org/10.1063/1.4962992.

Crabtree, B., Dempsey, P., Johnson, I., Whitehead, M., 2008. The development of a risk-based approach to managing the ecological impact of pollutants in highway runoff. Water Sci. Technol. 57 (10), 1595–1600. https://doi.org/10.2166/wst.2008.269.

De Paolis, F., Kukkonen, J., 1997. Binding of organic pollutants to humic and fulvic acids: influence of pH and the structure of humic material. Chemosphere 34 (8), 1693–1704. https://doi.org/10.1016/S0045-6535(97)00026-X.

European Commission, 2000. Directive 2000/60/EC of the European Parliament and of the Council Establishing a Framework for Community Action in the Field of Water Policy (Water Framework Directive). EUR-Lex Available from: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32000L006.

European Parliament and the Council, 2008. Directive 2008/105/EC on Environmental Quality Standards in the Field of Water Policy, Amending and Subsequently Repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and Amending Directive 2000/60/EC of the European Parliament and of the Council. Available from. https://eur-lex.europa.eu/resource.html?uri=cellar:5c835afb-2ec6-4577-bdf8-756d3d694eeb.0004.02/DOC_1&format=PDF.

Flanagan, K., Branchu, P., Boudahmane, L., Caupos, E., Demare, D., Deshayes, S., Gromaire, M.-C., 2019. Retention and transport processes of particulate and dissolved micropollutants in stormwater biofilters treating road runoff. Sci. Total Environ. 656, 1178–1190. https://doi.org/10.1016/j.scitotenv.2018.11.304.

Florence, T.M., 1982. Development of physico-chemical speciation procedures to investigate the toxicity of copper, lead, cadmium and zinc towards aquatic biota. Anal. Chim. Acta 141, 73–94. https://doi.org/10.1016/S0003-2670(01)95312-7.

Genç-Fuhrman, H., Mikkelsen, P.S., Ledin, A., 2016. Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater using high-efficiency industrial sorbents: effect of pH, contact time and humic acid. Sci. Total Environ. 566–567, 76–85. https://doi.org/10.1016/j.scitotenv.2016.04.210.

Gnecco, I., Lanza, L.G., 2013. Review of hydrologic processes and transport of pollutants operated by stormwater runoff in urban environment. In: Overland Flow and Surface Runoff. Nova Science Publishers, pp. 287–320. http://www.novapublishers.org/catalog/product_info.php?products_id=20137.

Herngren, L., Goonetilleke, A., Ayoko, G.A., 2006. Analysis of heavy metals in road-deposited sediments. Anal. Chim. Acta 571 (2), 270–278. https://doi.org/10.1016/j.aca.2006.04.064.

Hiraide, M., Ogoh, M., Itoh, S., Kageyama, T., 2002. Selective collection of inorganic iron (III) colloids in water with oxine-impregnated water-in-oil emulsion. Talanta 57 (4), 653–660. https://doi.org/10.1016/S0039-9140(02)00070-X.

Hofmann, T., von der Kammer, F., 2009. Estimating the relevance of engineered carbonaceous nanoparticle facilitated transport of hydrophobic organic contaminants in porous media. Environ. Pollut. 157 (4), 1117–1126. https://doi.org/10.1016/j.envpol.2008.10.022.

International Organization for Standardization (ISO), 2017. ISO 22412:2017 Particle Size Analysis - Dynamic Light Scattering (DLS). ISO, pp. 34. https://www.iso.org/standard/65410.html.

Jonsson, A., Fridén, U., Thuresson, K., Sörme, L., 2008. Substance flow analyses of organic pollutants in Stockholm. Water, Air, & Soil Pollution: Focus 8 (5–6), 433–443. https://doi.org/10.1007/s11267-008-9185-7.

Kalbe, U., Krüger, O., Wachtendorf, V., Berger, W., Hally, S., 2013. Development of leaching procedures for synthetic turf systems containing scrap tyre granules. Waste and Biomass Valorization 4 (4), 745–757. https://doi.org/10.1007/s12649-013-9248-5.

Kalmykova, Y., Björklund, K., Strömvall, A.M., Blom, L., 2013. Partitioning of polycyclic aromatic hydrocarbons, alkylphenols, bisphenol A and phthalates in landfill leachates and stormwater. Water Res. 47 (3), 1317–1328. https://doi.org/10.1016/j.watres.2012.11.054.

Kalmykova, Y., Moona, N., Strömvall, A.M., Björklund, K., 2014. Sorption and degradation of petroleum hydrocarbons, polycyclic aromatic hydrocarbons, alkylphenols, bisphenol A and phthalates in landfill leachate using sand, activated carbon and peat filters. Water Res. 56, 246–257. https://doi.org/10.1016/j.watres.2014.03.011.

Kole, P.J., Löhr, A.J., Van Belleghem, F.G.A.J., Ragas, A.M.J., 2017. Wear and tear of tyres: a stealthy source of microplastics in the environment. Int. J. Environ. Res. Public Health 14 (10), 1265. https://doi.org/10.3390/ijerph14101265.

Kraft, D.J., De Folter, J.W.J., Luigjes, B., Castillo, S.I.R., Sacanna, S., Philipse, A.P., Kegel, W.K., 2010. Conditions for equilibrium solid-stabilized emulsions. J. Phys. Chem. B 114 (32), 10347–10356. https://doi.org/10.1021/jp102659b.

Kretzschmar, R., Sticher, H., 1997. Transport of humic-coated iron oxide colloids in a sandy soil: influence of Ca2+ and trace metals. Environ. Sci. Technol. 31 (12), 3497–3504. https://doi.org/10.1021/es970244s.

Kulawik-Pióro, A., Tal-Figiel, B., 2017. Influence of preparation method on size distribution of the dispersed phase of primary emulsions. Chemical Engineering & Technology 40 (2), 412–420. https://doi.org/10.1002/ceat.201500746.

Lamprea, K., Bressy, A., Mirande-Bret, C., Caupos, E., Gromaire, M.-C., 2018. Alkylphenol and bisphenol A contamination of urban runoff: an evaluation of the emission potentials of various construction materials and automotive supplies. Environ. Sci. Pollut. Res. 25 (22), 21887–21900. https://doi.org/10.1007/s11356-018-2272-z.

Leads, R.R., Weinstein, J.E., 2019. Occurrence of tire wear particles and other microplastics within the tributaries of the Charleston Harbor Estuary, South Carolina, USA. Mar. Pollut. Bull. 145, 569–582. https://doi.org/10.1016/j.marpolbul.2019.06.061.

Månsson, N., Sörme, L., Wahlberg, C., Bergbäck, B., 2008. Sources of alkylphenols and alkylphenol ethoxylates in wastewater—a substance flow analysis in Stockholm, Sweden. Water, Air, & Soil Pollution: Focus 8 (5–6), 445–456. https://doi.org/10.1007/s11267-008-9186-6.

Markiewicz, A., Björklund, K., Eriksson, E., Kalmykova, Y., Strömvall, A.-M., Siopi, A., 2017. Emissions of organic pollutants from traffic and roads: priority pollutants selection and substance flow analysis. Sci. Total Environ. 580, 1162–1174. https://doi.org/10.1016/j.scitotenv.2016.12.074.

Markiewicz, A., Strömvall, A.-M., Björklund, K., Kalmykova, Y., 2019. Emissions of Organic Pollutants, Nano- and Microparticles from Vehicles. (To be published).

Massoudieh, A., Ginn, T.R., 2008. Modeling colloid-enhanced contaminant transport in stormwater infiltration basin best management practices. Vadose Zone J. 7 (4), 1215–1222. https://doi.org/10.2136/vzj2007.0179.

Miljöförvaltningen, G.S., 2013. Miljöförvaltningens Riktlinjer Och riktvärden för utsläpp Av förorenat Vatten till Recipient Och Dagvatten (the Environmental Management Guidelines and Benchmarks for the Discharge of Polluted Water into the Receiving Waters and Stormwater). R 2013:10). pp. 24. https://goteborg.se/wps/wcm/connect/fee9bd22-ed19-43ed-907c-14fc36d3da16/N800_R_2013_10.pdf?MOD=AJPERES.

Mo, S., Shao, X., Chen, Y., Cheng, Z., 2016. Increasing entropy for colloidal stabilization. Sci. Rep. 6, 36836. https://doi.org/10.1038/srep36836.

Ngai, T., Bon, S.A.F., 2015. Particle-stabilized emulsions and colloids-formation and applications. In: The Royal Society of Chemistry, Electronic Book, pp. 322. https://doi.org/10.1039/9781782620143.

Nielsen, K., 2015. Characterisation and Treatment of Nano-Sized Particles, Colloids and Associated Polycyclic Aromatic Hydrocarbons in Stormwater. Doctoral thesis. Technical University of Denmark, Lungby, pp. 81. http://orbit.dtu.dk/files/110852891/Katrine_Nielsen_PhD_thesis_WWW_Version.pdf.

Nielsen, K., Kalmykova, Y., Strömvall, A.-M., Baun, A., Eriksson, E., 2015a. Particle phase distribution of polycyclic aromatic hydrocarbons in stormwater — using humic acid and iron nano-sized colloids as test particles. Sci. Total Environ. 532, 103–111. https://doi.org/10.1016/j.scitotenv.2015.05.093.

Nielsen, K., Mørch-Madsen, A., Mikkelsen, P.S., Eriksson, E., 2015b. Effect of disc filtration with and without addition of flocculent on nano-and micro-particles and their associated polycyclic aromatic hydrocarbons in stormwater. Water (Switzerland) 7 (3), 1306–1323. https://doi.org/10.3390/w7031306.

Nowack, B., Bucheli, T.D., 2007. Occurrence, behavior and effects of nanoparticles in the environment. Environ. Pollut. 150 (1), 5–22. https://doi.org/10.1016/j.envpol.2007.06.006.

OKQ8, 2017. OKQ8 Diesel Miljöklass 1. OKQ8, pp. 2. http://www.energipartnerab.se/Diesel%20MK1%20_%20PDB.pdf.

Pensini, E., Tchoukov, P., Yang, F., Xu, Z., 2018. Effect of humic acids on bitumen films at the oil-water interface and on emulsion stability: potential implications for groundwater remediation. Colloids Surf. A Physicochem. Eng. Asp. 544, 53–59. https://doi.org/10.1016/j.colsurfa.2018.02.024.

Pettersson, T.J.R., Strömvall, A.-M., Ahlman, S., 2005. Underground sedimentation systems for treatment of highway runoff in dense city areas. In: Eriksson, E., Genc-Fuhrman, H., Vollertsen, J., Ledin, A., Hvitved-Jacobsen, T., Mikkelsen, P.S. (Eds.), Proceedings of the 10th International Conference on Urban Drainage, August 21–26 2005.

Pichot, R., 2010. Stability and Characterisation of Emulsions in the Presence of Colloidal Particles and Surfactants. Doctoral thesis. University of Birmingham, Birmingham, pp. 219. http://etheses.bham.ac.uk/3271/1/Pichot12PhD.pdf.

Polukarova, M., Markiewicz, A., Björklund, K., Strömvall, A.-M., Galfi, H., Andersson Sköld, Y., Gustafsson, M., Järlskog, I., Aronsson, M., 2019. Organic Pollutants, Nano- and Microparticles in Street Sweeping Road Dust and Washwater. Chalmers University of Technology, pp. 30 (Submission in progress).

Roy, S.B., Dzombak, D.A., 1998. Sorption nonequilibrium effects on colloid-enhanced transport of hydrophobic organic compounds in porous media. J. Contam. Hydrol. 30 (1–2), 179–200. https://doi.org/10.1016/S0169-7722(97)00040-5.

Schijf, J., Zoll, A.M., 2011. When dissolved is not truly dissolved—the importance of colloids in studies of metal sorption on organic matter. J. Colloid Interface Sci. 361 (1), 137–147. https://doi.org/10.1016/j.jcis.2011.05.029.

Shaker, A.M., Komy, Z.R., Heggy, S.E.M., El-Sayed, M.E.A., 2012. Kinetic study for adsorption humic acid on soil minerals. J. Phys. Chem. A 116 (45), 10889–10896. https://doi.org/10.1021/jp3078826.

Solans, C., Izquierdo, P., Nolla, J., Azemar, N., Garcia-Celma, M.J., 2005. Nanoemulsions. Curr. Opin. Colloid Interface Sci. 10 (3–4), 102–110. https://doi.org/10.1016/j.cocis.2005.06.004.

Strömvall, A.-M., Norin, M., Inanta, H., 2007. Reactive Soil Barriers for Removal of Chromium(VI) from Contaminated Soil. Paper Presented at the Highway and Urban Environment, Dordrecht. Available from. https://link.springer.com/content/pdf/10.1007%2F978-1-4020-6010-6.pdf.

Tadros, T.F., 2013. Emulsion formation, stability, and Rheology. In: Emulsion Formation and Stability. Wiley-VCH Verlag GmbH & Co. KGaA, pp. 1–75. https://doi.org/10.1002/9783527647941.ch1.

The United Nations Economic Commission for Europe, 1998. Protocol to the 1979 Convention on Long-RangeTransboundary Air Pollution on Persistent Organic Pollutants. pp. 60. (EB.AIR:1998:2). Available from. https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/273273/6757.pdf.

Tong, K., Zhao, C., Sun, D., 2016. Formation of nanoemulsion with long chain oil by W/O microemulsion dilution method. Colloids Surf. A Physicochem. Eng. Asp. 497, 101–108. https://doi.org/10.1016/j.colsurfa.2016.02.039.

Unice, K.M., Bare, J.L., Kreider, M.L., Panko, J.M., 2015. Experimental methodology for assessing the environmental fate of organic chemicals in polymer matrices using column leaching studies and OECD 308 water/sediment systems: application to tire and road wear particles. Sci. Total Environ. 533, 476–487. https://doi.org/10.1016/j.scitotenv.2015.06.053.

Unice, K.M., Weeber, M.P., Abramson, M.M., Reid, R.C.D., van Gils, J.A.G., Markus, A.A., Vethaak, A.D., Panko, J.M., 2019. Characterizing export of land-based microplastics to the estuary - part II: sensitivity analysis of an integrated geospatial microplastic transport modeling assessment of tire and road wear particles. Sci. Total Environ. 646, 1650–1659. https://doi.org/10.1016/j.scitotenv.2018.08.301.

Vermeer, A.W.P., Van Riemsdijk, W.H., Koopal, L.K., 1998. Adsorption of humic acid to mineral particles. 1. Specific and electrostatic interactions. Langmuir 14 (10), 2810–2815.

Wagner, S., Hüffer, T., Klöckner, P., Wehrhahn, M., Hofmann, T., Reemtsma, T., 2018. Tire wear particles in the aquatic environment - a review on generation, analysis, occurrence, fate and effects. Water Res. 139, 83–100. https://doi.org/10.1016/j.watres.2018.03.051.

Wei, Z., Simin, L., Fengbing, T., 2013. Characterization of urban runoff pollution between dissolved and particulate phases. The Scientific World Journal, Article ID 964737, 6. https://doi.org/10.1155/2013/964737.

Zgheib, S., Moilleron, R., Saad, M., Chebbo, G., 2011. Partition of pollution between dissolved and particulate phases: what about emerging substances in urban stormwater catchments? Water Res. 45 (2), 913–925. https://doi.org/10.1016/j.watres.2010.09.032.

Zgheib, S., Moilleron, R., Chebbo, G., 2012. Priority pollutants in urban stormwater: part 1 – case of separate storm sewers. Water Res. 46 (20), 6683–6692. https://doi.org/10.1016/j.watres.2011.12.012.

Zhang, W., Zhang, S., Yue, D., Wan, C., Ye, Y., Wang, X., 2008. Characterization and loading estimation of polycyclic aromatic hydrocarbons in road runoff from urban regions of Beijing, China. Environ. Toxicol. Chem. 27 (1), 31–37. https://doi.org/10.1897/07-030.1.

Zhou, J., Wang, L., Qiao, X., Binks, B.P., Sun, K., 2012. Pickering emulsions stabilized by surface-modified Fe3O4 nanoparticles. J. Colloid Interface Sci. 367 (1), 213–224. https://doi.org/10.1016/j.jcis.2011.11.001.