Polycyclic aromatic hydrocarbons in stormwater ponds

Assessment of removal efficiency and monitoring methods

Master's thesis in Civil Engineering and Water Management

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Abstract

To reduce the impact of stormwater runoff pollution on receiving waters and to achieve Environmental Quality Standards, stormwater ponds are commonly used pollutant control measures for settling of particles and attached pollutants. In stormwater, many organic pollutants, such as the most frequently detected polycyclic aromatic hydrocarbons (PAHs), may partition into the truly dissolved and colloid-bound phases, and may therefore not be removed in stormwater ponds. The objectives of this thesis were to: (1) assess the removal efficiency of PAHs in stormwater ponds with special regard on the pollutants' partitioning; (2) test monitoring methods to evaluate the cost and efficiency of monitoring approaches. Monitoring was performed at the inlet and outlet of a stormwater pond using two passive sampling methods (SorbiCell samplers and semi-permeable membrane devices - SPMDs), sediment sampling and volume-proportional automatic sampling. The results obtained by automatic sampling revealed lower removal rates of total PAH concentrations ranging from -75% to 46% for single storm events compared to previous reports for the same pond where removal efficiencies around 70% were registered. The SPMD method was able to detect several PAHs present in the truly dissolved phase, although these were not found in the water samples collected by automatic sampling. However, contradictory results regarding the removal efficiency were observed. The SorbiCell technology revealed issues with low sampling rates, which resulted in analytically not detectable analyte accumulation. This thesis illustrates the possibilities and limitations of different approaches for monitoring highly dynamic stormwater discharges. It shows that passive sampling presents a simple and cheap opportunity to obtain information about bioavailable pollutant concentrations present at low concentrations in stormwater runoff. However, reliable methods for the estimation of the total concentration based on passive sampling results are needed, or alternatively, adaptions of the WFD are necessary to take the pollutant's partitioning into account and bring these methods more into use.

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1   Introduction

Stormwater management has traditionally been aiming at the prevention of flooding. Today, contaminated stormwater is regarded as one of the biggest pressures on aquatic ecosystems worldwide (Malmqvist & Rundle, 2002). Organic pollutants and metals commonly occur in runoff from urban areas and traffic is regarded as the most relevant source of contamination, although e.g. construction, building materials and commercial activities also give rise to both organic pollutants and metals in urban runoff (Markiewicz, et al., 2017; Zgheib, et al., 2012; LeFevre, et al., 2015). Traffic-related pollutants are emitted from nonpoint sources such as exhaust gases, vehicle and tyre wear, and abrasion of road surfaces and are transported from urban surfaces into sewer systems, subsequently into stormwater treatment facilities, if they exist, and then into receiving waters. Among those organic pollutants are for example polycyclic aromatic hydrocarbons (PAHs); very stable compounds that are known of having negative effects on human health such as carcinogenicity and reproductive disorders (Björklund, 2011; Zgheib, et al., 2012; Eriksson, 2002).

Frequently applied stormwater treatment facilities such as for example stormwater ponds are designed to remove particles. Since many organic pollutants are hydrophobic by definition they are expected to be mainly present attached to particles; however, studies show that many of these compounds are also detected in the colloid-bound and dissolved phase in stormwater (Crunkilton & DeVita, 1997; Kalmykova, et al., 2013; LeFevre, et al., 2015). Considering this knowledge, removal efficiencies of treatment facilities must be investigated, and the associated environmental risks have to be evaluated (Nielsen, et al., 2015; Kalmykova, et al., 2013; Zgheib, et al., 2011).

The requirements of the European Water Framework Directive include quality monitoring of aquatic environments in order to observe trends, assess the effectiveness of control strategies and to identify significant pollutant sources (Roig, et al., 2007). Monitoring of urban stormwater runoff, recognized as on the most relevant pollutant sources for surface waters (Björklund, 2011), is challenging due to the large number of possible pollutants and the dynamics in runoff flows. Commonly, stormwater quality is monitored using automatic samplers for taking grab samples or composite samples in a flow- or time-proportional manner. These approaches normally involve many practical difficulties and can be expensive. Consequently, alternative methods are requested. In contrast to automatic samplers, passive samplers work in a real time-integrative manner and allow continuous monitoring in aquatic environments over an extended time frame. Most passive samplers are based on accumulating only truly dissolved compounds which represent the most bioavailable phase (Birch, et al., 2012).

1.1   Aim and research questions

The aim of the thesis was to monitor the occurrence of PAHs, in influent and effluent water as well as sediment in a stormwater pond. The PAHs are commonly detected in urban runoff and cover a range of physical-chemical properties, hence may represent other organic pollutants. In the course of this, different monitoring strategies were tested and assessed.

The objectives of this thesis were to:

- monitor the occurrence of PAHs in influent and effluent water as well as in sediment in the stormwater pond
- investigate the partitioning of PAHs in stormwater, including particle-bound, colloid-bound and truly dissolved phases

- identify relevant removal processes for PAHs in the pond
- study the pollutant removal efficiency of the pond, with regard to both total and truly dissolved concentrations of PAHs
- test and assess the effectiveness of different sampling methods in terms of collecting reliable data and cost

Thus, the following questions are to be answered:

- How do pollutant occurrence and rain characteristics, such as antecedent dry period, rain intensity and rain depth, correlate?
- Is particle settling the major process for the removal of organic stormwater pollutants in the studied pond and which other removal processes are relevant?
- What removal efficiency on PAHs is achieved in the pond (total concentration and individual species) and is the removal of PAHs correlated to e.g. suspended solids and organic carbon removal?
- Are passive sampling and/or sediment sampling useful methods for monitoring stormwater ponds and assessing compliance with water quality standards and/or guidelines?

To answer these questions a case study was performed at the Järnbrott pond in the south of Gothenburg, Sweden.

1.2   Limitations

- Only one pond and one catchment were studied.
- The study only included PAHs although there were other organic pollutants which exhibit other physical-chemical properties that could be relevant from a stormwater perspective.
- Due to restrains in time and economy, monitoring using automatic samplers was performed from October to January and resulted in monitoring seven storm events. Therefore, no seasonal changes were covered and only a very limited number of storm events were observed.
- Also, passive sampling was performed only during two sampling periods of 3-4 weeks each.

1.3   Outline of the thesis

This report is organized into five chapters. After the introduction and definition of the aims and contents of the thesis in chapter 1, chapter 2 provides background information about stormwater pollutants, stormwater management and monitoring of stormwater runoff quality.

Chapter 3 describes the applied methodology. In this chapter, the study site where the monitoring campaign was performed is explained, giving information about the catchment and the studied pond. Chapter 3 also discusses the used sampling methods at the site, the performed analytical methods in the laboratory and the applied statistical methods.

Chapter 4 deals with the results of the performed monitoring programme. This chapter is divided into three parts: i) at first, the observed storm events are described; ii) after that, the results on the studied removal efficiency of PAHs, TSS/VSS and TOC/DOC are presented and discussed; iii) lastly, the tested sampling strategies are compared in terms of effectiveness and cost-efficiency.

In Chapter 5 conclusions are drawn and points out which questions should be answered by further research.

2   Background

2.1   Stormwater Pollutants

2.1.1   Sources and groups of stormwater pollutants

Worldwide about 600 compounds have been detected in stormwater runoff and rainwater (Eriksson, 2002). Both wet deposition of atmospheric pollutants and the wash-off from urban surfaces result in stormwater pollution (Butler & Davies, 2011). These pollutants include both inorganic and organic substances that are present as particles, attached to colloids and in the dissolved phase. Traffic is seen as a major contributor to contamination of urban stormwater (Revitt & Ellis, 2008). Markiewicz et al. (2017) identified the main traffic-related sources of organic pollutants; among them are vehicle exhaust, tyre wear, brake linings, spills of fuels, oils and lubricants, and abrasion of road surfaces. Furthermore, traffic is also regarded as a significant source of metals (Sörme, et al., 2001). Beside traffic, leaching building materials, such as metals from roofs, wood facade impregnations or concrete have been identified as important emitters of inorganic and organic pollutants to stormwater (Björklund, 2011; Van Metre & Mahler, 2003). Table 1 gives an overview of commonly detected stormwater pollutants including possible sources.

Stormwater runoff quality can be highly variable in its constituents and concentrations; average runoff concentrations can vary from one site to another by several levels of magnitude and this may occur even at the same site between storm events. Traffic intensity, road surface characteristics, antecedent dry periods, effectiveness of street sweeping, rainfall intensity and geographical location of the site are known as relevant factors that strongly influence runoff quality (Björklund, 2011; Butler & Davies, 2011).

The so-called pollutant build-up phase starts with the deposition from traffic and atmospheric fallout (dry deposition) on surfaces such as roads and roofs. This is often described by two simplified approaches; a linear accumulation with a constant time-dependent increase of pollutants, or an asymptotic process which assumes that pollutant build-up is limited due to an equilibrium between build-up and wash-off (Egodawatta, et al., 2009). After the accumulation phase, the subsequent wash-off process depends on the rain intensity and the pollutant's binding characteristics; dissolved pollutants may be washed-off at a storm event of lower intensity than pollutants bound to particulates. The pollutants are washed off the surface and subsequently transported to the sewer system which leads the water either directly into receiving waters or, before that, into stormwater treatment facilities (Björklund, 2011; Butler & Davies, 2011).

Table 1. Pollutant groups in stormwater (Björklund, 2011; Barbosa, 2012).

Pollutant group	Parameter	Sources	Relevance & effects
Solids	TSS	Pavement wear, winter road maintenance, corrosion of vehicles and building materials; construction sites; atmospheric fallout; anthropogenic wastes	Important for transportation of contaminants; increased turbidity: reduced light penetration; interference with aquatic organisms
Organic matter	BOD_5 and COD	Fertilizers; degradation of organic material; animal and human waste; combined sewer overflows (CSOs), atmospheric deposition	Increased oxygen demand: low levels of dissolved oxygen or even anoxic conditions in receiving waters
Nutrients	N (TKN, NO_x, org.-N); P (total-P, soluble-P)	Fertilizers; degradation of organic material; animal and human waste; CSOs, atmospheric deposition	Eutrophication: increased plant growth which leads to increased demand in dissolved oxygen and reduced light penetration
Metals	e.g. Cu, Zn, Cd, Pb, Ni and Cr	Corrosion of vehicles, tire wear, fuels and lubricant oils, traffic signs; industry; metallic roofs and other building materials	Toxic effects on aquatic plants and humans
Organic pollutants	e.g. PAHs, PCBs	Incomplete combustion of organic material, tire wear, fuels and lubricant oils; facades and roofs	Many organic pollutants are carcinogenic, mutagenic and persistent against degradation
Pathogens	e.g. total coliforms, E. coli	Animal and human feces; natural occurrence in soil and water	May cause disease in plants, animals or humans
Ions	Ca, Cl, Na	De-icing; atmospheric fallout	Potential groundwater contamination

2.1.2   Consideration of stormwater pollution in the European Water Framework Directive

The Water Framework Directive (WFD) of the European Union was put in force in 2000. The objectives of the WFD include ensuring sustainable use of drinking water resources, protection of aquatic ecology, protection of natural habitats and preventing degradation of the aquatic environment due to pollution and artificial barriers (European Commission, 2000). Based on a chemical and ecological quality assessment, the WFD aims at achieving a "good status" for all surface water and groundwater bodies. The WFD determines the good chemical status using Environmental Quality Standards (EQS) (European Commission, 2000) – emission limits defined as annual average and maximum allowable total concentrations. Only the limit values for metals are determined referring to the dissolved fraction (Vignati, et al., 2009).

Pollution of surface water caused by diffuse sources, such as stormwater discharges, is not directly mentioned in the WFD. However, to achieve a good water quality status pollution control of diffuse pollution sources is necessary. The WFD established a list of 33 priority pollutants (PPs) which present a significant risk to or via aquatic environments (Annex X, Decision 2455/2001/EC). Of the 33 PPs, 11 are regarded as priority hazardous substances with the goal of eliminating them from discharges. The

PP list includes metallic and organic compounds like biocides and substance groups like PAHs (European Commission, 2016). However, stormwater quality research has focused in the past predominantly on the fate of metals, in contrast to organic substances (LeFevre, et al., 2015; Björklund, 2011).

2.1.3 Polycyclic aromatic hydrocarbons in stormwater

This study focuses on polycyclic aromatic hydrocarbons (PAHs) since they are commonly detected in urban runoff and cover a range of physical-chemical properties, hence may represent other organic pollutants. In the following paragraphs, chemical properties, sources, occurrence and environmental effects of PAHs are described.

Physicochemical properties and health effects

The PAHs constitute a class of very stable organic molecules. More than 100 different compounds belong to the PAH group. They consist of fused aromatic rings, where the simplest form is naphthalene, based on two benzene rings. Depending on their number of aromatic rings, PAHs are commonly divided into three groups following the categorization of the Agency for Toxic Substances and Disease Registry (ATSDR): low-molecular-weight (LMW) PAHs having 2 to 3 aromatic rings (naphthalene, acenaphthene and acenaphthylene), medium-molecular-weight (MMW) PAHs with 3 and 4 rings (fluorene, phenanthrene, anthracene, fluoranthene and pyrene) and high-molecular-weight (HMW) PAHs having 4 to 6 rings (benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene and indeno[1,2,3-c,d]pyrene) (Neilson, 1995).

The PAHs are non-polar, and most compounds are highly hydrophobic (Neilson, 1995), i.e. the octanol-water partitioning coefficient log K_{OW} > 3. Therefore, PAHs also show a high affinity for organic carbon (Hylland, 2006; Nielsen, et al., 2015), why organic sediments are considered as an important sink for these compounds in aquatic environments (Krein & Schorer, 2000). Studies in the past decades have shown that selected PAHs may exhibit acute toxicity, carcinogenicity and reproductive effects on aquatic organisms (Agency for Toxic Substances and Disease Registry, 1995; Neilson, 1995). Moreover, due to their high persistence against biological and chemical degradation, PAHs show the ability to bioaccumulate in aquatic organisms and are forwarded in the food chain (Jones & De Voogt, 1999).

Sources

The PAHs are released from anthropogenic activities as well as natural sources. They occur naturally e.g. in coal tar and crude oil and are produced when organic matter, such as oil, gas, coal and wood is combusted incompletely (Neilson, 1995). Several studies identified traffic as a major PAH source; exhaust gases, tyre wear (mainly from HA oils), lubricant oils and abrasion of road surface are regarded as possible polluters (Markiewicz, et al., 2017; Björklund, 2011; Watts, et al., 2010). Markiewicz et al. (2017) estimate in a highway case study that 990-3900 µg PAHs are emitted per vehicle kilometre. Consequently, stormwater runoff from roads and other urban surfaces is recognized as a main contributor of PAHs to receiving waters. Crunkilton and DeVita (1997) for example, reported increased PAH concentrations during storm events up to 20 times higher than measured in base flow, which demonstrates the possible influence of stormwater on the water quality of the river.

The US Environmental Protection Agency (US EPA) published in 1976 a list of 16 PAHs of special concern (also "priority PAHs", "16 EPA PAHs" or "PP PAHs"). The list was created considering toxicity of the substances, availability of analytical methods and knowledge about their occurrence. Today, 40 years after its publication, the list has still a tremendous role since the defined 16 PAHs are routinely investigated in the majority of environmental studies (Andersson & Achten, 2015). Eight of these 16 EPA PAHs are included in Annex X of the EC Water Framework Directive (European Commission, 2000) as priority substances, for which EQS are defined for total concentrations. According to Birch (2012), this shows that there is a lack of knowledge about the PAH's partitioning behaviour since the dissolved phase of the PAHs are considered as the most relevant fraction from a toxicological point of view (European Commission, 2000).

According to today's knowledge, however, highly relevant PAHs are not included among the 16 EPA PAHs. There are discussions whether if and how the list should be expanded since the list does not cover three groups of polycyclic aromatic compounds (PACs): larger PAHs, alkylated PACs and compounds containing heteroatoms (Andersson & Achten, 2015).

2.1.4 Partitioning in water

Partitioning is the distribution of a compound between phases in water. These include the truly dissolved, colloid-bound and particle-bound phase. Colloids are often defined as inorganic and organic (e.g. humic acids) particles < 1 µm, which do not settle (however, there is no strict definition) – therefore, they are more difficult to remove from contaminated waters than particles that settle. The distribution between phases depends on water quality parameters, other environmental factors and the compound's physical-chemical properties. In the case of PAHs and other organic contaminants, their hydrophobicity is of particular importance. Partitioning has severe impacts on a compound's mobility, bioavailability and risk for the environment (LeFevre, et al., 2015; Kalmykova, et al., 2013).

A substance's partitioning behavior may be characterized by its partitioning rate, equilibrium constant or accumulation factor. To describe the distribution of organic compounds between the aqueous and particulate phase, the octanol-water partition coefficient K_{OW} is commonly used as an indicator (1) (Connell, et al., 1997). It is defined as:

$$K_{OW} = \frac{C_O}{C_W} \qquad (1)$$

where:
C_O is the concentration of the chemical in octanol ($C_8H_{17}OH$) [µg/l].
C_W is the substance's concentration in water at equilibrium [µg/l].

Non-polar, lipophilic compounds prefer octanol (large K_{OW} values) while polar, hydrophilic compounds prefer water (small K_{OW} values). Normally, $K_{OW} > 100$ is considered as lipophilic, which means that the compound is more likely to bioaccumulate (Connell, et al., 1997).

In theory, hydrophobic organic compounds (log $K_{OW} > 3$), such as PAHs, mainly distribute among organic phases driven by absorption and adsorption. Contrarily, hydrophilic compounds (log $K_{OW} < 3$) can be ionic or non-ionic and therefore can also form complexes with other ions, molecules, colloids or particles by sorption-desorption processes (Birch, et al., 2012). The log K_{OW} values of PAHs range from 3.45 (Naphtalane) to approximately 6.90 (Dibenzo[ah]anthracene) (Huckins, et al., 1999). However, several studies investigating the partitioning behavior of PAHs report that even highly hydrophobic organic compounds (i.e. the HMW PAHs) are present not only in the particulate, but also to a considerable part in the colloidal and dissolved phase (LeFevre, et al., 2015; Kalmykova, et al., 2013).

This knowledge stands in contrast to the assumption that hydrophobic compounds predominantly bind to particulates.

Generally, the partitioning behavior of PAHs is known to strongly depend on the molecular weight: LMW and MMW PAHs are reported to be detected in the filtrated fraction partly (= truly dissolved and colloid-bound fraction), while more HMW PAHs were observed in the particulate phase (Nielsen, et al., 2015). This finding is consistent with their expected behavior according to their hydrophobicity. Further, the presence of colloids, often measured as DOC, is expected to decrease the particulate-bound fraction (Nielsen, et al., 2015).

Since the WFD only determines limit values for organic substances as total water concentrations to comply with the EQS, partitioning between particle-bound, colloid-bound and truly dissolved contaminant species is not considered (Vignati, et al., 2009). This issue is further discussed in Chapter 4.3.2

2.2 Stormwater management

2.2.1 Sustainable drainage systems

Traditionally, water running off from impervious surfaces is collected either in storm sewers or combined sewers which drain into receiving waters. Increasing urbanisation leads to more frequently overloading of these existing piped systems. For many years, the only answer to this problem was to increase the transport capacity of the sewer systems and to reduce peak discharges by retention systems. This can be achieved by measures such as building new transport pipes, additionally to the existing sewers, or constructing detention and retention facilities. Generally, these measures are associated with high capital and maintenance costs (Stahre, 2006; Butler & Davies, 2011).

In the last decades, alternative approaches to the previously described so-called "grey infrastructure" have been developed and are widely used today. The sustainable drainage systems (SuDS), as they are commonly called in Europe, aim at disposing stormwater more naturally and locally. They are characterized as low-tech solutions using processes such as infiltration, percolation, detention in ponds and wetlands. In other parts of the world, terms such as "green infrastructure", "best management practices" (BMP) or "ecological stormwater management" may be more commonly used (Stahre, 2006). Beside reducing the pressure on the existing storm- and wastewater infrastructure, SuDS involve additional benefits such as water quality improvement by physical and biological treatment, contribute to a sustainable groundwater management and may help in irrigation problems especially in urban areas. Additionally, stormwater facilities may also entail aesthetic, economical and recreational values (Stahre, 2006).

However, it is important to mention that SuDS must not always present the most sustainable solution. Butler & Davies (2011) state that the ultimate goal is always to "find the right tools for the job, used in the best combination". Therefore, conventional drainage systems should not be ignored and may still present or be part of the best solutions for certain issues (Butler & Davies, 2011).

2.2.2 Pollutant removal in stormwater ponds

Stormwater ponds are control systems that are designed for slow release and treatment of stormwater runoff. They may be constructed as dry or wet ponds. Dry ponds (or detention ponds) are designed to store stormwater runoff temporarily and drain the whole amount of stored water. In contrast, wet ponds (or retention ponds) permanently store a certain water volume since the outflow is positioned at a higher elevation relative to the pond bottom. The outflow can be equipped with or without a control system in

both types of ponds (Erickson, et al., 2013). Stormwater retention and detention influence both stormwater quantity and quality: The slow drainage of the pond reduces the peak discharge while the reduction of flow velocities leads to settling of particles and associated pollutants (Butler & Davies, 2011).

Beside the technical use, stormwater ponds may also represent aesthetic and recreational features of an urban area. However, when the pond is open to the public, safety precautions have to be considered (Stahre, 2006). Further, water quality aspects may restrict other uses (e.g. recreation) strongly (German & Svensson, 2005). Another common problem of stormwater ponds is growth of algae; the problem may be reduced by measures such as emptying and cleaning the pond or reducing the incoming nutrient concentrations (Stahre, 2006).

Removal of suspended solids

Sedimentation (or settling) presents the primary pollutant removal process in stormwater ponds for suspended solids which are considered as a main vector for many pollutants occurring in stormwater runoff. According to Chebbo and Bachoc (1992), 84-89% of the COD load, 77-95% of the BOD load, and > 86% of the hydrocarbon load is detected attached to particles. However, in the study no further information is given which hydrocarbons specifically were studied. The settling process is described by Stokes' Law (1851); it derives the sedimentation rate and applies for small particles under quiescent conditions (2) (Erickson, et al., 2013):

$$v_S = \frac{g\,(s-1)\,d^2}{18\,\nu} \qquad (2)$$

where:
v_S is the terminal settling velocity of the solid particle [m/l].
s is the specific gravity of sediment [N/m^3].
g is the gravitational acceleration [m/s^2].
d is the diameter of the particle [m].
ν is the kinematic viscosity of the fluid (depending on the fluid temperature and salt concentration).

Figure 1 shows that the relationship between settling velocity and particle size strongly differs with varying particle density.
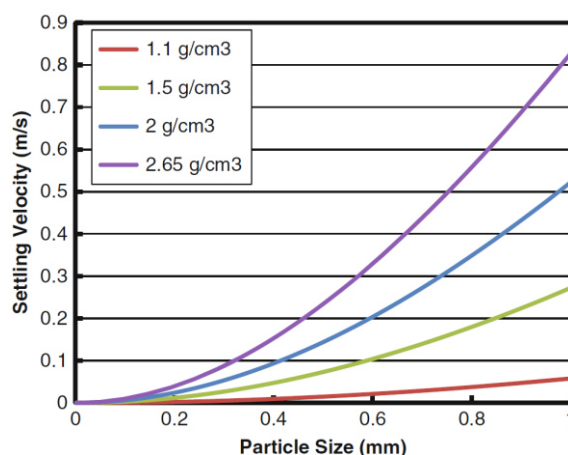
Figure 1. Settling velocity according to particle size and particle density (Erickson, et al., 2013)

It must be considered that Stokes's Law is determined for spherical particles, which may not be true in nature. Particle settling is influenced by the particle's shape, size and density as well as the fluid's

kinematic viscosity, which depends on temperature and density of the fluid. Thereby, the impact of the temperature increases with increasing particle size, while a higher temperature results in a higher settling velocity (Erickson, et al., 2013). Ferguson and Church (2004) developed an equation based on Stokes' Law (1851) that applies for larger particles (3):

$$v_S = \frac{g\,(s-1)\,d^2}{18\,v + (0.75\,Cg\,(s-1)\,d^3)^{1/2}} \qquad (3)$$

where:
C is a constant depending on the form of the particle (0.4 for spheres, 1.0 for typical sand grains) [-].

Comparing the two equations, it is apparent that particles bigger than approximately 0.5 mm are represented more accurately by the equation developed by Ferguson and Church (2004), whereas both equations (3) and (4) derive the same results for particles smaller than 0.5 mm.

Theoretically, the hydraulic condition resulting in the minimum treatment efficiency is the completely mixed tank, while plug-flow (i.e. constant velocity over one cross-section) results in the maximum treatment efficiency. For plug-flow it is assumed that the water flows through the tank laminarly and particles are not pushed backward or upward. In reality, hydraulic conditions are something between those two ideal cases since a pond is influenced to a certain degree by turbulences caused e.g. by the inflow, groundwater infiltration or wind, which leads to mixing of the water column. These factors may also cause resuspension of already settled particles into the water body (Erickson, et al., 2013; Andradottir, 2017). Figure 2 presents examples how the removal efficiency of a settling pond may vary at different temperatures and different particle densities. It demonstrates that particle density has a stronger influence on the removal efficiency than the fluid temperature.
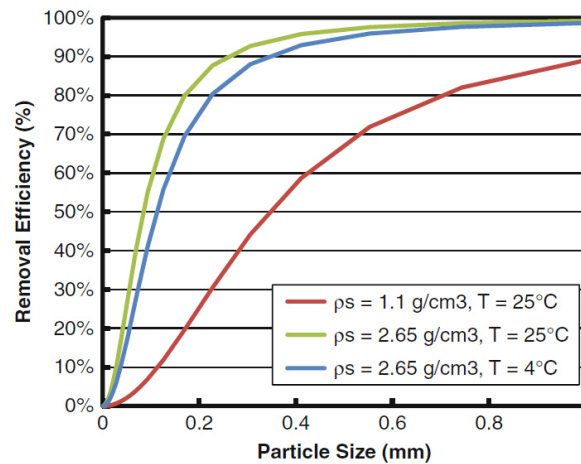
Figure 2. Removal efficiency of stormwater ponds depending on particle size, particle density and water temperature (Erickson, et al., 2013)

The removal efficiency may be highly variable between single storm events. It is influenced significantly by rain characteristics such as retention time (i.e. time between two storm events) or rain intensity. Therefore, the removal efficiency should always be considered for longer periods including several storm events. Since more than 90% of the removal process are expected to take place during periods between two storm events, removal efficiency is strongly decreased by a high storm frequency due to shorter residence time (Pettersson & Svensson , 1998). The pond geometry and the catchment load (or specific pond area; i.e. the catchment's impervious area related to the pond surface area) are regarded as the most influential factors on the removal efficiency. This conclusion was drawn by Pettersson (1999), who reviewed different stormwater ponds in southern Sweden, investigating their removal

efficiencies. Pettersson reported that ponds with a high catchment load usually achieve removal efficiencies for suspended solids ranging from 20% to 40%, while ponds with a low catchment load remove particles by 80% to almost 100%. It was shown that increasing the specific pond area up to 250 m²/ha improves the removal efficiency; however, this value is regarded as being dependent on hydrological and climatic conditions. The removal efficiency of the Järnbrott pond investigated in 1997 was 70% for total suspended solids (TSS) and 60% for volatile suspended solids (VSS) (Pettersson, et al., 1999).

Removal of heavy metals

The metals commonly analysed in stormwater are Cd, Pb, Cu and Zn. Since metals are not degraded, they accumulate in sediments, plants and organisms. The removal of heavy metals from stormwater largely depends on the metals' partitioning behaviour. Many metals are detected in the dissolved phase and may bind to solid particles or colloids due to their negatively charged surface (LeFevre, et al., 2015). Consequently, these compounds are effectively removed by sedimentation. Factors such as characteristics, properties of the metal, and characteristics of the water in the pond (pH, metal concentration, etc.) influence the extent of the sorption process. Organic matter plays an important role for the fate of metals since they are known to strongly adsorb certain metals. However, once a metal ion is attached to organic matter, it can be mobilized again by processes that result in metal leaching, such as dissolution or biotransformation. In addition to sorption, metals may also be removed by plants. Although studies have shown that certain plant species are able to capture metals, their role as significant removal factors is not commonly accepted (LeFevre, et al., 2015). The removal efficiency for the Järnbrott pond (without consideration of the overflow) on metals ranges from 50% for Pb, 30% for Cu and Zn, and 10% for Cd (Pettersson, 1999).

Removal of organic matter and nutrients

Under aerobic conditions, heterotrophic microorganisms (organisms that rely on organic compounds as source of energy and carbon) are able to degrade organic carbon in aquatic environments (Burton & Stensel, 2004). The concentration of dissolved oxygen (DO) in natural waters depends on factors like water temperature, activity of the microorganisms or reaeration rate and is normally between 0 to 10 mg O_2/L. When the concentration of DO is lower than 1.0 mg O_2/L the degradation process starts to shift towards an anoxic degradation (which may occur in deep ponds), where nitrate-bound oxygen substitutes molecular oxygen. In zones where neither dissolved, nor bound oxygen is available, anaerobic degradation occurs. Heterogenic organisms are able to degrade organic substances under anoxic conditions. These processes are in general slower with lower energy yields and bacterial growth rates than aerobic degradation. Heterogenic microorganisms need an additional source of nutrients, such as nitrogen or phosphorus, which often is the limiting factor for the anoxic degradation process (Burton & Stensel, 2004). Generally, a very common parameter to quantify microbial degradation is the biochemical oxygen demand (BOD). It is defined as the amount of DO demanded by microorganisms for breaking down organic matter during a certain time period and at a defined temperature of 20°C (Burton & Stensel, 2004).

By definition, nutrients are compounds that organisms use for their sustainment and are utilized in their metabolism. However, the term is often used for two of the essential elements, nitrogen and phosphorus (Butler & Davies, 2011). Nitrogen mainly occurs in stormwater as ammonium and ammonia (NH_4^+ and NH_3), bound to oxygen (NO_x) and organic compounds. 30-50% of the total nitrogen in urban stormwater runoff consists of dissolved inorganic nitrogen compounds (LeFevre, et al., 2015). The natural nitrogen cycle strongly depends on microbial activity: Nitrification is the bacterial oxidation process of ammonium (NH_4^+) to nitrate (NO_3^-) and is performed by autotrophic organisms in two steps: the

oxidation of ammonium to nitrite (NO_2^-) and the degradation of nitrite to nitrate (NO_3^-) where both steps require aerobic conditions (Burton & Stensel, 2004). As oxygen is consumed and not renewed in undisturbed sediments, the nitrification process gets strongly inhibited (Lavieille, 2005). Under anoxic conditions, where oxygen is predominantly only available bound to nitrate (NO_3), nitrate is transformed into molecular dinitrogen (N_2) which finally evaporates. This process, called denitrification, is performed by certain heterotrophic organisms and some autotrophic organisms, while additional organic substrate is needed for oxidation (Burton & Stensel, 2004).

Since phosphorus is usually the limiting nutrient in freshwater bodies, phosphorus removal presents the most efficient way to avoid eutrophication of stormwater. In the aquatic environment, phosphorus is present either as organic phosphorus in organic materials or inorganic orthophosphates - the only dissolved form of phosphorus. Orthophosphates include the phosphoric acid H_3PO_4, and its conjugate bases ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}). Phosphates are mainly bound to particles which makes them settleable in stormwater ponds. However, phosphorus is likely to resuspend into the pore water of the sediment bed and consequently into the pond water; this is explained with the low redox potential in sediments that results in the dissolution of the metal oxides. This process can lead to the release of phosphorus into the pond years after the compound has settled (Butler & Davies, 2011). Beside sedimentation, biological uptake is considered as a main removal mechanism of phosphorus in stormwater ponds (Wetzel, 2001).

At the Järnbrott pond, a removal efficiency for nitrogen of 7% and 40% for phosphorus are reported (Pettersson, et al., 1999). The Krubban pond, also investigated in the study of Pettersson et al. (1999) and approximately double the size of the Järnbrott pond, exhibit significantly better values: 33% removal efficiency of nitrogen and 74% for phosphorus.

Removal of polycyclic aromatic hydrocarbons

In aquatic environments, the persistence of PAHs against chemical and biological degradation strongly depends on their number of aromatic rings. Generally, PAHs are known to show an increase in electrochemical stability and consequently a higher persistence with increasing number of benzene rings (Kanaly & Harayama, 2000). As stated before, PAHs bind to particles to a certain extent, due to their high affinity to organic matter and hydrophobic behaviour (Figure 3). However, the compounds show different affinities to different particle sizes. However, studies investigating this aspect show different results (Krein & Schorer, 2000; Nielsen, et al., 2015).

As illustrated in Figure 3 (Lavieille, 2005), after settling, aerobic and anaerobic biodegradation presents the first degradation path of PAHs in a pond. It occurs in sediments when microorganisms are able to use PAHs as energy and carbon source or in the course of co-metabolism, which means that microorganisms, such as algae, bacteria and fungi, consume PAHs through ingesting organic material, degrading the PAHs to simpler compounds and under certain prerequisites until mineralization. The compound's bioavailability, which depends on partitioning between dissolved and particulate phases, plays a significant role in the biological transformation process (Haritash & Kaushik, 2009).

Since PAHs have a strong ultraviolet and visible radiation absorption, they are highly degradable by sunlight in combination with dissolved oxygen in the water. This second pathway of PAH degradation, called photoreaction, is reported to be able to significantly reduce the half-lives of PAHs from weeks to hours. The third way of degradation, oxidation, occurs using e.g. hydroxyl radicals, peroxides or singlet oxygen as oxidants (Neilson, 1995).

In previous studies at Järnbrott, removal of PAHs was investigated: A reduction of total PAH concentrations by factor 10 was observed from the inlet to the outlet; the highest removal rates were

noted for the dissolved fraction (< 0.7 µm) (Nielsen, et al., 2015). Further, Lavieille (2005) found removal rates ranging from >30% to >75%.
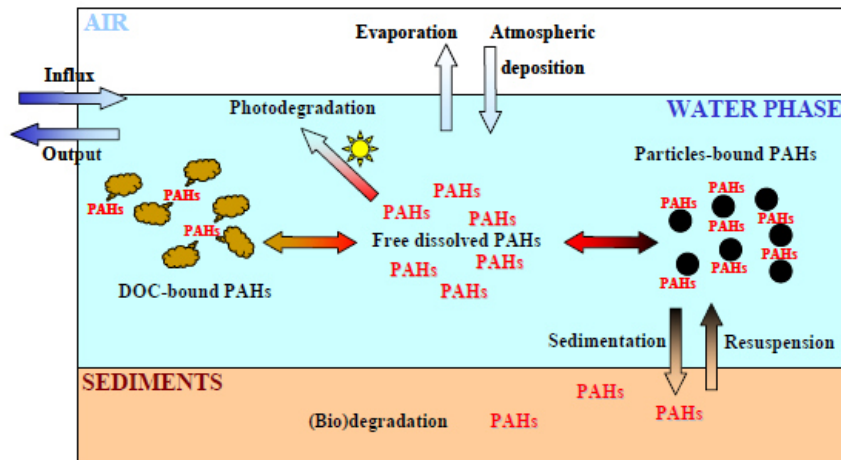
Figure 3. *PAHs degradation pathways in the aqueous environment where DOC-bound PAHs correspond to colloid-bound PAHs. According to Lavieille (2005).*

2.2.3 Other stormwater management options

Sustainable stormwater management intends to use different drainage techniques in series to reduce pollutant concentrations and peak flow discharges (Lavieille, 2005; Butler & Davies, 2011). In Table 2, common types of stormwater management practices beside stormwater ponds are presented. The measures are characterized according to their location within the so-called "management train". The idea behind this concept is to preferably use techniques as close to the top as possible. It starts with solutions preventing runoff locally (local disposal and inlet control), followed by techniques treating the water at site (site control) and finally "end-of-pipe facilities" that are intended for stormwater retention and treatment outside densely populated areas (regional control) (Butler & Davies, 2011).

Table 2. *Stormwater management options* (Lavieille, 2005; Butler & Davies, 2011).

Option	Examples	Advantages	Disadvantages
Local disposal	Vegetated surfaces (e.g. swales; green roofs)	+ Runoff delay and reduction + Pollution reduction + Low capital costs + Groundwater recharge	- Maintenance costs - Groundwater pollution
	Pervious pavements	+ Groundwater recharge + Pollution reduction + Runoff reduction of minor storms	- High capital and maintenance costs - Clogging - Groundwater pollution
Inlet control	Rooftop ponding	+ Runoff delay + Cooling effect on building	- Structural loading - Outlet blockage
	Downpipe storage (e.g. water butts above/below ground)	+ Runoff delay + Reuse of stormwater	- Small capacity
Site control	Infiltration and bioretention devices (e.g. infiltration trenches, drains or basins; soakaways)	+ Groundwater recharge + Pollution reduction + Runoff reduction of minor storms	- High capital costs - Groundwater pollution - Clogging
	Stormwater basins (and ponds)	+ Runoff delay + Pollution reduction + Aesthetics + Other uses (recreation, wildlife)	- High capital and maintenance costs - Large footprint - Pest breeding potential
	Oversized sewers	+ Runoff delay + Low space requirement	- Maintenance costs - Access difficulties - Large footprint
	Filtration devices (e.g. surface/underground sand filters)	+ Pollution reduction	- Clogging - Maintenance costs
	Underground sedimentation systems	+ Pollution reduction + Low space requirement	- Maintenance costs - Access difficulties - Large footprint
Regional control	Constructed wetlands	+ Low capital costs + Pollution reduction + Runoff delay + Other uses (recreation, wildlife)	- Great space requirements - Maintenance costs

Non-structural practices

In contrast to the previously stated engineered measures (structural practices), non-structural measures include different kinds of management practices, such as maintenance programs (e.g. street sweeping) or restricting the use of certain substances (Butler & Davies, 2011). Non-structural measures are not explained more in detail since this would go beyond the thesis' scope.

2.3 Monitoring of stormwater runoff quality

As stated before, the WFD requires the control of several substances and further to achieve defined EQSs. Since stormwater is a major transport route of many relevant pollutants, there is a need to monitor stormwater runoff quality for different reasons. The WFD lists three mandatory monitoring programs:

- *Control surveillance* aims at providing information to observe trends and assess long term effects of both natural and human activities on selected catchments. The catchments are selected based on their size, significance or special location (e.g. water bodies that cross borders to member states).
- *Operational surveillance* assesses the effectiveness of measures supposed to reduce emissions of certain PPs in catchments that are likely not to comply with the EQSs. Removal efficiencies of stormwater treatment facilities or CSOs may be investigated.
- *Investigative surveillance* is performed when the significant sources of high concentrations of PPs and reasons exceeding the EQSs are not known or to investigate the effects of accidents (Pettersson, et al., 2010).

Two common ways to characterize to report the pollutant concentration in stormwater runoff are

- the event mean concentration (EMC), which represents the total mass of a pollutant in one specific storm event divided by the total runoff volume of that event (4):

$$EMC = \frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \ [\mu g/l] \tag{4}$$

- the site mean concentration (SMC) is the total pollutant mass divided by the total runoff volume during a defined period of time (for example months) weighted after runoff volumes of single events (5):

$$SMC = \frac{\sum_{i=1}^{n} EMC_i V_i}{\sum_{i=1}^{n} V_i} \ [\mu g/l] \tag{5}$$

The goal of most sampling programs is to collect data of high accuracy and precision at the lowest costs. Considering that a substance's concentration may change within a relatively short time and also differs over the cross-section of a water body significantly, it is clear that certain simplifications or assumptions are necessary for every sampling method. In the following, different approaches for water sampling with special focus on PAH quantification are presented.

2.3.1 Conventional sampling methods for stormwater

Grab sampling, time- and volume-proportional sampling belong to the most commonly used stormwater sampling methods. Time- and volume-proportional sampling is performed by collecting either discrete or composite samples, consisting of two or more sub-samples that are pooled to one representative sample, which is subsequently analyzed for certain contaminants. Time- and volume-proportional sampling are performed using automatic sampling devices, whereas grab sampling is performed

manually. Since these sampling methods collect single water samples, either composed or not composed, they only represent a simplification of the real conditions and an instantaneous image of e.g. the PAH concentration at one specific spot. Additionally, uncertainties due to chemical and biological modifications during sampling, storage and transportation need to be considered (Nollet & Gelder, 2014).

Manual grab sampling

In this thesis, "grab samples" are considered as "snapshot" samples of a fixed volume taken manually, representing the current conditions at a specific point and time. Grab sampling can be performed at relatively low costs (Birch, et al., 2012). However, it is only representative for a very limited time and provides only a picture of the current chemical conditions. This can be counteracted by increasing the number of grab samples to improve the information value, but this leads to a large increase in costs due to high analysis and staff costs (De Jonge & Rothenberg, 2005). Data from a series of grab samples are typically highly variable and strongly affected by the time during the storm event when the samples were collected.

Since the water runoff volume at the beginning during a storm event are expected to transport the highest pollutant concentrations ("first flush effect"), samples collected at the beginning of a storm event may show higher pollutant concentrations than the event mean concentration (EMC). Therefore, they are representative only for the peak concentration. Moreover, this effect is reinforced in regions with long dry periods where the "seasonal first flush" may occur. If mean concentrations are needed, samples collected in the assumed middle of the storm event are preferred (Lee, et al., 2007). A study on the accuracy of common sampling strategies revealed that grab sampling requires at least 30 samples per storm event to estimate EMCs within 20% average error. The average error can be reduced by collecting grab samples at equal discharge volume intervals (Ma, et al., 2009).

Time-proportional sampling

Time-proportional sampling means that a fixed volume is collected at regular time intervals, producing either discrete samples or a composite sample (Figure 4). Compared to grab sampling, advantages of time-proportional sampling include extended information value since the samples represent an extended time interval and reduced logistic expenses. Disadvantages of this method include heavy and comparably expensive equipment and installation of equipment, which requires knowledgeable staff. Furthermore, the success of the time-proportional sampling method strongly depends on the design of the sampling volumes which requires detailed knowledge about the site's precipitation characteristics (Birch, et al., 2012; Wehrstein, 2017).
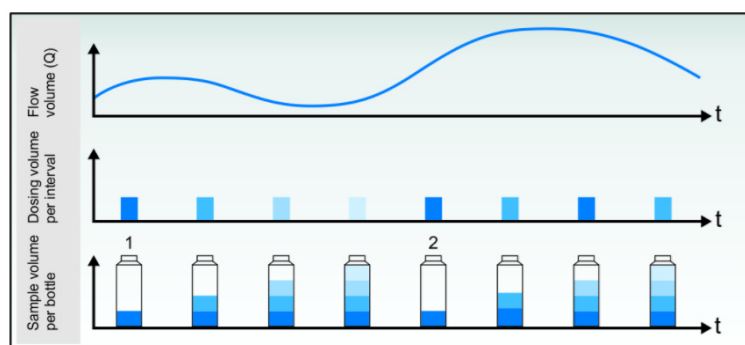
Figure 4. Time-proportional sampling mode according to Wehrstein (2017).

Volume-proportional sampling

Volume-proportional sampling is performed by collecting constant sample volumes at time intervals that vary according to the water flow what is measured by a flow meter (Figure 5). This means that a sample is taken after a certain water volume that has passed the sampling point. The collected samples are more representative for varying flows than time-proportional samples. This method also entails heavy and expensive equipment, a great installation effort is involved, and it strongly depends on knowledge about the local weather characteristics since the volumes of the single samples need to be defined (Birch, et al., 2012; Wehrstein, 2017).
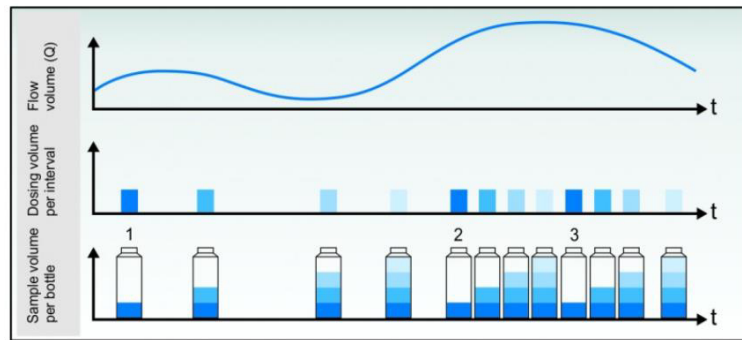
Figure 5. Volume-proportional sampling mode according to Wehrstein (2017).

Flow-proportional sampling

Flow-proportional sampling also uses the input of a flow meter. The current flow what determines the sample volume while time intervals remain constant (Figure 6). As for time-proportional and volume-proportional sampling, expensive and heavy equipment in addition to knowledgeable staff is needed (Birch, et al., 2012; Wehrstein, 2017).
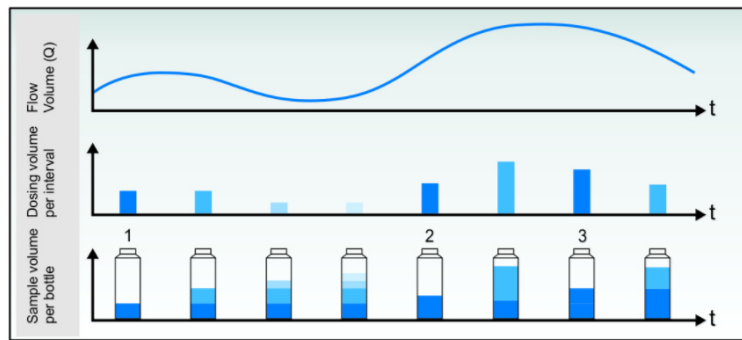
Figure 6. Flow-proportional sampling mode according to Wehrstein (2017).

2.3.2   Passive sampling of organic pollutants

The total concentration of a contaminant only supplies very limited information about its ability to harm aquatic organisms or human health (Férard & Blaise, 2013). It is proven that the presence of e.g. colloids, particulates and DOC may reduce the bioconcentration of many pollutants in various organisms significantly because of reduced bioavailability (Vignati, et al., 2009). From an ecological and toxicological point of view, investigations of water contamination therefore require data on the bioavailable concentration, which is defined as the compound fraction available for uptake by organisms via several uptake routes. Generally, the truly dissolved concentration is regarded as the only bioavailable fraction. The partitioning behavior is strongly influenced not only by a contaminant's

chemical structure but also by several environmental factors (as previously described in 2.1.4) and the affected organism itself (Figure 7) (Férard & Blaise, 2013).

Information on the bioavailability of pollutants can be acquired using two methods (assuming that the previously discussed sampling methods are not capable of delivering appropriate data for this issue):

- By using indicator organisms, a contaminant's bioavailability may be measured by determining the concentration of a certain compound contained in different organisms. The bioconcentration may provide, in combination with other measured parameters, information on a contaminant's toxicity, physiological and enzymatic effects (Figure 7) (Férard & Blaise, 2013). However, results from biomonitoring are difficult to interpret due to varying uptake rates of the organisms and further, this method is often not applicable for highly contaminated sites (Björklund Blom, 2002).
- Alternatively, passive sampling aims at collecting only certain species of the target compound by accumulating them on a receiving phase that shows high affinity for these constituents. This method imitates the uptake of a natural organism. The time-integrative manner makes the detection of even very low concentrations possible and allow to draw conclusions on long-term trends. Additionally, by using in-situ sampling techniques, such as passive sampling, uncertainties regarding modifications of the sample during collection, transport and handling before analysis can clearly be reduced (Björklund Blom, 2002). In the following, the passive sampling technique is discussed more in detail since this method was tested within this project's case study.
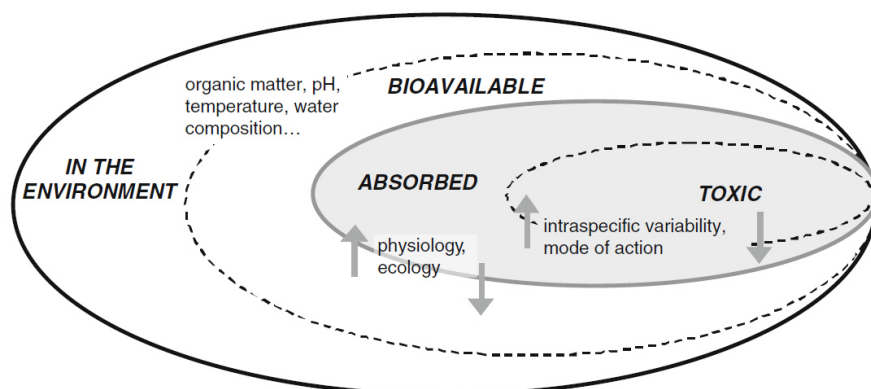
Figure 7. *Relationship between presence, bioavailability and toxicity of a contaminant according to Férard & Blaise (2013).*

Diffusive passive sampling using semi-permeable membrane devices

Most passive samplers are based on diffusion; they work without the need for external energy sources, only driven by the difference of the chemical potential between the sampled medium (water) and the receiving medium (Vrana, et al., 2005). Contrary to the previously discussed sampling methods, diffusive passive samplers target only a compound's truly dissolved phase, which is considered to be the most relevant for compound in terms of bioavailability and toxicity. Thus, passive sampling gives information about a pollutant's ability to enter the food chain and affecting human health. Further, passive samplers are exposed for an extended time period of several weeks, which allows them to provide a true image of the present bioavailable compounds and long-term trends (Tusseau-Vuillemin, et al., 2007).

In the case of semi-permeable membrane devices (SPMDs), before an analyte is adsorbed by the receiving medium it needs to pass the aqueous layer between the water phase and the semi-permeable

membrane – the diffusion boundary layer where the water turbulence is reduced (Figure 8). Subsequently, the diffusion layer must be passed by the analyte which is a semi-permeable membrane in case of the SPMDs. The diffusion limiting layer and the diffusion boundary layer are referred to as the diffusion pathway (Knutsson, 2013).
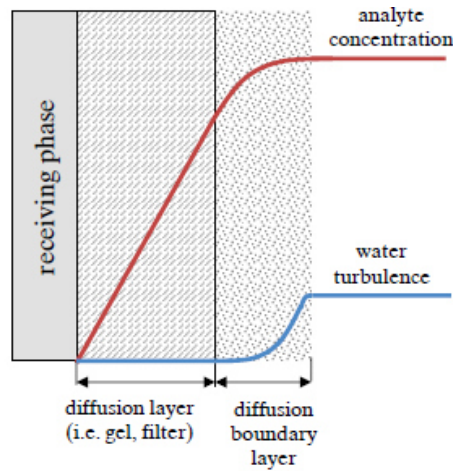
Figure 8. Scheme of the behaviour of the analyte concentration and the water turbulence at the sampler-water interface according to Knutsson (2013).

The time needed for passing the diffusion pathway limits the accumulation rate of a passive sampling device (PSD). The required time depends on the length of the diffusion pathway and the diffusion coefficient D [m²/s] which is described by the Stokes-Einstein equation (6):

$$D = \frac{k_b T}{3\pi\mu d} \qquad (6)$$

where:
k_b is the Boltzmann constant (1.38 x 10-23 J/K).
T is the temperature [K].
μ is the dynamic viscosity [g/s m].
d is the ionic diameter of the analyte [m].

The membrane may be selective, thus only selected compounds are able to pass, and is only permeable for dissolved compounds. The receiving phase may be an organic solvent, a resin or a polymer coating and shows, depending on its chemical or physical properties, a high affinity for the target compound. The receiving phase selectively accumulate target compounds when the sampler is deployed in the water phase (Pettersson, et al., 2010; Stuer-Lauridsen, 2005; Knutsson, 2013).

In the following, two different types of diffusive passive sampling – equilibrium and kinetic passive sampling – and advective passive sampling are presented. Equilibrium samplers are deployed until an equilibrium between the water and the collecting medium is established. They are characterized by a rapid equilibration time of hours to days and give information about the instant concentration of truly dissolved constituents. Their pollutant uptake regime is described by equations (7) and (8) (Vrana, et al., 2005).

$$C_{Water} = C_{SPMD}\frac{k_E}{k_U} = \frac{C_{SPMD}}{K_{SPMD}} \qquad (7)$$

while the relationship between K_{SPMD}, k_U and k_E is

$$K_{SPMD} = \frac{k_U}{k_E} = \frac{R_S}{k_E * V_{SPMD}} \qquad (8)$$

where:

C_{SPMD} is the measured analyte concentration in the SPMD [µg/l]

C_{Water} is the analyte concentration in the water [µg/l].

K_{SPMD} is the partition coefficient [-].

V_{SPMD} is the volume of the lipid and the membrane [ml].

k_U is the uptake rate [1/t].

k_E is the elimination rate or exchange coefficient [t$^-$].

R_S is the sampling rate (water volume cleared per time unit by a standard triolein SPMD) [l/d].

Therefore, to calculate the concentration of the analyte in water (C_W) only the partition coefficient K and the analyte concentration in the receiving medium (C_S) are necessary. Two prerequisites regarding the PSD are necessary for this method: i) the capacity of the sampler is bigger than the inherent concentration of the water, so that an early depletion of the receiving medium is prevented and ii) the response time of the sampler is shorter than fluctuations of the concentration in the water phase. Examples of available equilibrium PSD for hydrophobic organic pollutants are SPMDs and *Empore®* disks (Stuer-Lauridsen, 2005; Vrana, et al., 2005).

In contrast to equilibrium passive samplers, kinetic passive samplers estimate the time-weighted concentration of the truly dissolved compounds for the time of exposure by accumulating the analyte continuously. This is an advantage for contaminants which are usually difficult to analyse due to detection limit problems (Tusseau-Vuillemin, et al., 2007). Kinetic passive samplers usually consist of a receiving medium which has a strong affinity for specific target compounds and a large capacity for the collection of analytes. Three main assumptions are necessary for kinetic passive sampling: i) no interactions between the diffusive layer and diffusing compounds, ii) no accumulation of the target compound at the interface of the receiving phase to maintain a concentration gradient and iii) the adsorption of the analyte species occurs in a plane sheet (Knutsson, 2013). The theoretical accumulation behaviour is described by a linear relationship between the sampler's uptake rate of the compound and the exposure concentration in the first section, which is followed by a non-linear curve until equilibrium is reached and the capacity of the receiving phase is full (Figure 9).
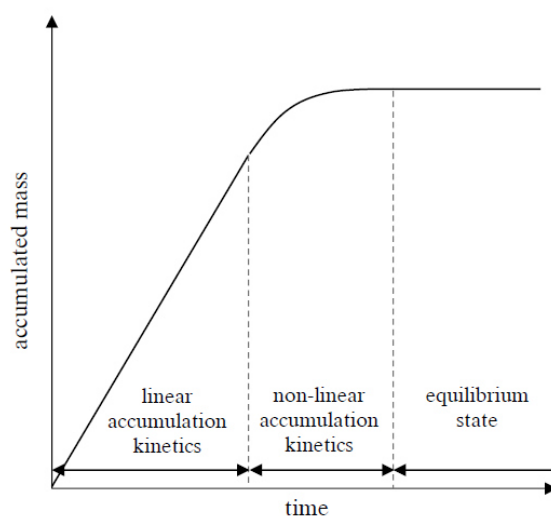
Figure 9. Theoretical uptake regime of passive samplers according to Knutsson (2013).

The linear uptake section of kinetic passive sampling is described by equation (9) (Huckins, et al., 1999).

$$C_{Water} = \frac{C_{SPMD} * V_{SPMD}}{R_S * t} = \frac{C_{SPMD}}{k_U * t} \tag{9}$$

R_S values for standard passive samplers can be found in the literature. Thus, C_{Water} can be calculated when M_S is determined in the laboratory and time t and R_S are known. R_S may be affected by biofouling, water flow turbulence and temperature (Stuer-Lauridsen, 2005; Vrana, et al., 2005).

In order to estimate the impact of environmental factors on the sampling rate R_S, Performance Reference Compounds (PRCs) - chemicals that do not interfere with the analytes - are added to membranes or the lipid phase of the diffusive passive samplers. When deployed, the PRCs leach due to their relatively high fugacity into the water phase. After exposure, the PRC loss can be used to derive the in-situ sampling rate of the PRC ($R_{S.PRC}$) (Huckins, et al., 2005). To adjust the sampling rates for the analytes, the Exposure Adjustment Factor (EAF) is used. To derive the EAF, the in-situ sampling rate of the PRC ($R_{S.PRC}$) is compared to the sampling rate determined during calibration studies ($R_{S.Cal}$) which is shown in equations (10) and (11) (Huckins, et al., 2005).

$$EAF = \frac{R_{S.PRC}}{R_{S.Cal}} \tag{10}$$

$$R_{S.2} = EAF * R_{S.1} \tag{11}$$

where:
$R_{S.PRC}$ is the in-situ sampling rate of the PRC, derived from the loss of PRC during a certain time period [l/d].
$R_{S.Cal}$ is the sampling rate determined in calibration studies [l/d].
$R_{S.1}$ is the analyte's sampling rate determined during calibration studies [l/d].
$R_{S.2}$ is the adjusted ("real") analyte's sampling rate [l/d].

Two key assumptions underlie the concept of PRCs: i) the sampler must obey first-order uptake- and loss-kinetics; ii) the loss rate constant (k_e) and uptake rate constant (k_u) must show a proportional relationship or should have similar half-lives, as illustrated in Figure 10 (Huckins, et al., 2005).
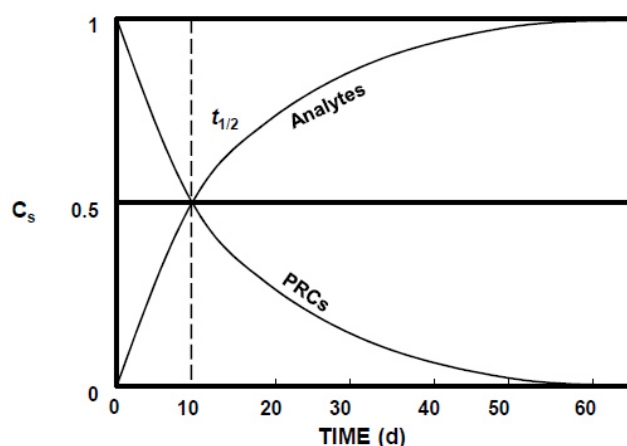
Figure 10. Uptake of analytes and release of PRCs of isotropic exchange kinetics according to Huckins, et al. (2005).

Various diffusion-based passive samplers are commercially available. Beside the previously described SPMDs which are used for hydrophobic compounds, most commonly used for kinetic passive sampling are polar organic chemical integrative samplers (POCISs) and Chemcatcher, which are available for different target constituents including polar and non-polar organic compounds or heavy metals (Pettersson, et al., 2010).

Advective passive sampling of organic pollutants

Beside diffusion-based passive samplers, which include kinetic and equilibrium-based passive sampling, advective (or flow-through) passive sampling presents another passive sampling technique. In this report, advective passive sampling is presented using the commercially available system SorbiCell (manufactured by Sorbisense A/S in Tjele, Denmark) as an example.

In contrast to the diffusion-based samplers, where the concentration gradient is the driving force, either the hydrostatic pressure or the water flow momentum creates a flow through the sampling device (depending on the installation method). For installation methods which work on hydrostatic pressure creating the advective flow, the method results in time-proportional sampling. When the SorbiCell is installed "in-stream", the flow momentum induces the flow through the cartridge which ends up in velocity-proportional sampling (Sorbisense A/S, 2017).

The SorbiCell sampler consists of a cartridge packed with two media: the one located upstream holds the receiving medium that adsorbs the compounds of interest, the second phase contains a tracer salt that is held by a filter and is leached dependent on the flow through the sampler (Figure 11). By determining the loss of tracer, conclusions on the passed through volume can be drawn by using equation and, subsequently, a time- or velocity-proportional analyte concentration can be derived (De Jonge & Rothenberg, 2005). Additionally, the sample volume ("field volume") is stored in the collection flask and can be measured after deployment to verify the sample volume calculated by the loss of tracer salt. The water concentration is therefore derived as followed (12):

$$C_{Water} = \frac{M_{ac}}{V_{water}} \qquad (12)$$

where:
M_{ac} is the accumulated analyte mass [µg].
C_{Water} is the derived analyte concentration [µg/l].
V_{Water} is the water volume that passed the cartridge (sample or field volume) [l].

Figure 11. SorbiCell cartridge (Sorbisense A/S, 2012).

The spheriglass filter (pore size from 60-100 µm holds back only larger particles from the sorbent medium, which means that not only truly dissolved compounds but also colloids and smaller particles may be included in the sample (Birch, et al., 2013). For ideal conditions, the tracer salt is washed out proportional to the flow through the sampler which results in a constant tracer concentration in the outflowing water (De Jonge & Rothenberg, 2005).

Five assumptions are necessary in order to regard Sorbicells as flow-proportional, although not all assumptions are fulfilled completely under certain conditions:

1. No uptake during no flow. However, during no-flow periods, analytes may in fact diffuse into the sampler without a wash-out of tracer salt. To limit this source of error, diffusion and flow into the sampler is only possible through a small opening (Birch, et al., 2013).
2. Linear relationship between water velocity and flow rate: This relationship mainly depends on the geometry of the monitored system (Birch, et al., 2013).
3. Water velocity through the sampler is representative for the entire cross section of the sampled water body: the relative depth and influencing currents have severe impacts on the sampler and should be considered for the installation. Relative depths of 0.1-1 have been shown to result in only little deviations (approximately ±10%) for turbulent flows (Birch, et al., 2013).
4. Linear relationship between water velocity at the site and the water flow through the sampler: Kronvang et al. (2010) reported that the relationship between velocity in a channel and flow through the sampler may change due to instant or slow clogging, or changes in hydraulics in the surroundings of the sampler (Birch, et al., 2013).
5. Sampling of the total concentration: Since the size of the entering particles is limited by the glass fibre filter (pore size 100 - 160 µm). This assumption cannot be fulfilled completely (Birch, et al., 2013). However, LMW and MMW PAHs are mostly detected in the filtrated fractions (i.e. dissolved and colloid-bound fractions), while only HMW PAHs are reported to mainly bind to particles > 0.7 µm (Nielsen, et al., 2015).

Passive sampling of PAHs – Review of previous studies

Previous studies found linear uptake regimes for less hydrophobic PAHs. Smaller variations in uptake rates of SPMDs are explained by different factors such as limits of analytical procedures or thickness of the boundary layer. This finding does not apply to highly hydrophobic compounds which are subject to greater impact of biofouling and thus, greater variations in uptake rates are reported. This explanation is also supported by the observed reduced uptake rates in SPMDs at higher temperature, which is suggested to increase the biological activity and consequently the extent of biofouling. However, the influence of temperature changes is assumed to be only of small effect for sampling with SPMDs. Also, salinity is not considered to affect SPMD sampling rates considerably but a compound's solubility and bioavailability (Huckins, et al., 1999).

Further, the less hydrophobic PAHs (i.e. LMW PAHs) reach the state of equilibrium within a shorter time than the more hydrophobic compounds (i.e. HMW PAHs), which show an extended linear uptake regime of typically several weeks (Tusseau-Vuillemin, et al., 2007). Huckins et al. (1999) report that performing SPMD sampling over 21 days, 8 of 16 PAHs achieved the equilibrium state.

As previously discussed, PAHs, and especially the HMW PAHs, are likely to bind to DOC. Since DOC colloids are too bulky to diffuse through the SPMD membrane, partitioning of PAHs to DOC strongly influences the performance of passive sampling since the more hydrophobic constituents are therefore less available for SPMD uptake (Tusseau-Vuillemin, et al., 2007). On the other hand, Stuer-Lauridsen (2005) reports that concentrations of LMW PAHs were partly underestimated, while some of the MMW

PAHs were overestimated. Komarova et al. (2006) report that sampling with SPMDs presents a more sensitive method compared to grab samples; 13 PAHs were detectable for SPMDs while only 6 PAHs were found with randomly collected grab samples. Thus, contradictory statements on SPMD sampling of different PAHs are found in the literature.

A study carried out on PAHs using SorbiCells indicates that the samplers are likely to overestimate the average concentration of small storm events where only the peak runoff is sampled. To counteract this issue, installing the passive sampling devices in a way that ensures high flow velocities also during the beginning of smaller storm events was suggested by the authors. In the study, dissolved LMW and MMW PAHs were detected, while HMW PAHs could not be determined with SorbiCells which was explained by the higher affinity of HMW PAHs to particles (Birch, et al., 2011).

3 Methodology

3.1 Description of the study area

The Järnbrott pond is situated 5 km south of Göteborg city centre (Figure 12) and was constructed in 1996 to improve stormwater quality. The pond is permanently filled with water. In Table 3, the technical specifications of the pond are presented (data on pond size refer to dry weather).

Table 3. Technical data of the Järnbrott pond (Pettersson, 1999).

Surface area	6200 m²
Depth	0.5 – 1.6 m
Volume	6000 m³
Specific pond area	40 m²/ha
Max. inflow rate	1100 l/s
Catchment area: Total	4.75 km² (475 ha)
Catchment area: Impervious surfaces - Commercial and industrial areas - Residential areas - Highway	1.57 km² (157 ha; 33% of total catchment area) Approx. 30% (0.47 km²) Approx. 70 % (1.10 km²) Annual daily traffic of 40 000 vehicles

The specific area of 40 m²/ha presents a small value with regard to the optimum value of 250 m²/ha. Therefore, an upstream overflow was constructed which discharges water directly to the river Stora Ån when the inflow exceeds 700 l/s. About 20% of the annual stormwater is spilled due to the overflow and therefore not treated before reaching the receiving water (Pettersson, 1999).

The highway presents one of the most significant sources of contamination (Pettersson, 1999). The catchment area drains into an overflow chamber that discharges via a steel pipe (DN 1000) into the pond. At the inlet, the steel pipe is submerged. The outlet overflow is designed as an 8 m broad concrete crest and effluent water discharges into the river Stora Ån. At the inlet, where the water depth is approximately 1.5 m, the pond bottom is constructed with a concrete slab to facilitate removal of accumulated sediments using a wheel-mounted loader. In the middle section, the bottom consists of gravel and water depth is approximately 0.5 m. At the outlet, the water depth is approximately 1.6 m and the bottom material is clay (Pettersson, 1999).
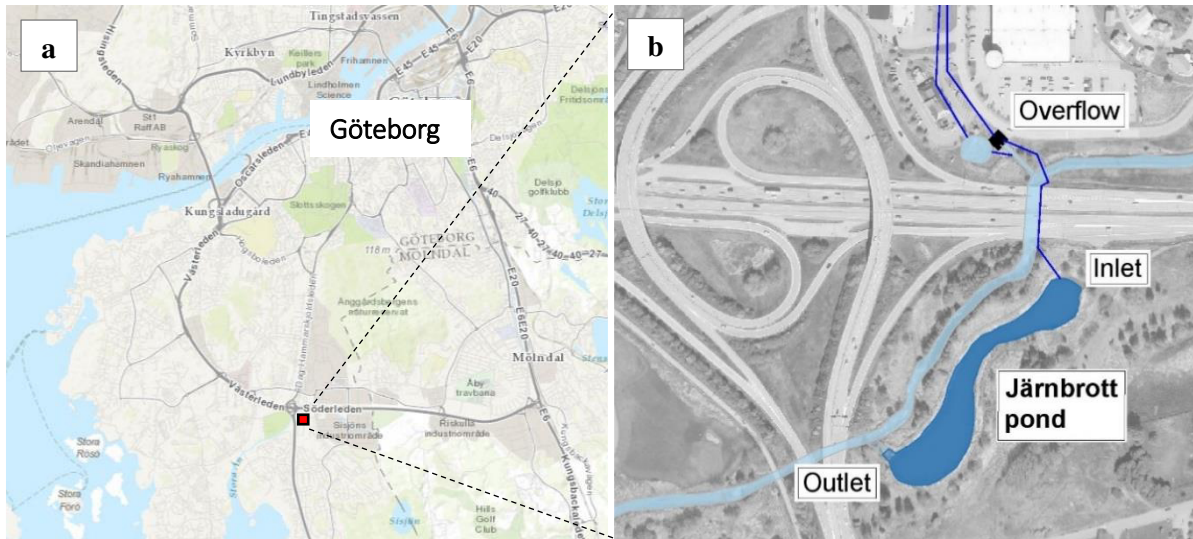
Figure 12. (a) Location of the study area in Göteborg; (b) Map of the pond, the receiving water Stora Ån, the upstream overflow and the connecting pipes.

3.2 Sampling and on-site measurement set-up
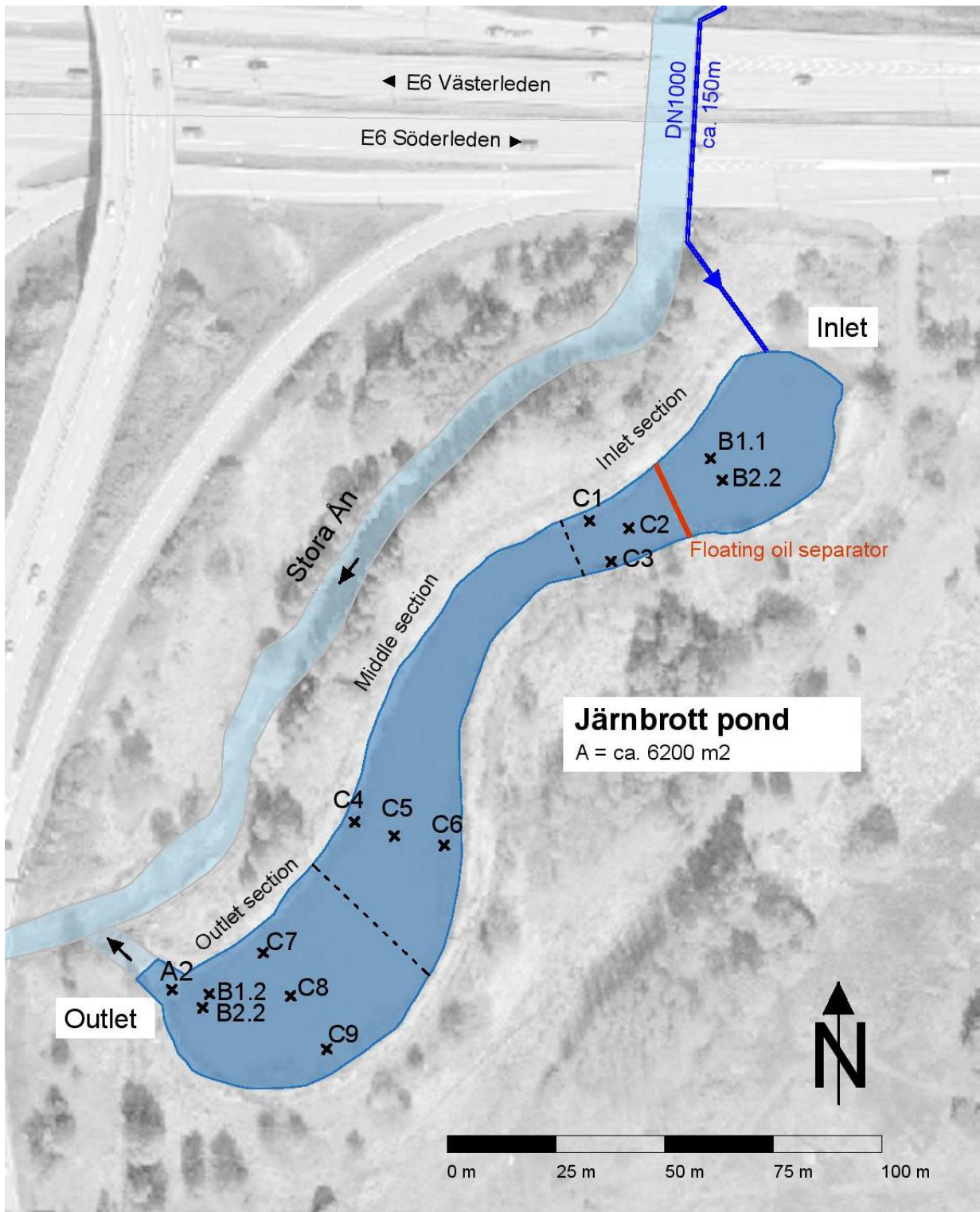
Figure 13. *Positions of automatic, passive and sediment samplers, where A2 is the automatic sampler at the outlet (A1 is not shown since it is located further upstream the inlet pipe); B1.1 & B1.2 are the SorbiCell passive samplers; B2.1 & B2.2 are the SPMD passive samplers; and C1-C9 are the sediment samplers.*

3.2.1 Automatic sampling
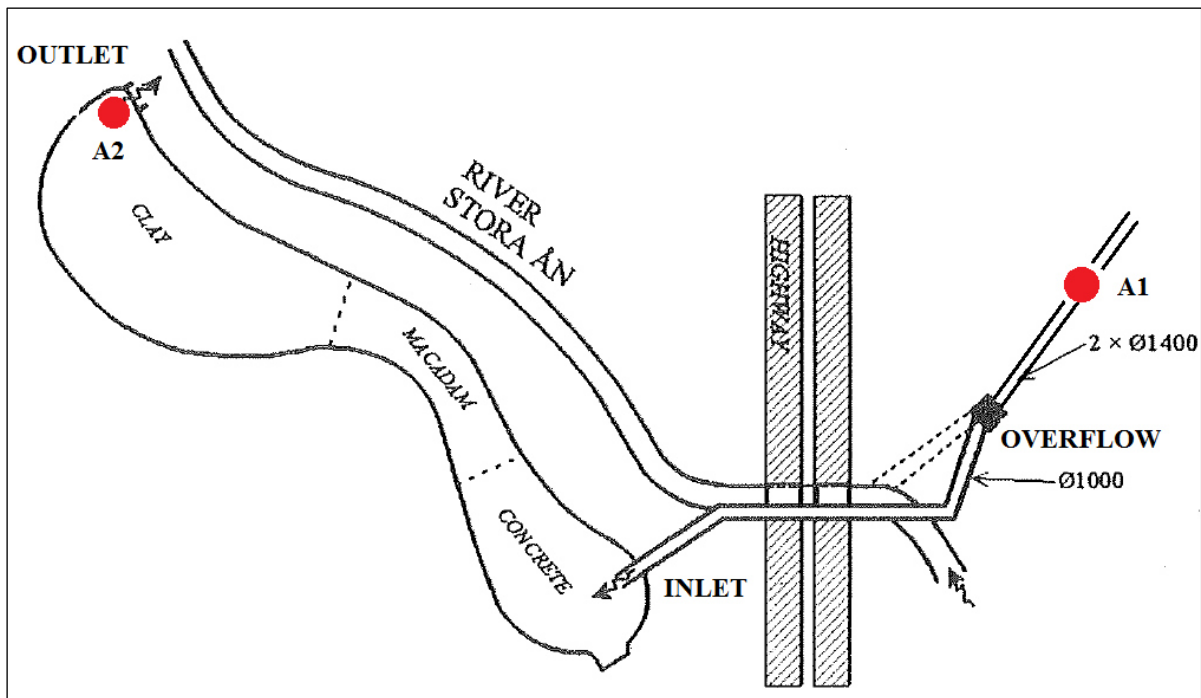
Figure 14. *Positions of automatic samplers, where A1 is the inlet sampler and A2 is the outlet sampler adapted from Pettersson (1999).*

Portable automatic samplers (Table 4) were used to collect "total samples" including the truly dissolved, colloid- and particle bound phase at the inlet and the outlet of the pond (Figure 13 and Figure 14). The automatic samplers used in this study can be connected to a series of modules for flow and parameter measurements and programmed to collect time- and volume-proportional samples.

To collect influent samples, the auto sampler was mounted into a manhole of the sewer which drains into the overflow and subsequently into the pond. The sampling point is located about 200 m upstream the overflow point. At this point, the sewer diameter is 1400 mm and the manhole is 2-3 m deep. A polypropylene strainer was used to avoid leaves and gross matter to enter the suction line, which may cause clogging. The strainer was placed about 10 cm below dry weather flow, at the sewer junction where high turbulences should provide a thorough mixing of the sampled water. A Teflon-coated hose was used as a suction line to prevent partitioning of PAHs to the plastic material. However, the pump tubing was silicone. The suction line was about 9.0 m long with a suction head of 3-4 m. In the pipe, a flow meter was used to measure the flow (Table 4). The probe is working on the principle of the Doppler effect; the module compares the frequency of a sound wave at the sending transducer and at the receiving transducer. The Doppler effects states that the degree of change of the sound wave frequency is proportional to the average flow velocity of the water (Teledyne Isco, 2013).

At the outflow weir, the sampler was positioned beside the outlet at the bank (Figure 15). The plastic strainer was placed at about 1 m upstream the top of the concrete weir and at level of dry weather. It was connected to the sampler via a 5.3 m long Teflon-coated suction line with a suction head of about 0.5 m; the pump tubing was used in silicone. To achieve the outlet flow, a pressure probe was used to measure the water level in the pond (Table 4), this was done in a well that is connected to the pond through a pipe. The probe measures the difference between the hydrostatic pressure and the inner pressure, which is referenced to the atmosphere (Teledyne Isco, 2013b). Consequently, the water level was measured and converted through a level-to-flow-rate formula. This relationship between water level in the pond [m] and flow rate [l/s] was determined in a previous study performed by Pettersson (1999).

At both the inlet and outlet, a maximum of 30 sub-samples were pooled to one composite volume-weighted sample in a 9.4 l glass bottle. Due to the low temperatures during fall/winter, cold storage of the samples until the collection was always ensured. Therefore, modifications through microbial activity during storage can be precluded. The stormwater volume passed between two sub-samples differed between inlet and outlet, in order to take the upstream overflow into account and therefore cover larger storm events to the same extend. The samplers were programmed to check flow conditions every minute and store data every 5 minutes by data loggers. All field data from the samplers and flow meters were downloaded after each storm event using a laptop computer with the software *Flowlink* installed.

Table 4. Specifications of the automatic sampling set-up.

	Inlet	**Outlet**
Sampler type	Teledyne Isco 6712 portable sampler	Teledyne Isco 6700 portable sampler
Duration of deployment	2017/10/11 – 2018/01/17 (both samplers)	
Flow measurement	Flow meter (Teledyne Isco 750 - Area Velocity Module)	Pressure probe (Teledyne Isco 720 – Submerged Probe Module)
Sampling condition	Water level > 0.200 m (equals to flow rate > 120 l/s)	Flow rate > 120 l/s
Stormwater volume passed between sub-samples	800 m³	600 m³
Number of samples and sample volume	Max. 30 sub-samples with 300 ml each (both samplers)	

Figure 15. Outlet automatic sampler with suction line and strainer (Björklund, 2017).

3.2.2 Passive sampling

Passive sampling was performed using two different passive sampling devices at both the inlet and outlet:

-   *Exposmeters Lipophilic for Water* (EWL) – hereafter referred to as "SPMDs" – applying the SPMD technology were used to obtain time-proportional information about the truly dissolved phase of PAHs.
-   SorbiCell samplers collected PAHs time-proportionally in the truly dissolved phase and attached to colloids and particles smaller than 60-100 µm.

Semi-permeable membrane device sampling

The SPMDs performed sampling of lipophilic compounds with log K_{OW} between 3.0 and 6.0 and included Performance Reference Compounds (PRCs) to estimate the in-situ sampling rate of the analytes. Before the field deployment, the sealed metal cans, in which the SPMDs were delivered, were stored at less than -15°C. The membranes of the SPMDs were installed on so-called "spiders" which were submerged into the pond protected by stainless steel deployment devices ("cages") (Figure 16).

The samplers were mounted to buoys 0.5 m below the water table (Table 5) and fixed to anchor weights on the bottom of the pond. At the inlet, the EWL (B1.1 in Figure 13) was located about 20 m downstream the pond inlet; the SPMD sampler at the outlet (B1.2 in Figure 13) was positioned about 10 m upstream the outlet weir. Berqvist & Zaliauskiene (2007) recommend a deployment duration of 21 days for monitoring PAHs. In this case study, the samplers were deployed for 21 and 17 days at sampling period 1 and sampling period 2, respectively. After the SPMDs were retrieved, the membranes were cleaned with pond water and then dried with clean tissue paper. Further, the extent of biofouling was estimated.

Figure 16. (a) SPMD membrane mounted on spider before deployment; (b) SPMD sampler with buoy; (c) Open protection cage after deployment; (d) Protection cage after deployment (Björklund, 2017).

In order to prevent accumulation of compounds from the atmosphere, the membranes were placed in the metal cans during transportation and storage. In addition to the deployed SPMDs, one field-control membrane was used to account for possible contamination from the air and the handling of the samplers during transport, deployment and retrieval. The field-control membrane was kept open while the normal SPMDs were deployed and retrieved. After both sampling periods, the samplers were covered strongly by biofilm, which was not considered as an influencing factor.

SorbiCell sampling

SorbiCell samplers of the type "VOC, 101" were used, where "VOC" specifies the target compounds, for example volatile organic compounds (VOCs), PAHs and pesticides; and "101" presents the lowest of three hydraulic resistance classes that is used for short measuring periods or shallow measuring depth. For installation, the SorbiCell cartridges were fitted in the polyethylene collection flasks WW-50 which are used for sampling in ponds with depths between 0.5 – 10 m. When using the WW-50, the water flow through the cartridge is induced by hydrostatic pressure. The flasks were attached to anchor weights and buoys (Figure 17).

At the inlet (B2.1 in Figure 13), the collection flask was attached to a buoy and anchor at 0.5 m below water level (the minimum recommended water depth is 0.5 m). The same set-up was used at the outlet (B2.2 in Figure 13), at about 10 m upstream the outlet weir. After each of the two sampling periods (Table 5), the sampling devices were retrieved from the pond and the SorbiCell cartridges were detached from the collection flasks. The collection flasks were emptied, and the field volume was measured in order to determine the water volume that passed through the sampler (to achieve volume-proportional sampling). For the second sampling period, new air vents were used. During transportation and shipping, the SorbiCell cartridges were resealed with the protection caps at both ends and detained in the transportation tube.
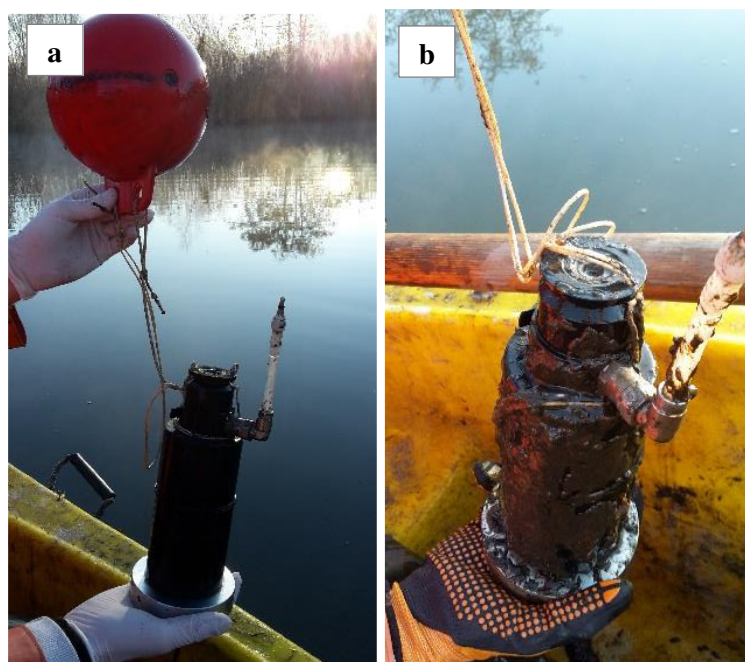
Figure 17. (a) SorbiCell sampler with buoy; (b) SorbiCell sampler after deployment (Björklund, 2017).

	SPMD samplers (inlet + outlet)	SorbiCell samplers (inlet + outlet)
Sampler type	Exposmeters Lipophilic for Water	SorbiCell VOC 101
Sampling period 1	21 days (2017/11/06 – 2017/11/27)	21 days (2017/10/31 – 2017/11/20)
Sampling period 2	17 days (2017/11/27 – 2017/12/14)	24 days (2017/11/20 – 2017/12/14)
Installation level	0.5 m below water level (SPMD and SorbiCell, inlet and outlet)	
Water level at point of installation (dry weather)	Inlet: 1.20 m Outlet: 1.20 m	
Relative water depth	Inlet: 0.4 Outlet: 0.4	
Sampled fractions	Truly dissolved	Truly dissolved + colloids (<60-100 µm)
Sampling method	Time-proportional	Time-proportional

3.2.3   Sediment sampling

To investigate the quantity of settling particles in the pond, three sediment traps were installed at the inlet, middle and outlet section of the pond, respectively. To keep the trap design as simple as possible, a trap design similar as presented in a study by Persson (2010) was applied. A metal jar (diameter 23 cm, height 8 cm) was thereby fixed to a metal pole (Figure 18) which was hit into the bottom of the pond for about 20-40 cm, holding the metal jar about 10 cm above the sediment surface. To prevent sediment from resuspending into traps during deployments, a boat was used for installation.

Since the concrete slab at the inlet section inhibited a penetration of the pole it was necessary to move the location of the three sediment traps representing the inlet section (C1, C2, C3 in Figure 13) towards the middle section. In this area, the pond bottom consists of gravel (as described in chapter 3.1) and clay below and appeared to have only little sediment accumulated on top (Table 6). The low sedimentation rate in this section can be explained by the pond shape: since this area presents the narrowest part of the pond the water velocity is expected to be relatively high, which counteracts an effective settling of particles. The water depth at this point is about 0.5 m (during dry weather flow conditions). Downstream the narrowest pond section, the sediment traps representing the middle section (C4, C5, C6 in Figure 13) of the pond were mounted. At the outlet section where the last three sediment samplers (C7, C8, C9 in Figure 13) were installed.

When retrieving the sediment traps, the water contained in the traps was carefully poured out, avoiding a significant loss of particles. Generally, a very high content of biofilm of the accumulated material was observed (inlet > middle > outlet). In each trap, the height of the accumulated sediment (including a certain water content) was measured. For each section, one representative sample was made by mixing the content of the three traps. The composite samples of each section were filled into glass jars. After about one hour of settling, the separated water was removed, and the jars were refilled with sediment.

Figure 18. (a) Sediment trap after deployment; (b) Sediment trap with accumulated sediment (Björklund, 2017).

Table 6. Specifications of the installation locations of the sediment traps.

Parameter	Inlet section	Middle section	Outlet section
Sampling period	23 days (2017/11/13 – 2017/12/06)		
Water depth (dry weather)	55-75 cm	65-118 cm	110-115 cm
Sediment depth of pond bottom	10-16 cm	60-85 cm	15-35 cm
Bottom material	gravel	clay	clay

3.2.4 Manual grab sampling and on-site measurements

Starting from November 6 until December 14, manual grab samples were collected at the inlet and outlet of the pond regularly (approximately two times a week; eleven measurements in total). Additionally, on-site measurements (temperature, DO and pH) were performed using the instrument *HANNA Multiparameter HI9829*.

3.3 Analysis and data treatment

3.3.1 Water samples

Observed flow data was downloaded from the inlet and outlet samplers using a laptop with the software Flowlink installed. Precipitation data was obtained by SMHI - station Askim D (SMHI, 2018).

The chemical analyses of PAHs in the water samples (collected by automatic sampling) were performed by certified laboratories. The results included the total concentrations of each compound and sum of LMW, MMW, HMW and carcinogenic PAHs, respectively. For events 5 – 7, more detailed partitioning studies were performed where the PAHs present in each fraction (dissolved, colloid-bound and particle-bound) were investigated. The experimental procedure to determine the partitioning of PAHs is described in Kalmykova et al. (2013). In short, the total water samples are analysed for PAHs, in parallel to filtered samples (representing the truly dissolved and colloidal phase) and samples passed through a

C18 SPE disk (representing the colloidal phase). The PAHs are concentrated using liquid-liquid extraction and analysed with GC-MS.

The content of suspended solids (TSS and VSS) were determined according to Swedish Standard Methods. Further, water samples were analyzed in the laboratory for the following parameters (used instruments in brackets):

- Turbidity (*HACH DR/890 Colorimeter*)
- Conductivity (*VWR MU 6100 L*)
- TOC and DOC (*SHIMADZU - TOC-V CPH Total organic analyzer*; based on the subtraction of the inorganic carbon (IC) of the total carbon (TC): TOC = TC – IC.

3.3.2 Passive samplers

The SorbiCell samples were analyzed by a certified laboratory (Eurofins Miljo A/S in Vejen, Denmark). The extraction method M 0345 GC-MS with a detection limit of 0.005 µg/sample, respectively was used, for which an uncertainty of 30% is stated.

The SPMD sample analyses were performed by Eurofins Environmental Sweden AB in Lidköping, Sweden. The method SOP 6.00 with a reported uncertainty of 30% was used.

3.3.3 Sediment samples

For each pond section, the triplicate samples were pooled in one jar where the depth of the accumulated sediment within the deployment of 23 days was measured. The measured depth was then converted into an accumulation rate representing the accumulation [cm] in one jar within one month. This value was used to estimate the accumulated mass per section [kg/week] by using the following equation (13):

$$m_{Sediment} = R * A_{Section} * \frac{TS}{100} * \rho \qquad (13)$$

where:
R is the measured sediment accumulation rate [cm/deployment time].
$A_{Section}$ is the area of the specific pond section [m²].
TS is the content of total solids [%].
ρ is the density of the accumulated sediment [kg m⁻³].

To analyze the water content of the sediment, the composite samples of each section were dried at 105° C using triplicates. The weight of the empty ceramic jar, and the jar including sediment before and after drying was measured (14).

$$W = \frac{m_{Sed1} - m_{Sed2}}{m_{Sed1} - m_1} * 100\% \qquad (14)$$

where:
m_1 is the mass of the empty ceramic jar [mg].
m_{Sed1} is the mass of the jar including the sediment before drying at 105° C [mg].
m_{Sed2} is the mass of the jar including the sediment after drying at 105° C [mg].

In order to analyze their loss of ignition (organic content), the samples were incinerated at 550° C, weighted again.

4 Results and discussion

4.1 Observed storm events

Between 2017/10/11 and 2018/01/17 seven storm events were monitored at the outlet whereas three events were monitored at the inlet of the Järnbrott pond using automatic samplers. Practical issues with the automatic sampling equipment at the inlet, which are further explained in Chapter 4.3.1, were the reason for collecting fewer inlet samples. In Table 7, some characteristics of the observed storm events are presented.

Table 7. Characteristics of the seven observed storm events. Hydrological data obtained by SMHI (2018), where the observation station "Askim D" was used. The dates represent the last day of sampling collection.

Parameter	Event 1 2017-11-19	Event 2 2017-11-23	Event 3 2017-11-27	Event 4 + Event 5 2017-12-9	Event 6 2017-12-13	Event 7 2018-01-11
Antecedent dry period [d]	1	-	2	2	3	6
Rain depth [mm]	7.0	25.8	30.4	18.9	21.0	8.9
Duration [d]	3	-	3.5	2	-	1
Collected samples	$Outlet_{Event.1}$	$Outlet_{Event.2}$	$Outlet_{Event.3}$	$Inlet_{Event.4}$ $Outlet_{Event.4}$ $Inlet_{Event.5}$ $Outlet_{Event.5}$	$Inlet_{Event.6}$ $Outlet_{Event.6}$	$Inlet_{Event.7}$ $Outlet_{Event.7}$

The sample $Outlet_{Event.1}$ represents three smaller storm events distributed over three days (4.3, 0.3 and 2.4 mm/d, respectively) and approximately one day with low flow conditions in between (Figure 19 b). For $Outlet_{Event.2}$, sampling started during high flow, not including the first flush and the peak discharge of the storm event (Figure 19 b). It represents an event with a rain depth of 3.3 mm/d, whereas the flow was still influenced by a large rain event (22.5 mm/d) which occurred on the day before. It should be considered that pollutant concentrations may be higher if the first flush and the peak discharge are included in the sample, but this sample is still included in the calculations. As shown in Table 7, it was not possible to determine the antecedent dry period and duration of the storm event since it was only monitored partly.

$Outlet_{Event.4}$ represents the first two of four peaks of a larger rain event (9.4 mm/d) (Figure 19 b). The first inlet sample, $Inlet_{Event.5}$, and $Outlet_{Event.5}$ cover the third and fourth peak of the same storm event (Figure 19 a and b). When calculating the PAH removal efficiency for event 5 it must be considered that the sampling program of $Inlet_{Event.5}$ lasted for about 1.5 days including 25 sub-samples, whereas $Outlet_{Event.5}$ only collected eight sub-samples during about 15 hours. Both samplers collected their first sub-sample at approximately the same time. Therefore, $Inlet_{Event.5}$ represents an extended part of the rain event.

Event 6 samples were collected during the beginning of large storm event including the peak discharge, therefore covering the largest storm event sampled in this study (Figure 19 a and b). Both the inlet and

outlet sample collected the maximum number of 30 sub-samples. The inlet sampler collected its first and last sub-samples shortly before the outlet sampler.

Event 7 presented only a smaller storm event of 8.9 mm/d (Figure 19 c and d) while the longest antecedent dry period of all studied storm events was registered.
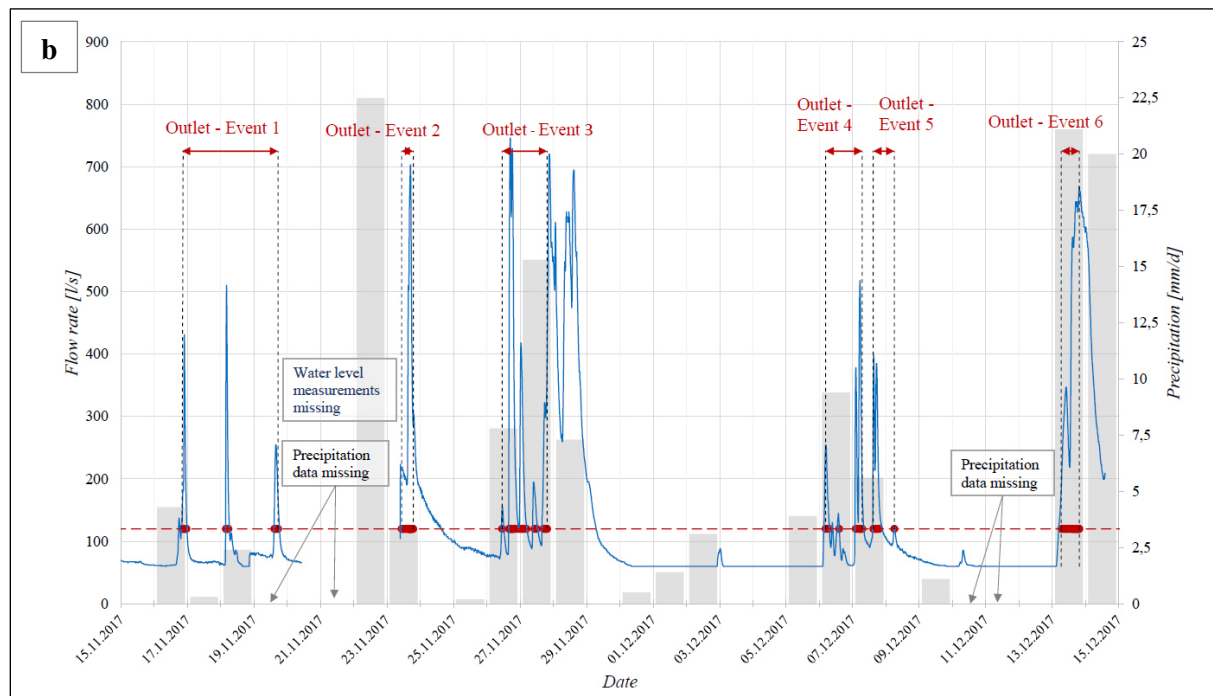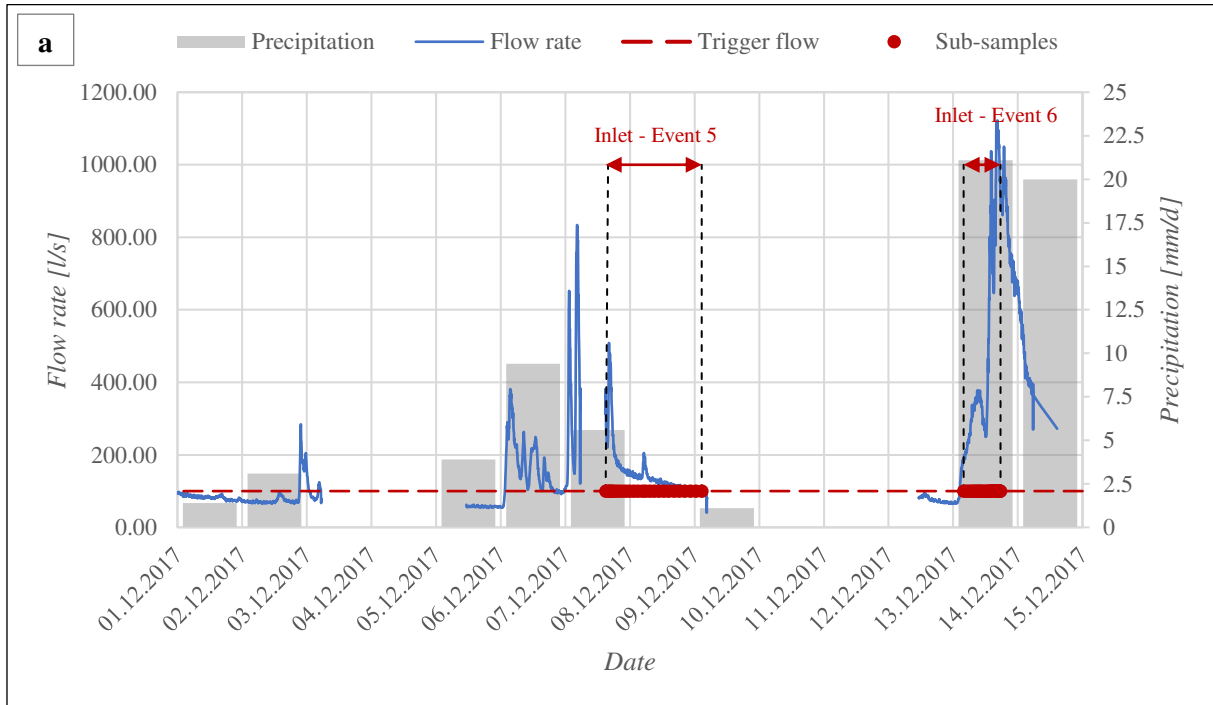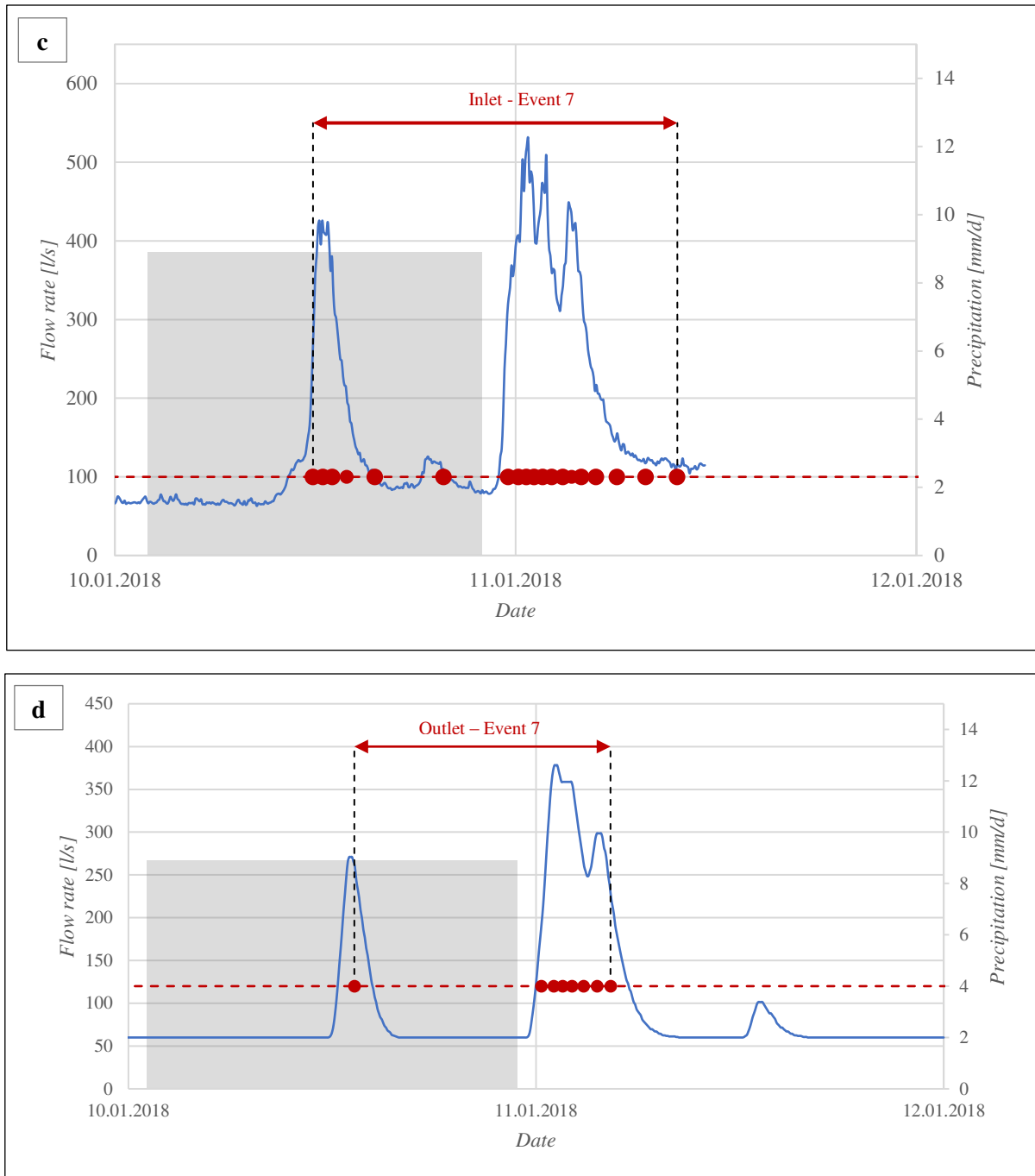
Figure 19. *Distribution of the individual sub-samples, corresponding flow rate and daily rain depths; **(a)** Inlet samples of events 5 and 6; **(b)** Outlet samples of events 1-6; **(c)** Inlet sample of event 7; **(d)** Outlet sample of event 7.*

4.2 Removal efficiency

4.2.1 Manual grab sampling and on-site measurements

The analysis of eleven grab samples and on-site measurements at the inlet and outlet showed great variations for most parameters (Table 8). Especially the turbidity and conductivity varied considerably; in several cases higher values were observed at the outlet than at the inlet for those parameters. Also, the dissolved oxygen (DO) tended to increase in the pond, while the water temperature decreased in the pond.

Table 8. Results from grab samples and on-site measurements (n=11).

Parameter		Inlet		Outlet	
		Mean	Std. deviation	Mean	Std. deviation
Temperature	[°C]	7.63	1.60	7.13	1.72
Turbidity	[FAU]	25	10	25	10
DO	[%]	72.6	15.4	79.2	16.8
Conductivity	[mS/cm]	585	447	541	270
pH	-	7.40	0.12	7.36	0.10
TOC	[mg/l]	8.83	0.83	7.45	1.61

4.2.2 Total concentrations of polycyclic aromatic hydrocarbons

Table 9 presents the calculated removal efficiencies based on EMCs for events 5-7, and the SMCs at the outlet. The observed values are compared to a previous study performed at the Järnbrott pond (Lavieille, 2005). For the same events, Figure 20 shows the observed inlet and outlet concentrations for four sum parameters.

For event 5, a $\sum$ 16 PAHs concentration of 0.28 µg/l was observed at the inlet; at the outlet 0.49 µg/l were observed (Figure 20 a). Ten of 16 PAHs showed negative removal rates ranging from -21% to -157% (Table 9). Only for one compound, naphthalene, a decrease in concentration from the inlet to the outlet was observed. Since the concentrations of the remaining five individual PAHs were below LOD at the inlet and outlet, the removal rates for these compounds were not calculated. The LMW PAHs were removed by > 25% where naphthalene was the only LMW compound detected above LOD at the inlet and outlet (values below LOD were counted as 0). Both the MMW and HMW PAHs showed a substantial increase in concentration of 69% and 170%, respectively (Table 9). The negative removal rates are explained by the very short residence time: Between event 4 and 5, a low-flow period (still above base flow) of less than 10 hours was registered. Thus, during event 5, the "untreated" water volume of event 4 was probably washed out of the pond. Since $Outlet_{Event.4}$ showed higher pollutant concentrations than $Inlet_{Event.5}$, a re-contamination of the water volume of event 5 was possible which might lead to the negative removal rate.

Event 6 revealed concentrations in the same range as observed at event 5 (Figure 20 b). However, positive removal rates for individual PAH compounds ranging from 17 – 70% were monitored. The HMW and MMW PAHs were removed to 55% and 36%, respectively (Table 9). The highest concentrations of single compounds were found for the MMW PAHs, for which also the highest removal rates were observed. The inlet and outlet concentrations of the LMW PAHs were below LOD.

For event 7, substantially higher PAH concentrations were detected: both inlet concentrations of the HMW and MMW PAHs were 0.5 µg/l, while the LMW PAHs were below detection limit (Figure 20c). Positive removal rates of 34% and 32% for the HMW and MMW PAHs, respectively, were noted (Table 9). In view of the considerably higher concentrations in $Inlet_{Event.7}$ and $Outlet_{Event.7}$, the relevance of the antecedent dry period and the rain intensity is clearly pointed out. Before event 7 (8.9 mm/d), pollutants may have accumulated during six days without precipitation (Table 7). That lead to an outlet concentration of 0.67 µg/l ($\sum$ 16 PAHs) which was the highest concentration observed at the outlet during the whole study. In contrast, $Outlet_{Event.1}$, representing a small event (4.3 mm/d) and only one antecedent dry day to allow for accumulation of pollutants, only pyrene was detected (0.02 µg/l) above LOD. This illustrates the high variability of PAH occurrence in stormwater runoff, depending on different rain characteristics such as rain intensity, rain duration and antecedent dry periods.
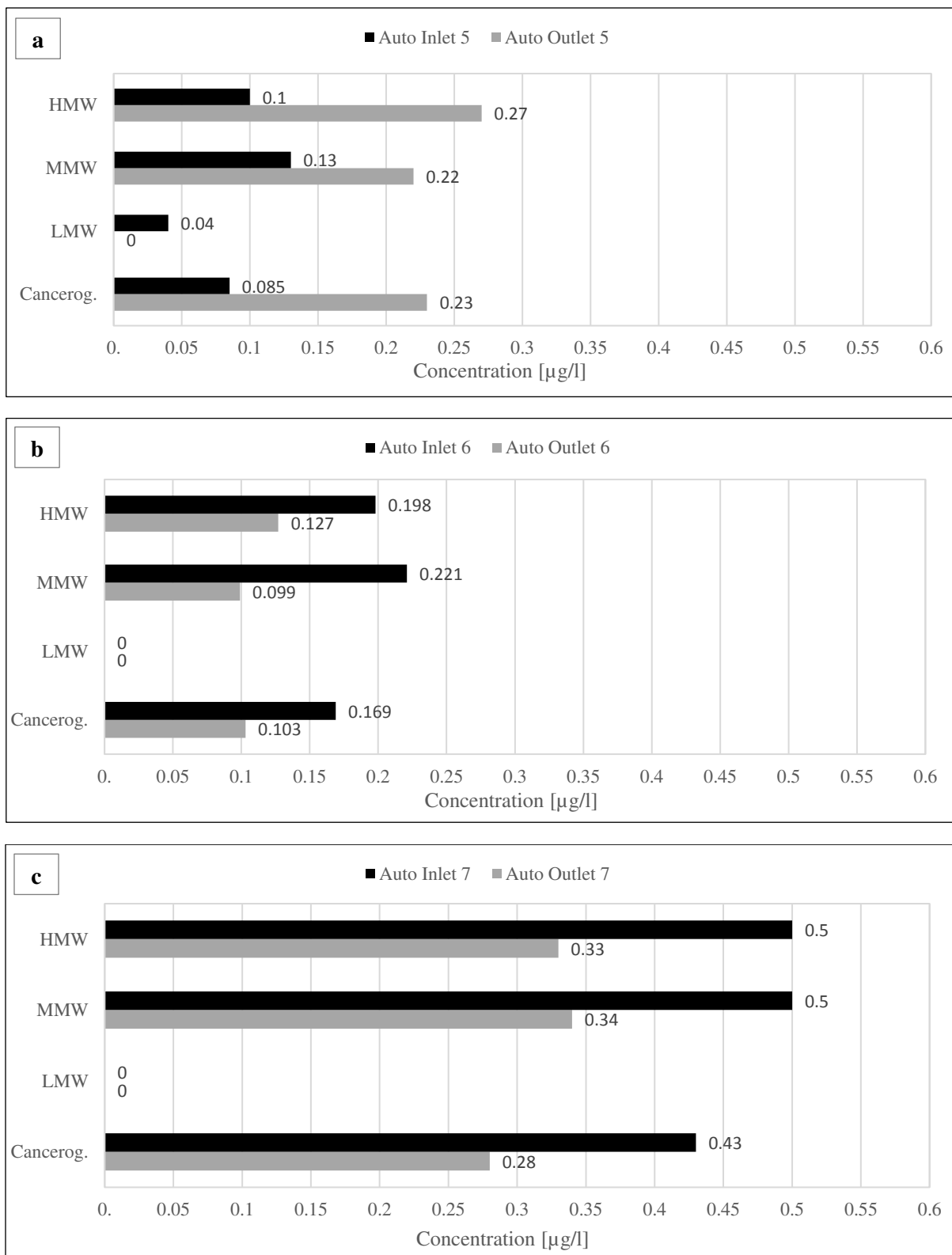
Figure 20. *Total concentrations monitored with automatic sampling at inlet and outlet.* ***(a)*** *Event 5;* ***(b)*** *Event 6;* ***(c)*** *Event 7.*

Table 9 shows the calculated site mean concentrations (SMCs) for the seven monitored outlet events. The SMCs for the individual PAHs range from < LOD (which mainly applies to two- and three-ring PAHs) to 0.082 µg/l (pyrene). The SMC_{OUT} for $\sum$ 16 PAH amounts to 0.35 µg/l while the $\sum$ 16 PAHs concentrations of the individual outlet events vary between 0.02–0.67 µg/l. In comparison, Lavieille (2005) found lower mean outlet concentrations than observed in this study. For example, the $\sum$ 16 PAH concentration calculated in this study is 70% higher than found by Lavieille; the $\sum$ cancerogenic PAH

concentration is > 100% greater. For the SMC at the inlet, Lavieille stated a ∑ 16 PAHs concentration of 0.73 µg/l (with EMCs between 0.24-1.20 µg/l), whereas in this study EMCs between 0.28-1.00 µg/l were observed. Therefore, the observed inlet concentrations in this study are in the same range as Lavieille's study which was also performed during fall, hence may represent comparable environmental conditions to the current study.

Table 9. SMCs of the outlet and removal efficiencies calculated in this study compared to values observed by Lavieille (2004). Removal efficiency reported by Lavieille was calculated with SMCs. Empty cells stand for compounds which were below LOD at the inlet and outlet. For compounds, which were below LOD either at the inlet or outlet, the removal efficiency was calculated conservatively using the LOD (result as "< / > removal efficiency [%]"). Yellow marked cells represent values below LOD.

Compound	SMC_OUTLET [µg/l]		Removal efficiency [%]			
	This study	Lavieille (2004)	Event 5	Event 6	Event 7	Lavieille (2004)
Naphthalene	0.02	< 0.02	> 25			
Acenaphthylene	< 0.01	< 0.01				
Acenaphthene	< 0.01	< 0.01				
Fluorene	0.01	< 0.01			0	
Phenanthrene	0.02	< 0.05	-21	70	28	> 30
Anthracene	< 0.01	< 0.01		> 11		
Fluoranthene	0.05	0.05	-67	54	33	60
Pyrene	0.08	0.06	-93	41	34	60
Benz(a)anthracene	0.03	< 0.02	-121	48	34	> 55
Chrysene	0.03	< 0.02	-81		28	> 65
Benzo(b)fluoranthene	0.05	< 0.03	-157	41	35	> 55
Benzo(k)fluoranthene	0.01	< 0.01		41	33	> 55
Benzo(a)pyrene	0.03	< 0.02	-142	32	35	> 65
Dibenz(ah)anthracene	< 0.01	< 0.01				
Benzo(ghi)perylene	0.03	< 0.01	-126	17	34	
Indeno(1,2,3-cd)pyrene	0.02	< 0.01		30	31	
PAH, ∑ 16	0.35	0.20	-75	46	33	70
∑ cancerogenic	0.17	< 0.08	-171	39	35	> 70
∑ non-cancerogenic	0.19	0.15	-37	51	32	65
∑ LMW	0.02	< 0.04	> 25			
∑ MMW	0.15	0.14	-69	55	32	
∑ HMW	0.20	0.05	-170	36	34	

In addition, the Lavieille study revealed higher removal rates compared to the removal rates for events 5 and 6. In Lavieille's study, seven events were used to calculate inlet and outlet SMCs, used for determining the average removal efficiency of the stormwater pond. In contrast, calculation of an average removal rate was not possible in this study due to lack of water quality data for the pond inlet. When comparing the results between the two studies, the widely differing characteristics of the observed storm events must be considered: Lavieille studied seven storm events with a rain depth between 4–20 mm and antecedent dry periods of 1–7.5 days. Compared to this study (Table 8), storm events tended to

be smaller and with longer dry periods, which is expected to have a positive effect on the pond's removal efficiency due to longer water residence time.

The short residence time experienced in this study, may be the main reason for the observed low pollutant removal rates. Previous studies found that, in stormwater ponds, 90% of the pollutant removal takes place during dry weather periods between storm events (Pettersson, 1999). Hence, mass balance calculations based on a series of events, such as the SMC approach, are required to investigate the long-term removal efficiency of stormwater ponds (Persson & Pettersson, 2009). These results highlight the high variability of the system and the issues with determining removal rates for single events.

4.2.3 Truly dissolved and colloid-bound fraction of polycyclic aromatic hydrocarbons

SorbiCell sampling

The testing of the SorbiCells resulted in low sample volumes (or "field volumes") and all studied PAHs were below the detection limit in all samples.

Between the two sampling occasions, the samplers showed great variations in field volumes; 125 and 225 ml at the inlet and outlet, respectively, during the first sampling period, whereas only 85 and 75 ml were measured for the second sampling period (Appendix A). A volume between 300–500 ml is recommended by the manufacturer and 50 ml is stated as the minimal volume necessary to perform analysis. When retrieving the SorbiCells after the first sampling period, the samplers (including the inlet of the cartridges) were covered by biofilm and probably fine sediments. The possible reasons for the high number of non-detected compounds is further discussed in Chapter 4.3.2.

SPMD sampling

During sampling period 1, the SPMD showed PAH concentrations of the truly dissolved phase ranging from < LOD to 3.90 ng/l (Table 10). For all detected compounds, a decrease in concentration from the inlet to the outlet was registered. However, for eight of the 16 compounds (two LMW and six HMW PAHs) it was not possible to calculate the removal rate since both the inlet and outlet concentrations were below LOD. This result is not surprising since HMW PAHs are known to be present predominantly associated to particles (Gustavson & Harkin, 2000).

Removal rates increased with the compounds' hydrophobicity: for acenaphtene, the only detected LMW PAH, a removal rate of 14% was registered; MMW PAHs were removed to 40% and HMW PAHs were reduced to 52%. Most of the studied carcinogenic compounds are below LOD at the pond inlet and outlet, resulting in ∑ 16 PAHs concentrations at the inlet and outlet of 1.95 and 0.93 ng/l, respectively (compounds with concentrations below LOD were excluded).

The considerable reduction of the truly dissolved PAHs in the pond indicate that there are other removal processes present, besides the settling of particulate pollutants. This may be explained by partitioning of PAHs, during their residence time in the pond, from the dissolved phase to particles. This hypothesis also goes in accordance with the finding of the highest removal rates for HMW PAHs, which show the highest affinity for particulate matter due to their high hydrophobicity. Beside that, degradation of the truly dissolved PAHs through photolysis may be a possible reason for the decreasing reduction of PAH concentration in the pond (Neilson, 1995). The second degradation route of PAHs, namely biological removal, may be excluded since temperatures of the pond water were constantly low (below 10°C).

Sampling period 2 showed a different outcome: outlet concentrations were higher than inlet concentrations for all detected compounds. None of the HMW PAHs was detected, whereas the MMW PAH concentrations at the inlet and at the outlet were almost 70 and 500% higher, respectively, than the

observed concentrations in sampling period 1 (Table 10). This resulted in a 77% increase in MMW PAH concentration from the inlet to the outlet. The LMW PAHs also show an increase close to 200% from the inlet to the outlet, but at lower concentrations compared to the MMW PAHs. The increase of the truly dissolved concentration may be explained by resuspension processes of particles present in the sediment to the water phase. This has also been reported in previous studies, which found rising PAH concentrations in the truly dissolved phase during dry periods (Neary & Boving, 2011). Increasing PAH concentrations during high flow conditions were also observed. This finding is based on resuspension of pollutants depending on shear stresses impacting the sediment while shear stress depends on factors including water density, velocity, bottom morphology and area. LMW PAHs were found to release faster from settled particles than MMW and HMW PAHs which is explained by their higher hydrophobicity (Feng, et al., 2008). However, it should be considered that the study was performed to simulate resuspension processes in rivers, with shear stresses between 0.2 and 0.5 N/m². Shear stresses were not investigated in the pond in the current study.

Generally, to prevent resuspension of PAHs into the aqueous phase regular maintenance is recommended; however, the results of SPMD and SorbiCell sampling in two sampling periods did not allow a clear statement about the removal efficiency of the truly dissolved PAH concentration in the pond. More inlet and outlet data on truly dissolved PAHs is necessary to assess the long-term removal efficiency and to draw conclusions on the relevant processes which are responsible for the observed negative and positive removal rates. For future projects, special attention has to be drawn on quality assessment of the monitoring methods; i.e. sampling is recommended to be performed using duplicates. The application of this method is further discussed in Chapter 4.3.2.

Table 10. Truly dissolved PAH concentrations and removal rates monitored by SPMD samplers. Yellow marked cells represent values below LOD.

Compound	Period 1			Period 2		
	Inlet [ng/l]	Outlet [ng/l]	Removal [%]	Inlet [ng/l]	Outlet [ng/l]	Removal [%]
Naphthalene	< 0.69	< 0.79		0.51	1.90	-273
Acenaphthylene	< 0.15	< 0.15		< 0.23	< 0.26	
Acenaphthene	0.72	0.62	14	1.20	1.40	-17
Fluorene	2.20	1	55	2.80	3.80	-36
Phenanthrene	2.20	1.9	14	5.50	11.00	-100
Anthracene	0.30	0.25	17	0.26	0.66	-154
Fluoranthene	0.98	0.41	58	3.70	4.80	-30
Pyrene	3.90	2.2	44	3.90	8.40	-115
Benzo(a)anthracene	1.70	0.77	55	< 0.080	< 0.27	
Chrysene	0.25	0.16	36	< 0.063	< 0.10	
Benzo(b)fluoranthene	< 0.069	< 0.050		< 0.11	< 0.15	
Benzo(k)fluoranthene	< 0.073	< 0.060		< 0.11	< 0.11	
Benzo(a)pyrene	< 0.083	< 0.053		< 0.13	< 0.18	
Benzo(g,h,i)perylene	< 0.10	< 0.046		< 0.12	< 0.15	
Dibenzo(a,h)anthracene	< 0.10	< 0.069		< 0.095	< 0.13	
Indeno(1,2,3-c,d)pyrene	< 0.097	< 0.061		< 0.098	< 0.12	
PAH, ∑16	12.3	7.31	40	17.9	32.0	-79
PAH, ∑LMW	0.72	0.62	14	1.71	3.30	-93
PAH, ∑MMW	9.58	5.76	40	16.2	28.7	-77
PAH, ∑HMW	1.95	0.93	52	< LOD	< LOD	

Automatic sampling: Partitioning study on polycyclic aromatic hydrocarbons

The partitioning behavior (i.e. concentration of the truly dissolved, colloid-bound and particle-bound fraction) of the analytes in the inlet and outlet water sample collected with automatic sampling during storm events 6 and 7 were studied. In both events, at the inlet and outlet, all 16 PAHs were below LOD in the colloid-bound phase (Appendix A); naphthalene was the only compound detected in the filtered fraction (i.e. <1.6 µm; truly dissolved and colloid-bound fraction), where a slight increase in concentration during event from the inlet (0.024 µg/l) to the outlet (0.028 µg/l) was registered. However, naphthalene was not detected in the total concentration of the same sample which implies an error.

Since the concentrations of the dissolved and colloid-bound phase are mostly below the detection limit, it is concluded that the studied PAHs were present in the particulate-bound fraction predominantly, as it may be expected due to their high hydrophobicity (Zgheib, et al., 2011). In contrast, the detection of several PAHs in the SPMDs is explained by the lower detection limits of the SPMD method compared to automatic sampling: In sampling period 1 (Table 10), the detected compounds showed time-averaged concentrations between 0.16 ng/l (0.00016 µg/l) and 3.90 ng/l (0.0039 µg/l), while the detection limit for automatic sampling is at 0.01 and 0.02 µg/l, respectively. In sampling period 2 (Table 10), the highest concentration was 0.011 µg/l (phenanthrene) which would have been the only measured SPMD concentration detectable by automatic sampling. However, this comparison only illustrates that the time-averaged PAH concentrations are very close or mostly below the detection limit of automatic sampling, while automatic samples were collected during peak discharges where generally higher pollutant concentrations are expected.

4.2.4 Total suspended solids and volatile suspended solids and the correlation to polycyclic aromatic hydrocarbon concentrations

For events 1–4, it was not possible to calculate TSS removal rates since only outlet samples were collected. The TSS outlet concentrations ranged between 15.3–58.0 mg/l, while the VSS were between 9.73–26.2 mg/l for these events (Appendix A).

Removal rates of TSS and VSS were calculated for event 5–7 (Figure 21) where, generally, great variations were observed. During event 5, TSS concentration increased in the pond which resulted in a negative removal rate of -121%, when also the PAH concentration showed an increase of 75% from the inlet to the outlet. The VSS concentration was 12.4 mg/l at the inlet and 18.5 mg/l at the outlet (removal rate of -50%). The reason for the negative removal rates are seen in the short residence time for the water volume of the previous storm event (as explained in chapter 4.2.2). In addition, resuspension processes due to high shear stress may be an explanation for it (Neary & Boving, 2011), although the upstream overflow definitely reduces the shear stress peaks and reduces in further consequence the impact of resuspension. In Outlet$_{Event.6}$ TSS was reduced by 68% compared to Inlet$_{Event.6}$. This finding is in accordance with the registered decrease of 46% in PAH concentration during this event. The VSS concentration was reduced from 70.2 at the inlet to 22.7 mg/l at the outlet (removal rate of 68%) during event 6. Event 7 showed a reduction of TSS from the inlet to the outlet of 40%. VSS were removed to 44%, while the inlet concentration was 33.3 mg/l; the outlet concentration was 18.75 mg/l (Appendix A).

This analysis indicates a correlation between the removal rates of TSS and PAH. The results were expected since PAHs are found to a high degree attached to particles. However, the results did not allow to draw conclusions from the TSS concentration on the PAH concentration; a high TSS concentration does not imply a high PAH concentration. TSS removal rates between -121% and 55% and VSS removal rates between -90% and 67% were observed. Previous studies found average removal rates for TSS between 70% (Pettersson, 1999) and 60% (Lavieille, 2005). VSS was reported to be removed to 60% (Pettersson, 1999) and 50% (Lavieille, 2005). The lower removal rates observed in the current study is

explained, once again, by the short retention time in the pond due to high rain frequency during the observation period (Pettersson, 1999) and resuspension processes (Neary & Boving, 2011).
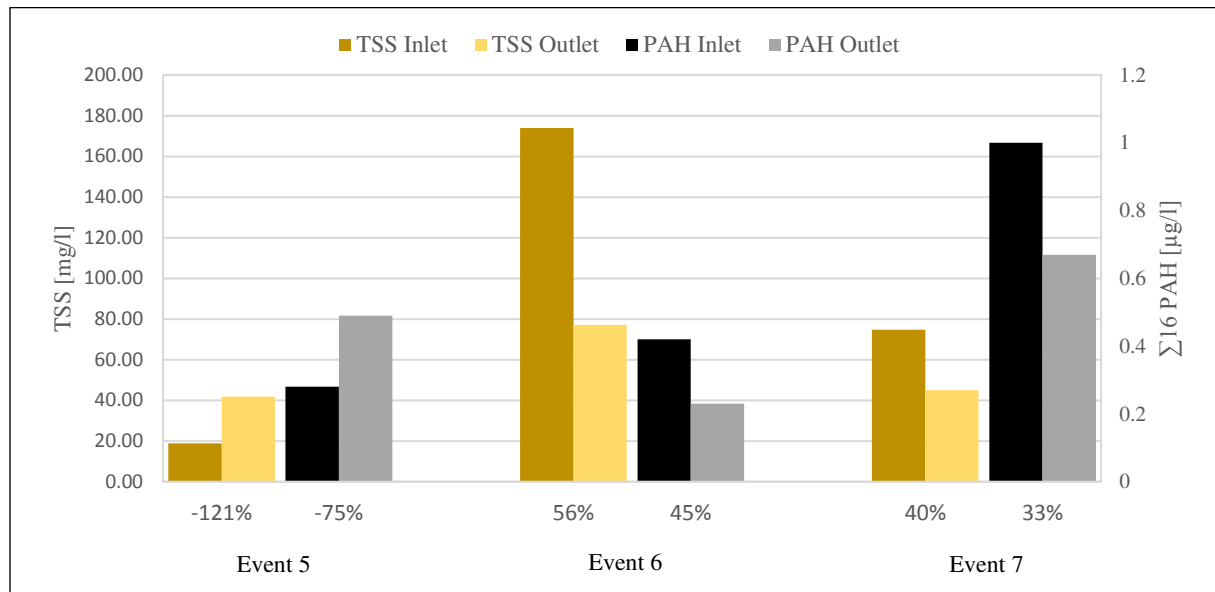
Figure 21. TSS inlet and outlet concentrations for events 5-7 with corresponding ∑ 16 PAH concentrations and removal rates.

4.2.5 Total organic carbon and dissolved organic carbon

The TOC and DOC concentrations of the collected water samples (manual grab sampling and automatic sampling) were measured. TOC concentrations showed a mean value of 8.83 mg/l (Table 8), whereas the DOC measurements did not lead to reliable results: DOC concentrations were higher than TOC concentrations in some cases, which is not possible. This clearly implies an error in the measurements. All TOC and DOC data is presented in Appendix A.

4.2.6 Accumulated sediment mass and accumulated mass of polycyclic aromatic hydrocarbons

As shown in Table 11, the average sediment accumulation rate decreased from the inlet and middle section to the outlet. In the middle section, accumulation was 20% lower than at the inlet, while it was almost 70% lower at the outlet compared to the inlet. The sediment collected at the outlet showed a considerably higher dry content. The organic content was between 26-30%, which appeared to consist of biofilm to a high degree. Generally, biofilm formation in the pond was observed to be very fast. Further, an average density of 704 kg/m³ was calculated for all pond sections. A previous study investigating the sediment of other stormwater ponds in Sweden reported sediment densities between 700–830 kg/m³ and organic contents between 6–16%, with a decrease from the inlet to the outlet (Persson, 2010), which was not observed in the current study. The middle section of the pond obtains very narrow parts, where a reduced flow area results in high flow velocities during a storm event. According to site observations, only very little sediment is accumulated on the top bottom layer. To take this into account, 50% of the middle section was estimated to obtain 0 cm accumulation.

In total, around 2700 kg sediment was accumulated within the deployment time in the entire pond, where a mass of around 70 g PAHs is estimated to be included. In comparison, the Persson study (2010) investigating metallic compounds in stormwater pond sediments, observed higher accumulation rates in different stormwater ponds. At the Steningedalen pond in Märsta in the south-east of Sweden, for example, which exhibits a similar surface area of 6600 m² compared to the Järnbrott pond, accumulation rates between 4.6-12.0 cm during a deployment time of seven weeks were observed with a comparable

sampling method, resulting in a total sediment accumulation of 94128 kg (Persson, 2010). This corresponds to an average accumulation rate of 2.0 kg/(m² x week); at the Järnbrott pond 0.15 kg/(m² x week) sediment were accumulated in average. The reasons for the great difference may be the used method and how the measurements were performed in detail, and factors such as rain characteristics, land use and main pollutant contributors in the catchment, pre-treatment facilities and specific pond area.

HMW and MMW PAHs were detected at similar concentration levels in the sediment; LMW were present only in small concentrations which is explained by lower hydrophobicity. The highest PAH concentrations occurred in the samples of the middle section, followed by the outlet samples; the inlet samples revealed only low PAH concentrations. Persson (2010) found the highest pollutant concentrations at the inlet sections of the studied ponds. One explanation for our finding may be the size of the particles: large particles settle at the inlet section, while smaller particles have lower settling velocities and settle at the middle and outlet section (Pettersson, 1999). Smaller particles generally exhibit a relatively larger surface area per mass than large particles and can therefore bind a larger load of contaminants. In the current study, the samplers for the middle and outlet section were placed quite close together, therefore large differences in PAH concentrations between those samples were not expected.

Due to too short duration of deployment and low accumulation rates, it is important to consider that these calculations can only be used as rough estimations. Further investigations are necessary to investigate other possible factors influencing the pollutant concentrations in the pond sediment. In Chapter 4.3.3, the used method is further discussed.

*Table 11. Results from sediment analysis and sediment mass calculations according to Chapter 3.3. PAH content refers to the sediment's dry weight (dw). * 50% of the middle section was estimated to have 0 cm accumulation. Yellow marked cells represent values below LOD.*

Parameter	Inlet section	Middle section	Middle section*	Outlet section	Total
Accumulation rate [cm/23 d]	0.7	0.5	-	0.2	
Section area [m²]	1750	1100	1100	2200	
TS content [%]	14.2	15.1	-	29,5	
Accumulated sed. mass [kg TS/23 d]	1130	605	-	1000	2735
PAH, $\sum$ LMW [mg/kg dw]	< 0.15	0.87	-	0.5	
PAH, $\sum$ MMW [mg/kg dw]	3,4	28	-	18	
PAH, $\sum$ HMW [mg/kg dw]	3,1	24	-	16	
PAH, $\sum$ 16 [mg/kg dw]	6,4	53	-	35	
Accumulated PAHs per month [g/23 d]	7.2	32.0	-	35.0	74.2

4.2.7 Compliance with environmental guidelines and standards

In Table 12, the total concentrations observed with automatic sampling at the outlet were compared with two guidelines for water quality assessment. These guidelines are:

- the Canadian Environmental Quality Guideline, which defines maximum pollutant concentrations for surface waters (CCME, 2011);
- the EU-WFD (European Commission, 2000), which includes the annual average concentration (AA) and the maximum allowable concentration in inland surface waters (MAC).

In the current study, samples collected by automatic sampling represent peak flows which are expected to include higher pollutant concentrations than the "average flow". Therefore, the EMCs are compared with the MAC values of the WFD-MAC and with the concentration limits by the Canadian quality guideline. The detected PAH concentrations of four compounds (fluoranthene, pyrene, benzo(a)anthracene and Benzo(a)pyrene) exceeded the Canadian guideline at least once during the studied period. The WFD-EQS for the maximum allowable concentrations (MAC) were not exceeded.

Table 12. Comparison of the observed event mean concentrations at the outlet (range and median of seven storm events) and EQS of the Canadian Freshwater Quality Guideline (maximum concentrations for surface freshwater) and WFD (AA: Annual average concentration, MAC: Maximum allowable concentration for inland surface waters). Yellow marked cells represent values below LOD.

Compound [µg/l]	Total conc. Outlet		Canadian Guideline	EU-WFD	
	Range	Median		AA	MAC
Naphthalene	<0.030-0.054	< 0.030	1.1	2.4	1.2
Acenaphthylene	< 0.010	< 0.010			
Acenaphtene	< 0.010	< 0.010	5.8		
Fluorene	<0.010-0.012	< 0.010	3		
Phenantrene	<0.020-0.055	0.025	0.4		
Anthracene	< 0.010	< 0.010	0.012	0.1	0.4
Fluoranthene	<0.010-0.122	0.061	0.04	0.1	1
Pyrene	0.02-0.151	0.086	0.025		
Benzo(a)anthracene	<0.010-0.043	0.019	0.018		
Chrysene	<0.010-0.066	0.038			
Benzo(b)fluoranthene	<0.010-0.074	0.054		∑ = 0.03	
Benzo(k)fluoranthene	<0.010-0.021	0.019			
Benzo(a)pyrene	<0.010-0.046	0.026	0.015	0.05	0.1
Dibenzo(a,h)anthracene	< 0.010	< 0.010			
Benzo(g,h,i)perylene	<0.010-0.046	0.029		∑ = 0.002	
Indeno(1,2,3-c,d)pyrene	<0.010-0.036	0.018			

4.3   Evaluation of sampling strategies: Practical issues and possible uses

4.3.1   Automatic sampling

Automatic, volume-proportional sampling included several practical problems which inhibited the collection of more samples. Six encountered practical issues are described more in detail:

1. Sampler installation: The installation of the samplers and flow-measurement equipment required site-specific expertise. Experience from previously performed studies at this site facilitated the installation and programming of the samplers significantly. Without that knowledge, an extended preparation and try-out phase would have been necessary.
2. Inaccessibility of the inlet sampler: to collect thoroughly mixed samples the inlet sampler was installed in an 2-3 m deep manhole of the inlet pipe. Therefore, the strainer of the sampler and the connected flow measurement probe was not accessible without certain safety equipment.

That resulted in the problem that a covering of the flow probe by a foreign object remained unnoticed for a certain time.

3. Power supply: The lack of constant power supply at the site and the short battery runtime required site visits 2-3 times a week, which resulted in high expenditures in working hours.

4. Distribution of the water samples: The inlet sampler was equipped with a 12-bottle system during October and November. The distribution of the water samples into the sampling bottles turned out to be very sensitive against an inclined position hanging in the manhole. The 1-bottle system appeared to be less prone to failure.

5. Sampler programming: The specification of the trigger flow (start/stop condition for sampling) and pacing (volume passing between two sub-samples) presents a key component for a successful sampling program, which requires site-specific experience and expertise. This issue appeared for example at event 5, where both the inlet and outlet samplers started sampling at the same time; however, the inlet sampler ran the program 1.5 days collecting 25 sub-samples, whereas the outlet sampler performed sampling only for approximately 15 hours collecting eight sub-samples. Thus, the samples are difficult to compare with regard to the removal rate, since the inlet sample represented an extended part of the event 5.

6. Inhomogeneity of the water samples: Flocks which probably include relatively high pollutant concentrations were seen as a possible error source. When they are contained in the water samples with generally low contaminant concentrations they can affect the analytical results disproportionally.

4.3.2 Passive sampling

SPMD sampling

The SPMD method allowed the detection of eight compounds in the truly dissolved phase which were not found in the partitioning study of the event 6. Among them were the two carcinogenic compounds benzo(a)anthracene and chrysene. Additionally, three compounds (acenaphthene, fluorene and anthracene) were present in the dissolved phase, although not detected in the total concentration in most of the automatic samples (acenaphthene: not detected; fluorene: detected during one event; anthracene: detected during one event). However, HMW PAHs were not detected in the SPMDs. This indicates that the SPMD approach, i.e. sampling in a time-integrative manner, presents a useful method in the case of stormwater pond sampling to determine certain compounds present at low concentrations in the truly dissolved fraction.

As previously discussed, the second sampling period showed contradictory results, as concentrations were higher at the outlet than at the inlet, although higher analyte masses (total mass per SPMD membrane) were observed for 50% of the studied compounds at the inlet. In the literature, the analyte accumulation during periods of no flow is identified as a considerable uncertainty of this method; i.e. samples may be more affected by the concentrations present in the stagnant water than by the concentrations occurring during peak discharges (Birch, et al., 2013).

SorbiCell sampling

The SorbiCell approach is based on an advective water flow through the sampler, which counteracts the problem of sampling volume determination. However, the method resulted in low sample volumes, and in combination with low pollutant concentrations, the accumulated analytes were not detectable in the sorbent. Three possible reasons can be identified for the too high hydraulic resistance that lead to low sample volumes: i) water depth; ii) clogging of filter inlet by biofilm; iii) clogging of filter by fine sediment.

The samplers were installed at a constant water depth of 0.5 m – this is stated as the minimal installation depth by the manufacturer. Since the sample volumes after sampling period 1 were in an acceptable range the level of installation was not changed for sampling period 2. Surprisingly, sampling period 2 revealed sample volumes to be 40% and 62% lower at the inlet and outlet, respectively, compared to sampling period 1. We conclude that either clogging by biofilm or by fine sediment increased the hydraulic resistance of the filter. To prevent too low sampling rates in future application of SorbiCells, either lower placement of the samplers or an extension of the air tubes (jutting out from the water) are seen as possible improvements.

Further, increased hydraulic resistance through covering of the SorbiCell cartridges by biofilm and fine particles is seen as a possible impact on the sampling rate. The problem with physical blocking was also stated by previous studies (Audet, et al., 2014; Jordan, et al., 2013). In addition, previous studies investigating the monitoring of nutrients identified the sampler's filter and desorption processes as possible sources of error (Jordan, et al., 2013). However, similar to the SPMD samplers, the advantages of a simple and quick installation also apply to this method. Thus, a high flexibility in changing sampling locations is given.

The two passive methods show great differences in reported PAH detection limits: the SorbiCell analysis offer LODs between 30–70 ng/l, while SPMD LODs are between 0.046–0.79 ng/l. The explanation for these varieties is, once again, the low sampling rate of the SorbiCells since the LOD is specified by the detectable analyte mass in the sorbent: SorbiCells show a detection limit of 5 ng/sampler, whereas the SPMDs require between 4.5–9.3 ng/sampler to detect specific compounds.

Estimation of the total concentration based on the observed truly dissolved concentration and total organic carbon

Based on Schwarzenbach, et al. (2003), the truly dissolved PAH concentrations obtained by SPMD passive sampling and TOC/DOC measurements were used to estimate the total concentration of the PAHs. The performed calculation steps are shown in detail in Appendix B.

However, the estimated total concentrations were more than 10 times higher than detected in the water samples from automatic sampling. It resulted in an estimated inlet concentration for $\sum$ 16 PAHs of 8.36 µg/l (max. concentration in water samples: 0.46 µg/l) and an outlet concentration of 7.06 µg/l (max. concentration in water samples: 0.49 µg/l). It has to be pointed out that the DOC concentration was assumed to be zero since no reliable results were available while the measured TOC concentrations seemed to be valid. To estimate the total concentration, however, the particulate organic carbon (POC = TOC-DOC) is required which may explain the overestimated total concentration.

Passive sampling for Water Framework Directive-compliant monitoring

Although no satisfying results were obtained by passive sampling, the two tested methods clearly showed various operational advantages in comparison to automatic sampling and manual grab sampling. Once again, the identified benefits of a simple and quick installation, no time effort for maintenance and replacement of water samples by a receiving phase are pointed out. Further, no electricity is required for these methods and the need of fewer samples to quantify average concentrations are mentioned as advantages of these methods.

However, the WFD currently only refers to total concentrations in regard to organic pollutants without consideration of partitioning of pollutants (Roig, et al., 2007). Passive samplers, as previously described, take account of this problem to some degree when sampling specifically certain species. In order to use passive sampling for compliance monitoring, either changes in the definition of EQS (Vignati, et al.,

2009) or more reliable methods to estimate the total concentrations from passive sampling results are necessary. Vignati, et al. (2009) see the benefits of passive sampling at the present situation mainly in observing temporal trends and identifying areas where extended monitoring efforts are necessary. This can be confirmed by this study to a high degree. Indeed, it is not possible to directly compare results from passive samplers with results from conventional sampling methods such as automatic sampling. Therefore, it is necessary to find another way of formulating EQS to allow monitoring with emerging methods and, in further consequence, to allow innovations in this area. In addition, the tested passive samplers require further development in quality assurance procedures (Vignati, et al., 2009).

4.3.3   Sediment sampling

Generally, the sampling period of 23 days allowed the accumulation of only little sediment, which did not allow a reliable quantification of the settled material in the pond, and it was therefore shown to be too short. Longer sampling periods are required to obtain useful information from this method. As a consequence, the results from this simple approach to measure the accumulated sediment mass over a defined time period can only be used as an estimation. The aim of this method was to account for the removed load of PAHs in order to perform a mass balance of the pond.

Multiple factors contributing to the method's high uncertainties are identified: i) The sediment traps' position: due to the trap design it was only possible to place traps where the pole (which was used to attach the jars) could be rammed into the pond bottom for at least 20 cm, which was inhibited at the inlet section by the concrete slab. Hence, the inlet traps were located further downstream and were not representing the inlet section accurately. ii) The installation: when submerging the sediment traps, the immersion depth had to be estimated in a way that the trap was placed just above the pond bottom, whereas too low placement resulted in sediment resuspension and settling in the jar during deployment. iii) The retrieval: when retrieving the sediment traps, pond water was decanted, which lead to a loss of accumulated material.

To improve the applied trap design according to the stated issues, the following measures may be taken: i) an alternative way of fixing the traps close to the pond bottom is needed for placing traps at sections with a hard pond bottom. For example, the metal jar could be fixed on top of an anchor (for example a concrete block) while a buoy is attached to retrieve the samplers. ii) When deploying traps at sections where the pole is used to fix the jar, the water and sediment depth need to be measured more accurately to adjust the height of the jar. Additionally, a lid on the jar can help to avoid resuspension during installation.

4.4   Comparison of method costs and labor effort

The costs and required working hours of the studied five sampling strategies were estimated for the current project (Figure 22). However, to make it comparable, manual grab samples were assumed to be analysed for PAHs, which was not the purpose in this study. The comparison of the methods referred to a sampling period of one month, including investment costs and expenses for analysis performed by a commercial laboratory. The investment costs were converted into annual costs considering an expected equipment lifetime (reported in Appendix B). Additionally, the labor effort is reported also including travelling time (for 20 km return trip, in this case).

Automatic sampling revealed the highest expenditure of time based on an average of two field visits per week for maintenance, and also the highest equipment costs. Compared to automatic sampling, both passive sampling strategies required less working hours at significantly lower equipment costs. The costs for analyses were calculated for the automatic samplers based on the assumption of four samples

per month at the inlet and outlet each, whereas both passive sampling approaches only require one analysis per month for the inlet and outlet each. However, the costs for one single analysis are highest for SorbiCells.

Sediment sampling revealed approximately the same number of expended working hours as passive sampling but was performed at lowest equipment costs. The analytical costs represent analysis of three samples (inlet, middle and outlet section). Manual grab sampling was assumed to be performed once a week. It excels by its very low equipment costs; however, a high labor effort and the highest number of samples are necessary to get a representative image of the temporal variability of the water quality.
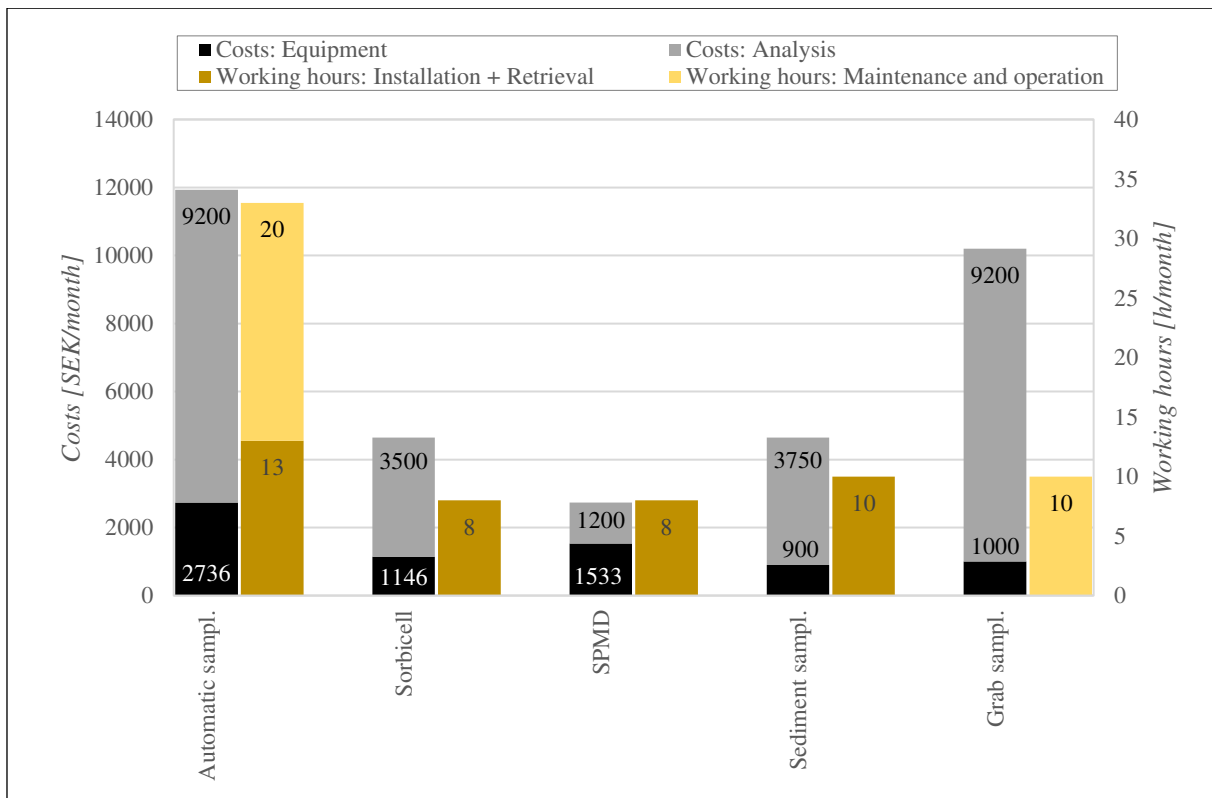
Figure 22. Required costs and working hours per month for five sampling methods.

In a previously performed study by Audet, et al. (2014), the costs of different sampling methods including SorbiCell, time-proportional automatic sampling and manual grab sampling were compared (Figure 23). SorbiCell sampling and time-proportional sampling were performed at similar costs (i.e. approximately EUR 3700 per year and site), while grab sampling was the cheapest method (EUR 2000 per year and site). The authors conclude that the SorbiCell method showed important advantages such as a high flexibility in sampler relocation and low equipment costs. Though, improvements may be necessary to make triplicate sampling unnecessary in order to reduce costs significantly. The reasons for the high differences in their findings compared to our study were found in their sampling methodology as well as in their approach to calculate the method costs. In contrast to our study, SorbiCell sampling was performed using triplicates which results in a threefold increase in equipment and analysis costs. However, a lifetime of 5 years and a discount rate of 4% was taken into account for the entire equipment whereas in this study lifetimes between 0.5 - 15 years and no discount rates were considered.
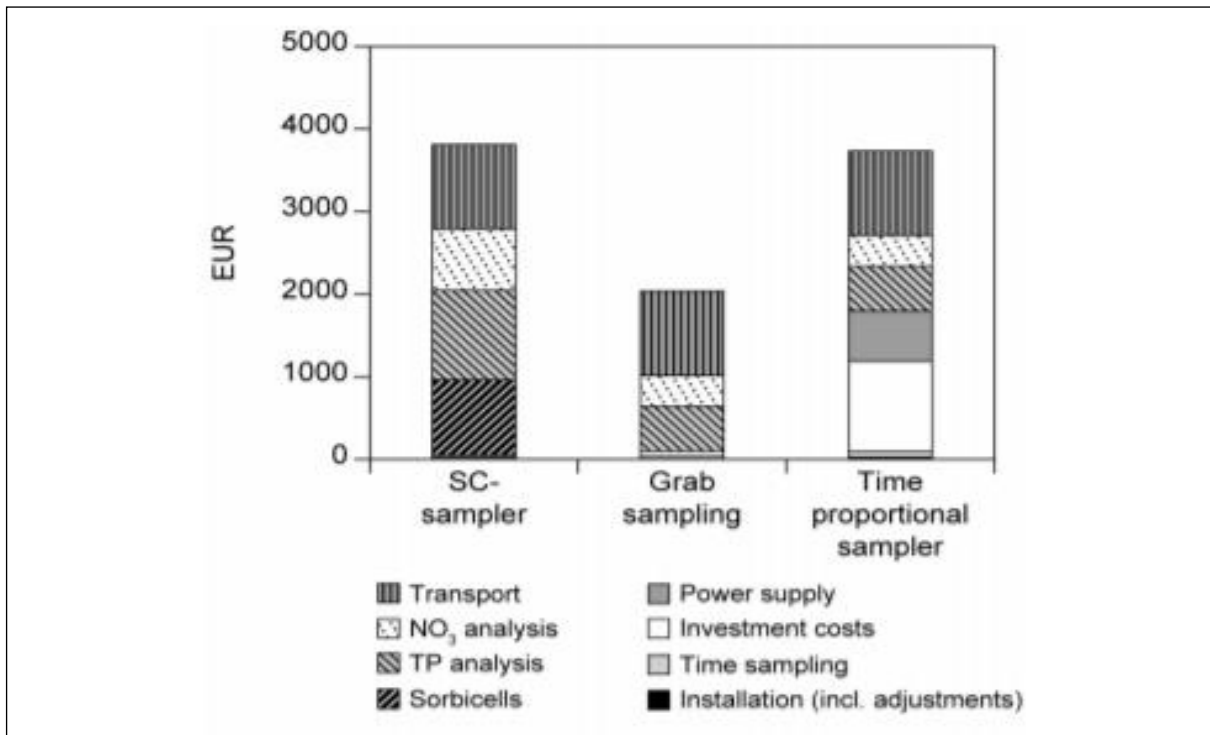
Figure 23. Comparison of the costs of sampling with SorbiCells, manual grab sampling and automatic time-proportional sampling of nutrients according to Audet, et al. (2014).

5 Conclusions

Different quality monitoring strategies at the inlet and outlet of the Järnbrott pond were used to investigate the pond's removal efficiency for PAHs. The results revealed great variabilities in the removal rates between three single storm events. The importance of observing a series of consecutive storm events to assess the long-term removal efficiency of a stormwater pond was pointed out. A comparison between the removal rates observed during the current study and previous studies at the Järnbrott pond demonstrated the great impact of water residence time on the removal rates. Therefore, the high rain frequency lead to reduced removal rates of PAHs. Removal rates for PAHs were found to be correlated to TSS/VSS removal, but not to the level of concentration; a high TSS concentration does not imply a high concentration of PAHs. Moreover, it was not possible to draw further conclusions on the correlation between occurrence of PAHs and rain data.

Two different passive sampling approaches were used to monitor PAHs present in the truly dissolved phase (SPMD), and in the truly dissolved phase as well as attached to colloids (SorbiCell). These pollutant phases are of special concern from an ecotoxicological point of view since they are the most bioavailable fractions. SPMD sampling showed contradictory results for the removal rates between two sampling periods and did not allow to draw a clear conclusion on the removal of truly dissolved PAHs in the pond. Positive and negative removal rates were found which indicates the presence of other processes in the pond beside particle settling, such as degradation, resuspension and partitioning. Further studies are needed to investigate the relevance of these processes in comparison to particle settling which was identified as the major removal process in the pond. The SorbiCell method resulted in observed concentrations below the detection limit for all studied compounds due to low sampling rates. Possible improvements for the SorbiCell for future projects were discussed to ensure higher sampling rates. Also, data from sediment sampling did not allow the calculation of a mass balance. Improvements of trap design and deployment time were suggested.

In addition to the investigation of the pond's removal efficiency, the tested methods were evaluated on effectiveness (providing reliable data) and costs. Several LMW and MMW compounds which were not found in the truly dissolved concentration of most samples collected by automatic sampling, could be detected in the truly dissolved phase, monitored using SPMD. Additionally, three compounds were detected by SPMD which were not even found in the total concentration of the samples collected by automatic sampling. Therefore, automatic sampling is likely to underestimate the concentration of the truly dissolved and colloid bound fractions. The cumulative sampling manner of the passive sampling method leads to one of the key advantages: the detection of compounds present at low concentrations. However, this finding did not apply to highly hydrophobic compounds. The method's major drawback is monitoring of the truly dissolved and colloid-bound phases alone, and that conclusions on the total concentration are not reliable. Thus, improvements of the passive sampling method that allow a reliable estimation of the total pollutant concentration are necessary to assess the ecotoxicological risk due to partitioning of PAHs into the most bioavailable fractions. Generally, PAHs are seen to partition predominantly in the particle-bound phase; however, it was also found to be present in the truly dissolved and colloid-bound fractions to a smaller extend. More detailed partitioning studies are necessary to quantify the partitioning behavior of PAHs in stormwater under the given circumstances.

The evaluation of method costs revealed the highest equipment and analysis costs for automatic sampling. Moreover, automatic sampling was the highest in labour effort. Both passive sampling methods and sediment sampling were performed at similar costs and working hours. Manual grab sampling is the lowest in equipment costs and time effort for installation but requires many analyses to obtain useful information on water quality.

The author concludes that applying cheaper monitoring programmes does not necessarily lead to lower infrastructure costs. Wrong assessment of the water quality may lead to immense additional costs (e.g. for building over dimensioned treatment facilities). Automatic sampling is still seen as the most reliable method when it comes to investigations of water quality in terms of the total pollutant concentration. However, passive sampling might present a useful alternative method for monitoring programmes where an average pollutant level or long-term trends are investigated. Also, passive sampling is seen as a better alternative for observing the bioavailable fraction of pollutants. Therefore, establishing effective and cost-efficient passive sampling methods may not replace automatic sampling completely for detailed observations, but may be performed in order to identify areas for detailed monitoring programmes and in cases where for example municipalities and other users would decide not to perform a sampling programme to avoid costs.

In future research projects, the passive sampling methods may be tested further for the monitoring of PAHs applying the recommendations presented in this thesis. Moreover, investigations are necessary to find reliable methods for the estimation of the total concentration based on passive sampling results. Alternatively, adaptions of the WFD quality standards are necessary to take the pollutant's partitioning into account. Since the current results did not allow profound statements on the removal efficiency of the Järnbrott pond and low removal rates during high rain frequencies were observed, long-term monitoring campaigns are needed to assess the removal of PAHs in the pond with special concern for the bioavailable fractions.

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Appendix A – Measurement results

Automatic sampling: Partitioning study

Compounds*	Event 6 SPE conc.		Event 6 filtered conc.		Event 7 SPE conc.		Event 7 filtered conc.	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]	[µg/l]
Naphthalene	< 0,020	< 0,020	0.024	0.028	< 0,020	< 0,020	< 0,020	< 0,020
Acenaphthylene	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010
Acenaphthene	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010
Fluorene	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010
Phenanthrene	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010
Anthracene	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010
Fluoranthene	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010
Pyrene	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010
Benz(a)anthracene	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010
Chrysene	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010
Benzo(b)fluoranthene / Benzo(k)fluoranthene	< 0,020	< 0,020	< 0,020	< 0,020	< 0,020	< 0,020	< 0,020	< 0,020
Benzo(a)pyrene	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010
Dibenz(ah)anthracene	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010
Benzo(ghi)perylene	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010
Indeno(1,2,3-cd)pyrene	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010	< 0,010

* Yellow marked cells represent values below LOD.

SorbiCell results

Compounds*	Period 1		Period 2	
	Inlet [µg/l]	Outlet [µg/l]	Inlet [µg/l]	Outlet [µg/l]
Naphthalene	< 0,03	< 0,03	< 0,07	< 0,06
Acenaphthylene	< 0,03	< 0,03	< 0,07	< 0,06
Acenaphtene	< 0,03	< 0,03	< 0,07	< 0,06
Fluorene	< 0,03	< 0,03	< 0,07	< 0,06
Phenantrene	< 0,03	< 0,03	< 0,07	< 0,06
Anthracene	< 0,03	< 0,03	< 0,07	< 0,06
Fluoranthene	< 0,03	< 0,03	< 0,07	< 0,06
Pyrene	< 0,03	< 0,03	< 0,07	< 0,06
Benzo(a)anthracene	< 0,03	< 0,03	< 0,07	< 0,06
Chrysene	< 0,03	< 0,03	< 0,07	< 0,06
Benzo(b+j+k)fluoranthene	< 0,03	< 0,03	< 0,07	< 0,06
Benzo(a)pyrene	< 0,03	< 0,03	< 0,07	< 0,06
Benzo(g,h,i)perylene	< 0,03	< 0,03	< 0,07	< 0,06
Dibenzo(a,h)anthracene	< 0,03	< 0,03	< 0,07	< 0,06
Indeno(1,2,3-c,d)pyrene	< 0,03	< 0,03	< 0,07	< 0,06
Flow Volume [l]	0.125	0.225	0.075	0.085

* Yellow marked cells represent values below LOD.

Chemical analysis of sediment

Compounds*	Inlet section [mg/kg TS]	Middle section [mg/kg TS]	Outlet section [mg/kg TS]
Naphthalene	< 0.100	0.472	0.284
Acenaphthylene	< 0.100	0.394	0.218
Acenaphthene	< 0.100	< 0.360	< 0.100
Fluorene	< 0.100	0.583	0.346
Phenanthrene	0.658	4.83	3.07
Anthracene	0.186	1.2	0.825
Fluoranthene	1.25	10.7	6.77
Pyrene	1.26	11	7.09
Benz(a)anthracene	0.459	3.82	1.98
Chrysene	0.488	2.1	2.8
Benzo(b)fluoranthene	0.661	5.24	3.56
Benzo(k)fluoranthene	0.211	1.84	1.12
Benzo(a)pyrene	0.497	4.5	2.83
Dibenz(ah)anthracene	0.076	0.66	0.441
Benzo(ghi)perylene	0.434	4.05	2.39
Indeno(1,2,3-cd)pyrene	0.232	1.78	0.948
PAH, $\sum 16$	6.4	53	35
PAH, $\sum$LMW	< 0.15	0.87	0.5
PAH, $\sum$MMW	3.4	28	18
PAH, $\sum$HMW	3.1	24	16

* Yellow marked cells represent values below LOD.

Appendix B – Performed calculations

Estimation of total PAH concentration based on SPMD results and POC concentration (Schwarzenbach, et al., 2003)

Step 1:

$$Log\ K_{OC} = a * \log K_{OW} + b \tag{1}$$

where:
K_{OC} is the soil organic carbon partitioning coefficient.
K_{OW} is the octanol/water partitioning coefficient.
$a\ and\ b$ are regression parameters.

Step 2:

$$K_{OC} = C_{OC}/C_W \ \rightarrow\ C_{OC} = \ C_W * K_{OC} \tag{2}$$

where:
C_{OC} is the amount of the analyte which is bound to 1 kg of organic carbon [µg$_{PAH}$/kg$_{oc}$]
C_W is the measured analyte concentration in the SPMD [µg/l].

Step 3:

$$C_{OC} = \ C_{Part}/P_{OC} \ \rightarrow\ C_{Part} = C_{OC} * POC \tag{3}$$

where:
POC is water concentration of particulate organic carbon [kg/l].
C_{Part} is the analyte concentration bound to POC [µg/l].

Step 4:

$$C_{Total} = C_{Part} + C_W \tag{4}$$

Appendix C – Technical information on the used passive samplers

SPMD: EWL-PRC – Exposmeter Lipophilic for water with PRCs

The EWL-PRC consists of a neutral, high molecular weight lipid such as triolein which is encased in a thin-walled lay flat polyethylene membrane tube.

<u>Performance:</u>

Detection level: Method specific. For PCB isomers sub-pg/L range

Selectivity: Truly dissolved concentrations of hydrophobic compounds with Kow from 3 to 6

Repeatability: Variability of sampling rates of replicate EWL-PRCs in the field is very small

Salinity range: no influence

Electrical: no power requires

Mechanical: recommended mounting device and protective cage

- Length: (between the welds) 91.4cm
- Width: 2.5cm
- Wall thickness: 70-95µm
- Tubing: lay flat low density polyethylene, additive free
- Triolein: 99% purity (l.0mL used for standard 91.4cm length)
- Membrane: surface area to total EWL-PRC volume (SA-V) ratio ≈90cm2 /mL or ≈460cm2 /mL of triolein
- Performance reference compounds: Phenenthrene-d10, Acenaphtene-d10, Chrysene-d12, Fluorene-d10, PCB3, PCB8, PCB37, PCB54, OCN internal standard.
- Lipid-to-membrane: mass ratio ≈ 0.2
- Weight of standard EWL-PRC: 4.4 to 4.6 grams

Technical information according to NyaExposmeter AB (2018).

SorbiCell: SorbiCell VOC – Product sheet

Technical product sheet according to Sorbisense (2010) attached on the following pages.

SORBICELL VOC

A novel patented technology for passive sampling of VOCs from water

Sorbisense A/S
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www.sorbisense.com
info@sorbisense.com

SORBISENSE

The **SorbiCell** is an effective patented sampling unit for use in Sorbisense mounting systems.
SorbiCells provide reliable and representative data whilst reducing cost, logistics and time associated with environmental monitoring of groundwater, surface water and drinking water.

The SorbiCell consists of a polypropylene cartridge containing:
a)   An effective sorbent, designed to adsorb volatile organic substances (VOCs) from water passing the cartridge.
b)   Environmentally friendly tracer salt that dissolves proportionally with the volume of water passing the cartridge.
c)   Special filters between sorbent and tracer salt compartments.

Flow direction
Filter
Filter
Filter
Sorbent
Tracer Salt
Tracer Salt
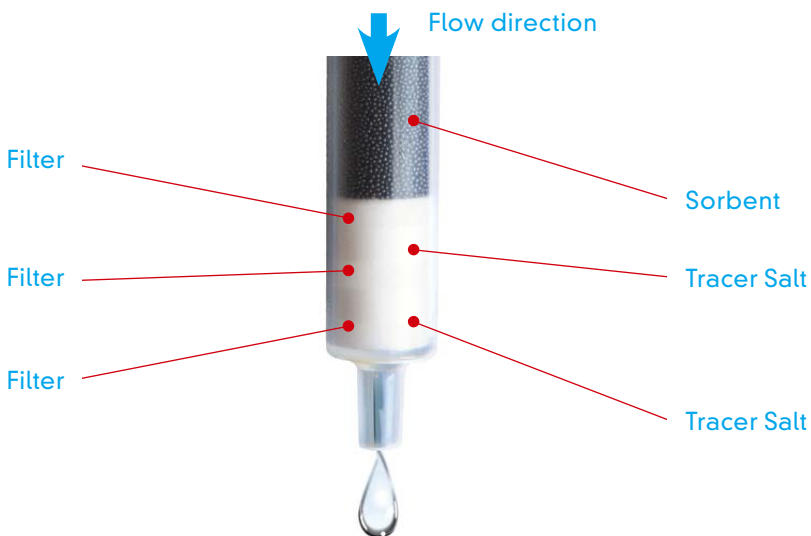
When the sampling period is over, the SorbiCell is sent to a laboratory for extraction and analysis. The analysis results give the average concentration of each contaminant (e.g., 10 ug/L of vinyl chloride).

Technical Specifications:

Diameter:	11 mm
Length:	75 mm
Weigth:	ca. 3 g
Volume:	3 ml
Material:	Polypropylene cartridge, polymer sorbent (styrene), environmental friendly tracer salt and polymer-/glass filters
Detection limit:	0.2 µg (per individual solute).
Measuring range:	0.1 – 0.5 litre of water.

SorbiCell's are supplied in packages of 6 cartridges.

SorbiCell (VOC) measures these Volatile Organic Compounds:

BTEX & MTBE	Chlorinated compounds "top 10"	Other compounds	
benzene toluene ethylbenzene p/m-xylene o-xylene 1,3,5-trimethylbenzene propylbenzene methyl tert-butyl ether (MTBE)	vinyl chloride 1,1-dichloroethene trans-1.2-dichloroethene cis-1,2-dichloroethene trichloromethane(chloro-form) 1,1,1-trichloroethane tetrachloromethane trichloroethene (TRI) tetrachloroethene (PER)	dichlorodifluoromethane trichlorofluormethane 1,1-dichloroethane 2,2-dichloropropane bromochloromethane 1,1-dichloropropene 1,2-dichloropropane dibromomethane bromodichloromethane c-1,3-dichloropropene t-1,3-dichloropropene 1,1,2-trichloroethane 1,3-dichloropropane dibromochloromethane 1,2-dibromoethane chlorobenzene 1,1,1,2-tetrachloroethane styrene bromoform cumen (isopropyl-benzene)	bromobenzene 1,1,2,2-tetrachloroethane 1,2,3-trichloropropane 2-chlorotoluene 4-chlorotoluene t-butylbenzene 1,2,4-trimethylbenzene sec-butylbenzene 1,3-dichlorobenzene p-cymen(4-isopropyltoluene) 1,4-dichlorobenzene 1,2-dichlorobenzene n-butylbenzene 1,2-dibromo-3-chloropropane 1,2,4-trichlorobenzene hexachlorobutadiene naphtalene 1,2,3-trichlorobenzene

We recommend limiting the number of compounds analysed to only relevant compounds and in accordance with standard analysis "packages" offered by the laboratory. Contact Sorbisense for further information.

SorbiCell VOC standard products:*

Product ID	Hydraulic resistance	Choose for
042-101	Low	Short measuring periods / shallow measuring depth
042-102	Medium	Medium periods / medium depths
042-103	High	Long periods / deeper measuring depth

*packaging 6 pcs

Table with recommended sampling times* in days, for different depths of installation.

Depth of installation (m):	0.5-1m	1-2m	2-5m	5-10m
SorbiCell 042-101:	8-40	1-4	1-2	n.r.
SorbiCell 042-102:	30-90	5-18	3-11	2-7
SorbiCell 042-103:	n.r.**	18-60	12-30	8-25

* sampling rates may be reduced in turbid water with high colloid loads
** n.r. = not recommended

Please observe the following:

All SorbiCells should be stored cool and out of light until use. SorbiCell's should be installed within three months from their production date printed on the package.
When installing SorbiCells, the adsorbent end should always be upstream to avoid contamination by the tracer salt.
Remove the protection caps from both ends prior to installation. Keep these protection caps – you can use them for sealing the SorbiCell after the measurement is finished.
SorbiCells must be kept wet until installation to avoid the hydraulic conductivity of the SorbiCells is changed e.g. by air-bubbles.
Pre-pumping is not necessary when measuring in groundwater.
SorbiCells are shipped to the laboratory e.g. in craft bubble envelope. If SorbiCells are stored before shipment they should be stored at +4degree C and out of light.
Unused SorbiCells may be disposed as household waste in accordance to local regulations. Used SorbiCells may be disposed as household waste in some cases. If in doubt the SorbiCells should be disposed of as chemical waste in accordance with local regulations.

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