UPPSALA
UNIVERSITET

15003
Examensarbete 30 hp
Februari 2015

Calibration and Application of Passive Sampling in Drinking Water for Perfluoroalkyl Substances

Caroline Persson

ABSTRACT

Calibration and application of passive sampling in drinking water for perfluoroalkyl substances

Caroline Persson

Perfluoroalkyl substances (PFASs) are global environmental contaminants and a need for monitoring levels has arisen due to their persistency and their ability to bioaccumulate. One relatively novel method of monitoring for both long and short time intervals and generating time-weighted average (TWA) concentrations is passive sampling for which no power, maintenance and supervision is required. The polar organic compound integrative sampler (POCIS) with a weak anion exchange (WAX) sorbent and the POCIS with a hydrophilic-lipophilic balance (HLB) adsorbent were calibrated for PFASs in a laboratory uptake experiment, and applied at a drinking water treatment plant (DWTP) in Stockholm, Sweden.

In the calibration study, all of the 14 studied PFASs were taken up by both passive samplers. Two and three out of the 14 studied PFASs had reached equilibrium after 28 days using POCIS WAX (PFBA and PFTeDA) and POCIS HLB (PFBA, PFPeA and PFTeDA), respectively. The sampling rate (R_s), which is the extracted water in liters per day, ranged between 0.003 and 0.10 L day^{-1} for the POCIS WAX and between 0.00052 and 0.13 L day^{-1} for the POCIS HLB. In general, R_s increased with increasing perfluorocarbon chain-length (C_4 to C_8) and for a perfluorocarbon chain-length longer than C_8, R_s decreased with increasing perfluorocarbon chain-length (C_8 to C_{13}) for both passive samplers. FOSA had the highest R_s-value (0.10 and 0.13 L day^{-1}) for both POCIS WAX and POCIS HLB, respectively. The POCIS WAX had a higher uptake for the short-chained PFASs PFBA (134 ng after 28 days), PFPeA (410 ng) and PFHxA (834 ng), compared to the POCIS HLB (0.5 ng, 58 ng, and 373 ng, respectively). For all other compounds, the accumulated amounts in the POCIS HLB were in the same range as in the POCIS WAX.

The application of the passive samplers at the DWTP showed that both passive samplers could detect ultra-trace (pg to ng L^{-1}) levels of PFASs. A comparison of the TWA concentration showed that the two passive samplers had a good linear correlation (R^2 = 0.63), but the TWA concentrations derived by POCIS WAX was approximately 40% higher compared to POCIS HLB. A comparison between the passive samplers and the grab samples did not show a correlation (R^2 = 0.24 for POCIS WAX and R^2 = 0.10 for POCIS HLB). The application also included a comparison of the removal efficiency in the conventional DWTP and a pilot plant with additional treatments steps of granulated activated carbon **(**GAC) and nanofiltration (NF). For the full-scale DWTP the average removal efficiency was 32% and high removal efficiency was observed for PFBA (81%). For the pilot plant, the removal efficiency was 100% for all the detected PFASs in the raw water.

Keywords: Perfluoroalkyl substances (PFASs), passive sampling, Polar organic compound integrative sampler (POCIS), sampling rate, calibration, application, drinking water

Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences (SLU), Lennart Hjelms väg 9, Box 7050, SE-750 07 Uppsala

REFERAT

Kalibrering och tillämpning av passiv provtagning i dricksvatten för perfluoroalkylsubstanser
Caroline Persson

Perfluoroalkylsubstanser (PFAS) har blivit uppmärksammade som globala miljöföroreningar, och ett behov av att övervaka dessa ämnens förekomst i miljön har uppkommit på grund av hög persistens i kombination med hög förmåga att bioackumulera. En relativt ny metod för tidsintegrerad provtagning är så kallad passiv provtagning. En adsorbent placeras i fält och ackumulerar PFAS från vattnet. Tillgång till elektricitet behövs inte, och behov av övervakning och underhåll är minimalt. I denna studie kalibrerades en så kallad 'polar organic compound integrative sampler' (POCIS) för mätning av PFAS genom upptagsexperiment med två olika adsorbenter: en svag anjons adsorbent (WAX) och en hydrofil-lipofil balanserad adsorbent (HLB). Metodiken tillämpades sedan på vatten från ett dricksvattenverk i Stockholm, Sverige.

Upptagsexperimenten utfördes med 14 PFAS och samtliga togs upp av båda adsorbenterna. Två respektive tre av de studerade PFAS uppnådde jämvikt efter 28 dagar för WAX (PFBS och PFTeDA) samt HLB (PFBA, PFPeA och PFTeDA). Upptagshastigheten (R_s), det vill säga den volym som extraheras per dag, varierade mellan 0,003 och 0,1 L dag^{-1} för WAX och mellan 0,00052 och 0,13 L dag^{-1} för HLB. Generellt ökade R_s med en ökande längd på kedjan av perfluorerade kol upp till C_8, för att sedan avta med ökande kedjelängd. FOSA hade det högsta R_s-värdet (0,10 och 0,13 L dag^{-1}) för både WAX och HLB. WAX hade ett högre upptag (upp till 134, 410 och 834 ng) för PFAS med kort perfluorerad kolkedja (PFBA, PFPeA respektive PFHxA) jämfört med HLB (upp till 0,5, 58, och 373 ng). Den ackumulerade mängden för alla andra PFAS överensstämde väl mellan de båda provtagarna.

Mätning av PFAS halter i dricksvattenverket med hjälp av POCIS WAX och POCIS HLB visade att även PFAS kunde detekteras även vid miljörelevanta halter. En jämförelse mellan de båda passiva provtagarna visade på ett linjärt samband ($R^2 = 0,63$), men där POCIS WAX hade en tendens att överskatta koncentrationen med ca 40%. En jämförelse mellan de passiva provtagarna och traditionell uppsamlingsprovtagning visade på låg överrensstämmelse ($R^2 = 0.24$ för POCIS WAX och 0.10 för POCIS HLB). Vid tillämpningen gjordes även en beräkning för reningseffektiviteten av PFAS i dricksvattenverket och i en pilotanläggning där ytterligare rening med granulerat aktivt kol (GAC) och nanofiltration (NF) används. I dricksvattenverket var den genomsnittliga reningen 32%, med den högsta reningseffektiviteten för PFBA (81%). I pilotanläggningen var reningen 100% för alla upptäckta PFAS i råvattnet.

Nyckelord: Perfluoroalkylsubstanser (PFAS), passiv provtagning, Polar organic compound integrative sampler (POCIS), provtagningsshastighet, kalibrering, tillämpning

Institutionen för vatten och miljö, Sveriges lantbruksuniversitet (SLU), Lennart Hjelms väg 9, Box 7050, SE-750 07 Uppsala

ACKNOWLEDGEMENT

This master thesis is the last part of the Master Programme in Environmental and Water Engineering of 30 ECTS at Uppsala University. It has been carried out on the behalf of the Department of Aquatic Science and Assessment at the Swedish University of Agricultural Sciences, SLU.

Lutz Ahrens acted as supervisor and mentor, Karin Wiberg was the subject reviewer and project owner, both at the Department of Aquatic Sciences and Assessment. Fritjof Fagerlund at the Department of Earth Sciences at Uppsala University acted as the final examiner.

First and foremost I would like to thank my supervisor Lutz Ahrens for his dedication to my project, for all his support and help throughout my project as well as for always taking the time to answer my questions. I would like to thank Karin Wiberg for help with my report. I would also like to thank the staff at SLU for being patient and helpful in the lab and answering all my questions. A special thanks also goes to the workshop at SLU for helping me with adjustment of equipment. Further, I would like to thank Per Ericsson at Norrvatten for taking on my project and to Sofia Wängdahl at Norrvatten for assisting and taking time off to help me through the application process. I would also like to thank Sophie Englund, fellow master thesis student, for all the support and interesting discussions. Lastly, I would like to thank my friends and family for all the support and encouragement through my thesis work.

Caroline Persson
Uppsala 2015

UPTEC W 15003, ISSN 1401-5764
Published digitally at the Department of Earth Sciences, Uppsala University,
Uppsala, 2015

POPULÄRVETENSKAPLIG SAMMANFATTNING

Perfluoroalkylsubstanser, även kallade PFAS, har under de senaste åren fått stor uppmärksamhet medialt då halter av PFAS har detekterats i dricksvatten. Livsmedelsverket gjorde en undersökning för att få en överblick av hur omfattande förekomsten av PFAS i dricksvatten var i Sveriges kommuner. Undersökning visade att 6% av alla dricksvattenanläggningar, främst lokaliserade i storstadsområden, hade PFAS i dricksvattnet. Det innebär att över 3,6 miljoner personer i Sverige har mätbara PFAS-halter i sitt dricksvatten.

PFAS används i stor utsträckning inom industrin på grund av deras unika förmåga att både avvisa vatten såväl som fett. Spridningen av PFAS är därför utbredd, och förutom att de finns i vatten har de också upptäckts i flora och fauna samt i mänskligt blod och bröstmjölk. Utbredningen av PFAS kan ge anledning till oro, eftersom PFAS bioackumulerar och kan ha toxiska effekter. När PFAS väl kommit ut i miljön är de svåra att bli av med, eftersom de inte bryts ner, och i dagsläget finns det ingen kostnadseffektiv metod att rena PFAS från dricksvatten. Troliga källor för PFAS i vatten är från industrin, läckage från soptippar, allmän användning av produkter som blivit behandlade med PFAS samt utsläpp från vattenreningsverk. Lokalt har platser för brandövningar visas vara bekymmersamma punktkällor. Utöver att PFAS finns i vissa typer av brandskum används de för ytbehandling på en mängd varor och produkter, allt ifrån papper till mattor.

Den mest kända PFAS, perfluoroktansulfonat (PFOS) är listad under Stockholmskonventionen sedan 2009. Det har därför blivit viktigt att kunna övervaka och reglera PFOS. Just övervakningen och insamling av halter i bland annat vatten är vikigt för att kunna göra en riskanalys för miljögifter. I dagsläget är den vanligaste vattenprovtagningsmetoden ett så kallat manuellt ögonblicksprov, vilket innebär att en viss volym vatten insamlas vid ett tillfälle. Detta provtagningssätt har sina begränsningar, eftersom endast en koncentration vid ett tillfälle erhålls. För att kunna göra en riskanalys som bygger på medelkoncentration över en längre tid behövs en annan metodik.

För detta ändamål kan man använda så kallad passiv provtagning, som är en relativt ny och enkel provtagningsmetod. Passiva provtagning kräver ingen ström och minimalt med övervakning och underhåll, vilket gör den till en lämplig metod för provtagning i naturen för både korta och långa tidsintervall. Metoden har också visat sig fungera för flertalet olika kemiska ämnen som är lösta i vatten. I detta examensarbete användes provtagare av typen POCIS för att mäta i PFAS i dricksvatten.

För att kunna få fram en genomsnittlig koncentration över tid för provtagning med POCIS krävs det att upptagshastigheten hos ämnet är känd för en specifik adsorbent. Upptagshastigheten definieras som den volym vatten som har extraherats per dag. Man får fram denna hastighet genom ett kalibreringsexperiment för den specifika adsorbenten som ska användas i POCIS-provtagaren. Kalibreringen i denna studie gjordes i en kontrollerad laboratoriemiljö genom att utsätta POCIS-provtagaren för en konstant koncentration av PFAS. Vid kalibreringen mättes halten i två olika adsorbenter i dubbelprov vid 0, 2, 4, 7, 21 och 28 dagar efter exponering. Det sig att de flesta PFAS var fortfarande i den så kallade linjära upptagsfasen efter 28 dagar, och upptagshastigheterna varierade mellan 0,003 och 0,1 L dag^{-1} för ena typ av POCIS och mellan 0,00052 och 0,13 L dag^{-1} för den andra typen. Upptagshastigheterna som togs

fram efter kalibreringen kunde sedan användas för koncentrationsmätningar av PFAS i riktiga vattenprover.

Efter kalibreringen gjordes fältmätningar av PFAS på Görvälnverkets dricksvattenverk i Stockholms kommun, där det både finns ett fullskaligt dricksvattenverk samt en pilotanläggning. Mätningarna gjordes dels för att testa om den passiva metoden med POCIS kunde detektera låga halter av PFAS och dels för att ta fram hur effektiv befintlig reningsteknik är för PFAS. Det visade sig att båda typerna av POCIS-adsorbenter kunde detektera låga halter av PFAS i vattnet, men där den ena hade en tendens att överskatta koncentrationerna. De koncentrationer som kundes tas fram för PFAS i dricksvattenverket från den passiva metoden överensstämde dock inte med de halter som erhölls genom manuell ögonblicksprovtagning.

Mätningarna av PFAS i dricksvattenverket gjordes mellan olika reningssteg både i det konventionella dricksvattenverket samt i den mindre pilotanläggningen. Mätpunkterna kunde då användas för att se om någon rening av PFAS sker och hur effektiv reningen är för respektive metod. Mätningarna visade att i det konventionella dricksvattenverket varierade reningen av PFAS mellan ingen rening alls och upp till 89%. Rening i pilotanläggningen varierade mellan två ytterligheter, ingen rening alls och en rening på 100%. Detta tyder på att pilotanläggningen är bättre på att rena PFAS än det konventionella dricksvattenverket. Anledningen till skillnaden i rening är att i pilotanläggningen fanns nyligen utbytta kolfilter. Nya kolfilter har i tidigare studier visat sig vara den reningsmetod som bäst renar PFAS. Problematiken med rening med kolfilter är att effektivitet avtar med tiden och varierar från fall till fall. Alltså kvarstår problemet med att det i dagsläget inte finns någon kostnadseffektiv reningsteknik för PFAS i dricksvatten.

ABBREVIATIONS

A	Water-sampler interfacial area
c_s	Concentration of a compound in a adsorbent
c_{PRC}	Concentration of PRC in the receiving phase after exposure
c_{PRC}^{0}	Initial concentration of PRC in the receiving phase
DOC	Dissolved organic carbon
DWTP	Drinking water treatment plant
FOSA	Perfluorooctane sulfonamide
HLB	Hydrophilic-lipophilic balance
GAC	Granulated activated carbon
K_{mw}	Membrane-water sorption coefficient
K_{pw}	Adsorbent-water sorption coefficient
k_m	Mass transfer coefficient of a membrane
k_o	Overall mass transfer coefficient
k_s	Mass transfer coefficient of the sorption phase
k_w	Mass transfer coefficient of the WBL
k_e	Elimination rate constant
m_s	Mass of adsorbent
NF	Nanofiltration
PES	Polyethersulfone
PFAA	Perfluoroalkyl acid
PFASs	Per- and polyfluoroalkylated substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonic acid
PFCA	Perfluorinated carboxylate acid
PFDA	Perfluorodecanoic acid
PFDoDA	Perfluorododeanoic acid
PFHpA	Perfluorohepanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonic acid
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFPnA	Perfluoropentanoic acid
PFSA	Perfluorinated sulfonic acid
PFTeDA	Perfluorotetradecanoic acid
PFUnDA	Perfluoroundecanoic acid
POCIS	Polar organic compound integrative sampler
PRC	Performance reference compound
RO	Reverse osmosis
R_s	Sampling rate
ρ_m	Density of a membrane
ρ_s	Density of a adsorbent
t	Time
$t_{1/2}$	Half-life time
TOC	Total Organic Carbon
TWA	Time-weighted average
WAX	Weak anion exchange
WBL	Water boundary layer
WWTP	Wastewater treatment plant

TABLE OF CONTENTS

1 INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are anthropogenic pollutants (Kaserzon et al., 2014) that are known to be persistent, bioaccumulative and potentially toxic (Ahrens, 2011; Buck et al., 2011; Wang et al., 2011; Glynn et al., 2012). Further, PFASs are hard to degrade which has led to a widespread contamination of PFASs in the environment (Mak et al., 2009). Levels of PFASs have been detected almost everywhere in the water cycle; in surface water and seawater, as well as in wastewater and drinking water all over the globe (Flores et al., 2013). Researchers have also found PFASs in wildlife as well as in human blood and breast milk (Mak et al., 2009; Post et al., 2013). This is a cause of concern given that PFASs have possible toxic effects on both humans and wildlife (Ahrens, 2011; Eschauzier et al., 2012; Fedorova et al., 2013).

The exposure pathways for PFASs into the environment are both point and nonpoint sources such as wastewater treatment plants (WWTPs) and atmospheric deposition (Ahrens, 2011). The recognition of perfluorooctane sulfonic acid (PFOS) as an environmental pollutant in 2009 by the Stockholm Convention has made it necessary to monitor and regulate levels of PFASs (Fedorova et al., 2013; Kaserzon et al., 2014). The regulation of PFOS for production has already begun and more PFASs are likely to be candidates for future monitoring. However, to be able to regulate PFASs in the future further risk assessments are needed (Zushi et al., 2012).

A risk assessment for any potentially harmful compound demands a large amount of environmental samples (Alvarez et al., 2004). The traditional method of sampling in water is grab sampling. However, grab sampling has the limitation of only reflecting one concentration at one point in time (Fedorova et at., 2012). For a risk assessment, the samples are preferred to be time-weighted average (TWA) concentrations (Kot-Wasik et al., 2007). TWA concentrations compensate for the fluctuation of concentrations in the environment over time, and therefore reflect the average concentration (Harman et al., 2011).

Passive sampling such as the polar organic compound integrative sampler (POCIS) is an effective and relatively novel sampling method for chemical contaminants in water (Alvarez et al., 2004). Passive sampling requires no power, maintenance or supervision (Alvarez et al., 2004). It is therefore an ideal technique for environmental sampling for both short and long time intervals (Bailly et al., 2013). The sampling technique has been proved to be efficient for a wide range of environmental contaminants including both neutral and ionized compounds (Kaserzon et al., 2012).

1.1 OBJECTIVES AND HYPOTHESES

The overall aim of this study was to calibrate and investigate the applicability of two passive sampler types (i.e. POCIS weak anion exchange (WAX) and POCIS hydrophilic-lipophilic balance (HLB)) as a sampling method for PFASs in drinking water. The following three hypotheses were investigated:

- The uptake in the passive samplers will differ depending on the chain length and functional group of PFASs.

- The passive samplers will be able to detect ultra-trace (pg to ng L^{-1}) concentrations of PFASs in a DWTP and the results will be comparable with grab sampling.

- The removal efficiency of PFASs is expected to be low in a DWTP using conventional treatment techniques and higher removal efficiency is expected with treatment techniques with granulated activated carbon (GAC) and GAC plus nanofiltration (NF) in a pilot plant.

This study was not intended to optimize passive samplers for PFASs, but instead the focus was to identify the applicability of passive samplers for low concentrations of PFASs. Further, the focus was to develop a calibration method with the objective to find sampling rates of the 14 studied PFASs, which were selected to represent commonly detected PFASs in drinking water. The calibration and application was limited to only two types of passive samplers, POCIS WAX and POCIS HLB with 200 mg of adsorbent.

2 BACKGROUND

2.1 PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs)

PFAS is a collective name for a family of per- and polyfluoroalkyl substances (Buck et al., 2011; Eschauzier et al., 2012; Rahman et al., 2014). The general structure of PFASs is a polyfluorinated alkyl chain (Fedorova et al., 2012) made up by one or more carbon atoms where hydrogen have been replaced by fluorine (Buck et al., 2011). The general molecular structure for a fully fluorinated PFAS is $(C_nF_{2n+1})^{-1}$. The stable and strong bond between the carbon and fluorine atoms creates a main structure of PFASs that is both chemically and thermally stable (Buck et al., 2011) as well as resistant to biological degradation (Mak et al., 2009). The structure of PFASs also leads to what makes them unique: the properties of water and oil repellency as well as thermal and oxidative resistance (Buck et al., 2011).

One large subgroup of PFASs are perfluoroalkyl acids (PFAAs) with a fully fluorinated alkyl chain in combination with either a carboxylic acid (-COOH) head group or a sulfonic acid ($-SO_3H$) head group (Buck et al., 2011; Eschauzier et al., 2012; Post et al., 2013). The two functional groups make up two large subgroups of the PFAAs; perfluorinated carboxylate acids (PFCAs, $C_nF_{2n+1}COOH$) and perfluorinated sulfonic acids (PFSAs, $C_nF_{2n+1}SO_3H$) (Table 1). A second large subgroup of PFASs is precursors compounds such as perfluoroalkyl sulfonamides (FASAs, $C_nF_{2n+1}SO_2NH_2$) (Buck et al., 2011; Flores et al., 2013).

PFASs are resistant to degradation, both physical and metabolic, which makes PFASs environmentally persistent (Flores et al., 2013). Two of the most investigated PFASs are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) (Flores et al., 2013; Kaserzon et al., 2013) that both tend to persist in water and can be formed as breakdown products of precursor chemicals (Fedorova et al., 2013). PFOA and PFOS have properties of ionic nature, high solubility and negligible vapor pressure when dissolved in water, which makes them highly mobile in water and thus a concern for the aquatic environment (Flores et al., 2013).

2.1.1 Physicochemical properties

All subgroups of PFASs can be divided into either long-chained or short-chained PFASs (Buck et al., 2011). For PFCAs the definition of long-chained is seven or more perfluorinated carbons and for PFSAs six or more perfluorinated carbons (Buck et al., 2011). In general, the polarity and solubility in water (S_w) increases with a decreasing carbon chain length for PFASs (Eschauzier et al., 2012).

PFCAs and PFSAs are primarily in the water phase or bound to particles due to high solubility and low vapor pressure of the ions (Ahrens, 2010). The shorter-chained PFCAs ($C<7$) are most likely in the water phase while longer chained PFCAs and PFSAs are more likely bound to particles (Ahrens, 2010; Du et al., 2014). PFAS precursors such as FASAs are less water-soluble as well as more volatile compared to PFCAs and PFSAs (Ahrens, 2010). Furhter, FASA and other PFAS precursors are not as persistent as PFCAs and PFSAs mainly due to an uncharged functional group (Buck et al., 2011). However, the FASAs can biodegrade and form PFCAs or PFSAs in the environment (Ahrens, 2011).

To determine a compound's hydrophobicity the octanol-water partitioning coefficient (K_{ow}) is used (Du et al., 2014). The higher the value of K_{ow} the more hydrophobic a compound is. However, for PFASs this poses a problem since PFSAs do not solve well in octanol (Du et al., 2014). PFASs have instead been known to aggregate in the interface between water and octanol (Kim et al., 2014). The estimation of K_{ow} for PFASs is therefore computed with models based upon experimental data and molecular descriptions, which generates a high uncertainty for all K_{ow}-values (Kim et al., 2014) (Table 1).

2.1.2 Production

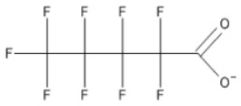
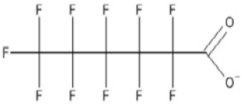
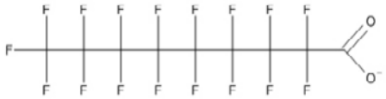
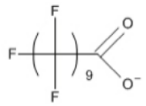
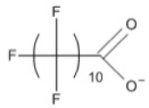
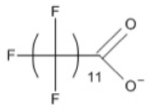
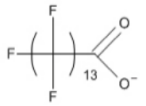
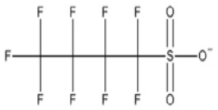
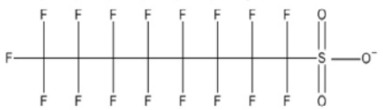
PFASs have been widely used in consumer and industrial applications for over 50 years (Ahrens, 2011; Kaserzon et al., 2012; Fedorova et al., 2013). They have been applied as water, oil and stain repellants for surface coating for textiles, furniture, paper products, paints, and fire retardants (Ahrens, 2011; Mak et al., 2009; Glynn et al., 2012; Fedorova et al., 2013; Flores et al., 2013). Before 2002, PFOA and PFOS were the most commonly used PFASs. However, since then PFOA and PFOS have been successively replaced by shorter-chained PFASs like perfluorobutanoic acid (PFBA) (Buck et al., 2011).

2.1.3 Exposure and toxicity

The assumed exposure ways of PFASs into the aquatic environment are from domestic and industrial wastewaters (Fedorova et al., 2013). One major point source of PFASs might therefore be WWTPs (Rahman et al., 2014). PFASs can also enter the environment from production of perfluorinated chemicals, processing industry and the use or disposal of material containing PFASs. Other contamination sources can be from fire-fighting foams and sewage sludge disposal (Flores et al., 2013). All of these different sources highlight that despite low concentration in water (range of pg L^{-1} to ng L^{-1}) (Rahman et al., 2014), the removal of PFASs presents a challenge especially since many are highly persistent (Fedorova et al., 2013). To add further to the contamination problem longer-chained PFAS precursors may degrade to shorter-chained PFASs, which are now more commonly used in production and application (Buck et al., 2011)

Recent studies have shown indications of serious health effects in animals for PFOA and PFOS (Flores et al., 2013). PFOS has been recommended by USEPA Science Advisory Board to be classified as likely human carcinogen (Flores et al., 2013; Post et al., 2013) due to that PFASs have been shown to accumulate in blood and protein-rich tissues after human exposure (Glynn et al., 2012). Further, levels of PFASs have been detected in human serum all over the world (Post et al., 2013). PFOA, PFOS and perfluorohexane sulfonic acid (PFHxS) have a half-life in humans that span over 3–8.5 years while other substances, like PFBA, have a half life of 2–4 days and perfluorobutanoic acids (PFBS) 10–20 days. This can explain the increasing levels of PFOA that have been reported in human serum over the last few years (Post et al., 2013). The exposure pathways for humans are diverse and include drinking water, food and food that have been in contact with materials containing PFASs as well as from breast milk and air (Buck et al., 2011).

Table 1. List of PFASs that were analyzed in this study along with their molecular structure (Naturvårdsverket, 2012), molecular weight (*MW*), the water solubility (log S_w) and the octanol-water partition coefficient (log K_{ow}).

Compound	Acronym	Structure	Chemical formula	MW (g mol^{-1})	log S_w (mol L^{-1})	log K_{ow}
Perfluorinated carboxylate acids (PFCAs)						
Perfluoro-butanoic acid	PFBA		C_3F_7COOH	213.04	0.42[a] -0.14[b]	0.76[b]
Perfluoro-pentanoic acid	PFPeA		C_4F_9COOH	263.05	-0.37[a] -0.95[b]	1.45[b]
Perfluoro-hexanoic acid	PFHxA		$C_5F_{11}COOH$	313.06	-1.16[a] -1.76[b]	2.15[b]
Perfluoro-hepanoic acid	PFHpA		$C_6F_{13}COOH$	363.07	-1.94[a] -2.59[b]	2.85[b]
Perfluoro-octanoic acid	PFOA		$C_7F_{15}COOH$	413.09	-2.73[a] -3.38[b]	3.55[b]
Perfluoro-nonanoic acid	PFNA		$C_8F_{17}COOH$	463.09	-3.55[a] -4.20[b]	4.24[b]
Perfluoro-decanoic acid	PFDA		$C_9F_{19}COOH$	513.10	-4.31[a] -5.00[b]	4.94[b]
Perfluoroun-decanoic acid	PFUnDA		$C_{10}F_{21}COOH$	563.11	-5.13[a] -5.80[b]	5.62[b]
Perfluorodo-decanoic acid	PFDoDA		$C_{11}F_{23}COOH$	613.12	-5.94[a] -6.63[b]	5.80[b]
Perfluorotetra-decanoic acid	PFTeDA		$C_{13}F_{27}COOH$	713.40	-7.42[a] -8.30[b]	7.05[b]
Perfluorinated sulfonic acids (PFSAs)						
Perfluorobutane sulfonic acid	PFBS		$C_4F_9SO_3H$	300.12	-1.00[a] -1.32[b]	1.15[b]
Perfluorohexane sulfonic acid	PFHxS		$C_6F_{13}SO_3H$	400.14	-2.24[a] 0.84[b]	2.91[b]
Perfluorooctane sulfonic acid	PFOS		$C_8F_{17}SO_3H$	500.16	-3.92[a] -4.56[b]	4.30[b]
Perfluoroalkyl sulfonamides (FASAs)						
Perfluorooctane sulfonamide	FOSA		$C_8F_{17}SO_2NH_2$	499.18	-5.05[a] -4.65[b]	4.33[b]

[a]Wang et al., 2011; [b]Kim et al., 2014

2.1.4 Legislative action and regulation

Since May 2009, PFOS has been added to the Stockholm Convention list of persistent organic pollutants (POPs) and is thus restricted globally in its production (Ahrens, 2011). Further, both PFOS and PFOA are on the Contaminant Candidate List (CCL) and are therefore considered candidates for regulation in the future. PFOS has also been included in Directives 2000/60/EC and 2008/105/EC in the European Parliament and the Environmental Quality Standard (EQS) have been set to 0.65 ng L^{-1} for the annual average of inland surface water (Flores et al., 2013). However, as of today none of the PFASs have any general European guidelines for concentrations in drinking water (Eschauzer et al., 2012). The USEPA has included PFBS, PFHxS, PFOS, PFHpA, PFOA and PFNA in a list of contaminants that should be under observation. For those six PFASs, it is required to have an occurring collection of data that can be used in any future risk assessments (Rahman et al., 2014).

Since there are no general guidelines for concentrations of PFASs in drinking water, some target values have been set up by Swedish agencies (Livsmedelsverket, 2013). The Swedish Environmental Protection Agency has set a target value for PFOS at 350 to 1 000 ng L^{-1} in drinking water. The target interval is based upon the parameters of tolerable daily intake, body weight and intake of drinking water. The tolerable daily intake was assumed to be in the range of 0.1 - 0.25 µg per kg body weight per day (Naturvårdsverket, 2008). Further, The Swedish National Food Agency has guidelines regarding seven PFASs (PFBS, PFHxS, PFOS, PFPeA, PFHxA, PFHpA and PFOA). The guidelines state that the sum of the seven PFASs should not exceed a measured limit of 90 ng L^{-1} in drinking water as well as not exceed a health-based guideline for the total daily intake of 900 ng L^{-1} water (Livsmedelsverket, 2014).

2.2 PFASs IN DRINKING WATER

Drinking water is a human exposure pathway for PFASs (Ahrens, 2011). It has therefore become relevant to monitor the presence of PFASs in drinking water as well as to find possible treatment techniques (Eschauzier et al., 2012). Due to the fact that PFASs are resistant to chemical, physical as well as biological degradation, conventional treatments such as coagulation, flocculation, sedimentation, oxidation, UV irradiation, filtration and biofiltration are not effective when it comes to removal of PFASs (Rahman et al., 2014). Further, preoxidation, sand filtration and ozonation have been shown to be inefficient in removing PFOA and PFOS (Flores et al., 2013; Post et al., 2013) which additionally proves that removing PFASs from drinking water is problematic (Eschauzier et al., 2012). To further add to the problem low levels of PFASs have been found in municipal drinking water (Kaserzon et al., 2012) from both surface and groundwater worldwide (Post et al., 2013). However, treatment techniques such as granular activated carbon filtration (GAC), reverse osmosis (RO) and nanofiltration (NF) show promise in removing PFASs from drinking water (Eschauzier et al., 2012; Flores et al., 2013).

GAC has been proved to remove PFOA and PFOS at a batch scale. However, it does not seem to be effective when applied (Eschauzier et al., 2012). Researchers have shown that GAC needs to be replaced or regenerated in frequent intervals in order to be able to remove PFOA and PFOS effectively (Rahman et al., 2014). To achieve removal above 70% for PFOA and PFOS, the GAC filters could not used more than nine months (Takagi et al., 2011), which entails large cost of operations (Rahman et al., 2014). The reason for the frequent regenerations of GAC are due to that dissolved organic carbon

(DOC) is competing for the adsorption sites in the GAC. The effectiveness of the GAC filters will therefore decrease when fouling occurs due to adsorption of DOC (Rahman et al., 2014).

The membrane techniques RO and NF have both successfully removed PFASs with long alkyl chains (Eschauzier et al., 2012). However, implementation is not widespread due to high costs and problems with disposal after treatment (Eschauzier et al., 2012). Further, the techniques needs to be improved when it comes to energy and operation efficiency as well as being able to be applicable for short-chained PFASs. The only technique that has shown promise to actually remove short-chained PFASs is that of a strong base anion resin; however contradicting trends for efficiency are a fact (Rahman et al., 2014).

2.3 PASSIVE SAMPLING

The basic principle of passive sampling is Fick's first law of diffusion (Kot-Wasik et al., 2007) based on the steady-state conditions assumption (Seethapathy et al., 2008). By utilizing the driving forces caused by a difference of compound concentration a free flow of molecules is created from a sampled medium to a collecting medium until equilibrium is reached. Usually, the permeation of the molecules occurs though a membrane that is incorporated in the passive sampling device. In a single step sampling, compound isolation and preconcentration are thus carried out (Górecki and Namiésnik, 2002).

The accumulation of a compound in a passive sampler is assumed to follow first-order kinetics, which consists of three phases: linear, curvilinear and equilibrium partitioning (Figure 1) (Alvarez et al., 2004). In the linear phase the adsorbent can be assumed to be an infinite sink (Górecki and Namiésnik, 2002; Alvarez et al, 2004). This assumption makes an estimation of the TWA concentration possible for a specific period of time (Alvarez et al., 2004).

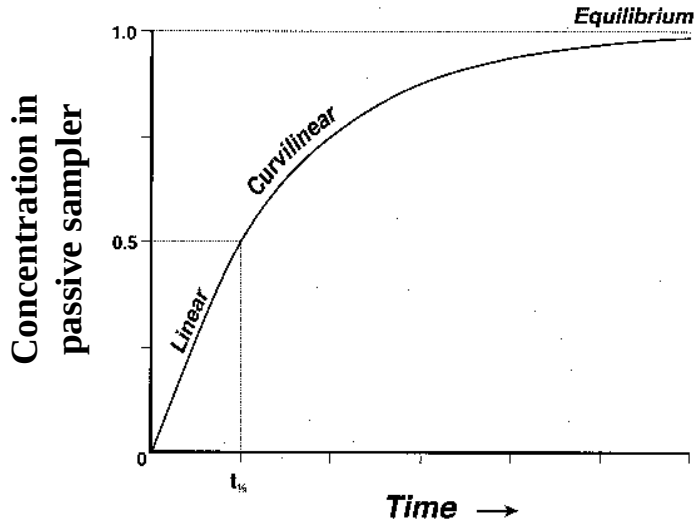


Figure 1. *First-order kinetics for accumulation of a compound in a passive sampler over time. The three phases (linear, curvilinear and equilibrium) and the half-life time ($t_{1/2}$) are shown (Huckins et al., 2002).*

The accumulation in a passive sampling device can be mathematically described with a first-order one-compartment model which includes the kinetics between the water and the sampler (equation 1) (Kot-Wasik et al., 2007; Kaserzon et al., 2012).

$$c_s = K_{pw} \cdot c_w \cdot \left[1 - \exp\left(-\frac{R_s t}{m_s K_{pw}}\right)\right] \quad (1)$$

where c_s (in ng g^{-1}) is the concentration of the compound in the adsorbent, K_{pw} (in L g^{-1}) is the adsorbent-water sorption coefficient, c_w (in ng L^{-1}) is the concentration of the compound in the water, R_s (in L $days^{-1}$) is the sampling rate, t (in days) is the time and m_s (in g) is the mass of the adsorbent (Kot-Wasik et al., 2007; Kaserzon et al., 2012).

The values for R_s and K_{pw} can be estimated by an unweighted nonlinear least-squares regression or by a calibration of the passive sampler (Kaserzon et al., 2012). During a calibration, first-order kinetic and the assumption that the adsorbent is an infinite sink can be used to simplify the equation of accumulation in the passive sampler. By determining the half-life time with equation 2:

$$t_{1/2} = \frac{\ln(2) \cdot m_s \cdot K_{pw}}{R_s} \quad (2)$$

where $t_{1/2}$ (in days) is the half-life time. The assumption of a linear uptake phase up until the half-life time can be used to reduce the expression for c_s from equation 1 to equation 3 (Fauvelle et al., 2012):

$$c_s = \frac{c_w R_s t}{m_s} \quad (3)$$

where the R_s can be estimated during a calibration and the TWA concentration can be deduced (Fauvelle et al., 2012). Further, R_s can also be determined mathematically, which is described in Appendix A.

The use of performance reference compounds (PRCs) during a calibration have proven to be an effective tool for determining the sampling rate for passive samplers (Mazzella et al., 2010: Belles et al., 2014). In general, the PRCs are loaded into the receiving phase before deployment. The dissipation of PRCs is then used to estimate the sampling rate for a compound (Belles et al., 2014) since the dissipation of PRC and the uptake of a compound are both in theory equally affected by the environmental factors (Mazzella et al., 2010). Mathematical formula for calculation with PRCs is described in Appendix A.

2.3.1 Calibration of a passive sampling device

A calibration of a passive sampler is necessary for individual compounds since there are no standard sampling rates (Harman et al., 2011). Different calibration methods have been described over the last years, which makes comparison between sampling rates hard (Harman et al., 2012) and leads to that an overall model is lacking for correlating different compounds and sampling rates (Harman et al., 2011).

In general, the calibration process involves measuring R_s and K_{pw}, which both are fundamental parameters for relating the accumulated amount into TWA concentration

as described above (Kaserzon et al., 2013). Studies have shown that the sampling rates are affected by environmental parameters such as the water flow rate, pH, salinity and fouling for which there is no common practice of how to adjust for (Fauvelle et al., 2012; Harman et al., 2012; Bailly et al., 2013). However, if a calibration is carried out in a laboratory, some of these affecting parameters can be controlled (Kaserzon et al., 2013) by maintaining a constant water temperature and a constant water flow and most importantly keeping a constant compound concentration (Kot-Wasik et al., 2007; Li et al., 2010a; Li et al., 2010b).

The basis of a calibration is that the passive sampler is placed in water for which a known concentration of the compound has been added (Harman et al., 2012). The sampling rate can then be estimated by the volume of water that was extracted by the sampler per unit time. One way of calibrating is to use a flow-through experiment. The aim is to keep the concentration of the compound constant over time. The calibration process achieves this by a continuously flow of spiked water into a tank, where the passive samplers have been placed. This way, all the samplers are exposed to approximately the same concentration of the compound. The passive samplers are then removed after different exposure times and the adsorbent is analyzed to calculate the uptake rate. Studies have shown that flow-through systems work for low concentrations (<100 ng L^{-1}), and large water samples will not affect the calibration since the compound is continuously added (Harman et al., 2012).

For passive samplers, it takes a while to reach the equilibrium stage (Alvarez et al., 2004), and the time needed is dependent on the capacity of the collecting phase (Kot-Wasik et al., 2007). The collecting phase in itself has close to no loss of the compound, it has a constant uptake and a sampling rate that is independent of environmental concentrations (Alvarez et al., 2004). Instead sampling rates varies for different compounds that in turn vary for different environmental conditions (Bailly et al., 2013). Temperature affects the sampling rate since the molecular diffusion constants increase with an increasing temperature, resulting in an increasing sampling rate with increasing temperature (Górecki and Namiésnik, 2002). Increasing water flow rates increase the water turbulence, which in turn increase the compounds uptake rates due to a reduction in the water boundary layer (WBL). How much sampling rates are affected by environmental conditions is hard to determine without the use of PRCs (Harman et al., 2011).

2.3.2 Polar organic compound integrative sampler (POCIS)

The polar organic compound integrative sampler (POCIS) developed by Alvarez et al. (2004) has been successfully applied to monitor over 300 compounds (Alvarez et al., 2004; Harman et al., 2011; Fauvelle et al., 2012; Metclafe et al., 2014). The POCIS has shown best results for hydrophilic compounds within the range of polarities of $0 < \log K_{ow} < 4$ (Alvarez et al., 2004; Fauvelle et al., 2012). A wide range of polar organic compounds (Mazzella et al., 2010), such as pharmaceuticals (Li et al., 2010a; Li et al., 2010b; Bailly et al., 2013), illicit compounds (Harman et al., 2011), pesticides, hormones (Li et al., 2010a; Li et al., 2010b) and industrial compounds (Kaserzon et al., 2012), have been proved to accumulate in the POCIS (Harman et al., 2011). The POCIS can therefore be seen as a part of a solution to the difficulty of measuring fluctuating and low concentrations of different contaminants (Harman et al., 2011; Metcalfe et al., 2014) as well as estimating the cumulative aquatic exposure (Alvarez et al., 2004).

The design of the POCIS is simple and consists of a collecting medium enclosed within two polyethersulfone (PES) membranes (Alvarez et al., 2004). The sandwich of the collecting medium and the PES membranes are in turn encompassed by two stainless steel plates (Figure 2). The stainless steel is chosen because it does not compete with the adsorbent and PES membranes when it comes to compound uptake (Alvarez et al., 2004).

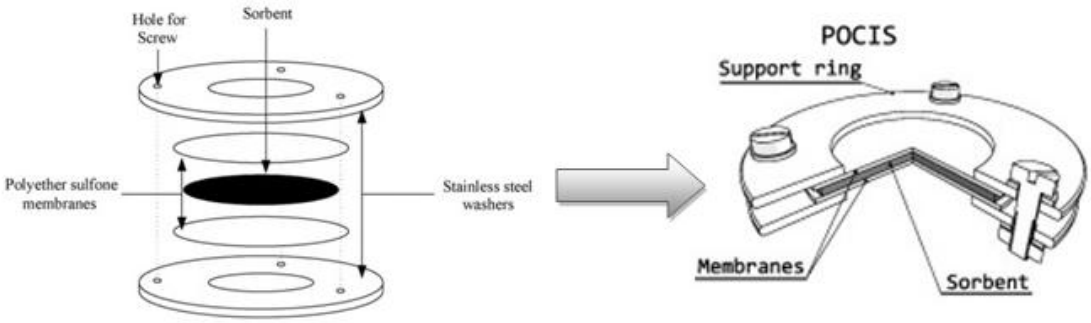


Figure 2. *The structure of a POCIS where stainless steel encompasses the PES membranes and the adsorbent in the middle (Kot-Wasik et al., 2007; Seethapathy et al., 2008).*

Two different types of POCIS are available on the market, "pharmaceutical" POCIS and "pesticides" POCIS (Harman et al., 2012). The "pharmaceutical" POCIS contains the adsorbent Oasis hydrophilic-lipophilic balance (HLB), whilst the "pesticides" POCIS contains a triphasic sorbet which is a mixture of hydroxylated polystyrene-divinylbenzene resin and a carbonaceous adsorbent (Harman et al., 2012). Oasis HLB is classified as a hyper-cross-linked porous polymeric adsorbent by its manufacturer, indicating that uptake and desorption does not by default follow first-order kinetics or pure isotropic exchange. Instead, the Oasis HLB can only follow first order kinetics under conditions where trace levels of the compound exists with a competing organic solute, the adsorbent is homogenous and adsorption sites are equivalent in energy for a particular solute. Under these conditions, the assumption of first-order kinetics is valid for the Oasis HLB (Mazzella et al., 2010).

A POCIS with Oasis HLB (POCIS HLB) interacts with compounds through van der Waals interactions, which makes POCIS HLB less favorable for acidic compounds since their high solubility generates a non-optimal thermodynamic situation (Fauvelle et al., 2012). An application of POCIS HLB for anionic compounds therefore requires a modification (Fauvelle et al., 2012). Oasis WAX is a modified version of Oasis HLB where poperazine groups have been added due to their weak anionic mechanisms (Kaserzon et al., 2012). A POCIS with Oasis WAX (POCIS WAX) has proven to be an effective adsorbent for the short-chained PFASs. However, both the Oasis WAX and Oasis HLB have shown similar performance for adsorbing PFASs (Kaserzon et al., 2012; Kaserzon et al., 2013; Kaserzon et al., 2014).

3 MATERIALS AND METHODS

3.1 CHEMICALS AND METERIALS

In this study 14 PFASs were used in the calibration for the passive samplers including PFBA (purity 98%), PFPeA (97%), PFHxA (≥97%), PFHpA (99%), POFA (96%), PFNA (97%), PFDA (98%), PFUnDA (95%), PFDoDA (95%), PFTeDA (97%), PFBS (98%), PFHxS (≥98%), PFOS (98%) and FOSA (purity not available) which were purchased from Sigma-Aldrich.

The components for the POCIS and the stainless steel cages used during the field deployment were purchased from Environmental Sampling Technologies Inc., Missouri, USA. The amount of the adsorbents Oasis HLB and Oasis WAX, respectively, was 200 mg in the POCISs. Both of the adsorbents had been spiked with PRCs before the passive samplers were assembled. 190 µL of PRCs were added to 19,935 g Oasis HLB and 200 µL of PRCs were added to 19,928 g Oasis WAX. The PRCs included 2-methyl-4-chlorophenoxyacetic acid (MCPA) D_3 (3,5-6-D3-phenoxy), acetamiprid D_3 (N-methyl D3), atrazine-desisopropyl D_5 (ethylamino D_5), diflufenican D_3 (3-trifluoromethylphenoxy-2,4,6 D_3), diuron D_6 (dimethyl D_6), beta-endosulfan D_4, imidacloprid D_4 (imidazolidin-4,4,5,5 D_4), chlorfenvinphos (ethyl) D_{10}, chlorfenvinphos (ethyl) D_{10}, γ-HCH D_6, simazine D_{10}, terbutryn D_5 (ethyl D_5), diclofenac-(acetophenyl ring-13C6) sodium salt hemi(nonahydrate).

Chemicals used throughout the laboratory work were as follows. Methanol (LiChrosolv, Germany, >99.9%), acetone (SupraSolv, Germany, >99.8%), Millipore water (Millipak, 0.22 µm filter), and ammonium acetate (Fluka, Netherlands, >99%).

Internal standards (ISs) were added to each sample for the passive sampling as well as the water samples right before the solid phase extraction. The IS for PFAS included $^{13}C_4$ PFBA, $^{13}C_2$ PFHxA, $^{13}C_4$ PFOA, $^{13}C_5$ PFNA, $^{13}C_2$ PFDA, $^{13}C_2$ PFUnDA, $^{13}C_2$ PFDoDA, $^{18}O_2$ PFHxS, $^{13}C_4$ PFOS, M_8FOSA, d_3-N-MeFOSAA, d_5-N-EtFOSAA, d-N-MeFOSA, d-N-MeFOSA, d-N-EtFOSA, d_7-N-MeFOSE and d_9-N-EtFOSE, all purchased from Wellington Laboratories (purity 99%).

3.2 PREPARATION OF PASSIVE SAMPLERS

In total 28 passive samplers were assembled for the calibration and 27 for the application in the DWTP. All the stainless steel parts were washed and rinsed three times with methanol and after drying wrapped in aluminum foil and stored until usage. The PES membranes were cut into squares with the side length of 8.9 cm. The cleaning procedure for the PES membranes was to put the PES membranes in 1 L of methanol and sonicate for 15 min after which the methanol was discarded and new methanol was added. The PES membranes were cleaned by repeating the same cleaning procedure three times. After cleaning, the PES membranes were dried under nitrogen gas and packed in aluminum foil and stored in a freezer at -20 ^{o}C until usage.

The passive samplers were assembled to mimic the POCIS that are available commercially with 200 mg of one of the adsorbents: Oasis HLB or Oasis WAX. The adsorbents were prepared before assembling the passive samplers by being dissolved one at the time in a solution of 200 mL acetone spiked with 200 µL PRC-solution. The solute was stirred at 500 rpm for 24 h and then the acetone was evaporated by heating the mixture and stirring it until the adsorbents were completely dried. The POCIS were

then assembled with the adsorbent (Oasis WAX or Oasis HLB) sandwiched between two PES-membrane and then held together by two stain-less steel plates. The components were sealed together with three screws (Figure 2). For the POCIS WAX, all heads of the screws faced the same direction while for the POCIS HLB, one screw faced the other way so that a distinction could be made between the two different types of POCIS.

3.3 LABORATORY CALIBRATION OF PASSIVE SAMPLERS

The setup for the calibration was specifically constructed to fit the needs of this project and was a modified flow through system with two aquariums with the capacity of 90 L (length = 80 cm, width = 35 cm, height = 40 cm). In tank 1 the passive samplers were deployed and tank 2 worked as a reservoir for tank 1 (Figure 3). In tank 1 two pumps were also deployed to create a continuous water circulation within the tank with the purpose to distribute the PFAS concentration homogeneously throughout the body of water. Both tanks were wrapped in aluminum foil to prevent UV-light penetrating into the water. The water in tank 1 and tank 2 were spiked to a concentration of 500 ng L^{-1} and 1000 ng L^{-1}, respectively of a mixture of 14 PFASs (average concentration for each PFAS was about 480 µg mL^{-1}).

The calibration setup was based upon having a constant concentration in tank 1 with the passive samplers. A compensation for the uptake of contaminants in the passive samplers was therefore necessary. The uptake for one passive sampler was assumed to be 0.25 L day^{-1} (roughly the mean sampling rate for PFASs and passive sampling obtained by Kaserzon et al. (2012)). With 24 passive samplers deployed in tank 1, the total uptake would be 6 L day^{-1}. With a concentration of 500 ng L^{-1} of PFASs in tank 1, the total loss each day would be 3000 ng absolute. Thus, 3000 ng of PFASs had to be added every day into tank 1 in order to maintain a constant concentration. By approximation, adding 3 L of water with a PFAS concentration of 1000 ng L^{-1} this would make up for the loss of PFASs in the passive samplers and keep the concentration constant. In the approximation, the concentration of the 3 L of water pumped out of tank 1 was not taken into account. Further, since the passive samplers were taken out after different time intervals, the total loss of PFASs from the water would decrease. The volume replaced in tank 1 was therefore adjusted to 2 L for the last week of the calibration study.

To compensate for losses of water due to evaporation, more than 3 L of water was added each day to tank 1. A mark was made on the glass of tank 1 representing the water level for the first day of the calibration study. The water that was pumped out of tank 1 was measured to 3 L and 2 L, respectively. However, the total amount of water replaced was targeted at where the water level was marked. To be able to get the measurements as accurate as possible at a low flow rate, a peristaltic pump (MasterFlex® L/S®, Cole-Parmer, Assembled by Thermo Fisher Scientific, USA) was used to pump the water.

The first day of the calibration a two POCIS WAX and two POCIS HLB were not deployed in the water. They were used as blanks and stored in a freezer at a temperature of -20 ^{o}C until they were analyzed. In total 24 passive samplers, 12 POCIS WAX and 12 POCIS HLB, were deployed into tank 1, where they were mounted in triples and then stacked on a pillar (Figure 3). In total four pillars were deployed with six passive sampler attached to each pillar. Two POCIS WAX and two POCIS HLB were taken out

at the same time at an interval of 2, 4, 7, 14, 21 and 28 days. Along with the passive samplers a 100 mL water sample was taken from tank 1 each sampling day.

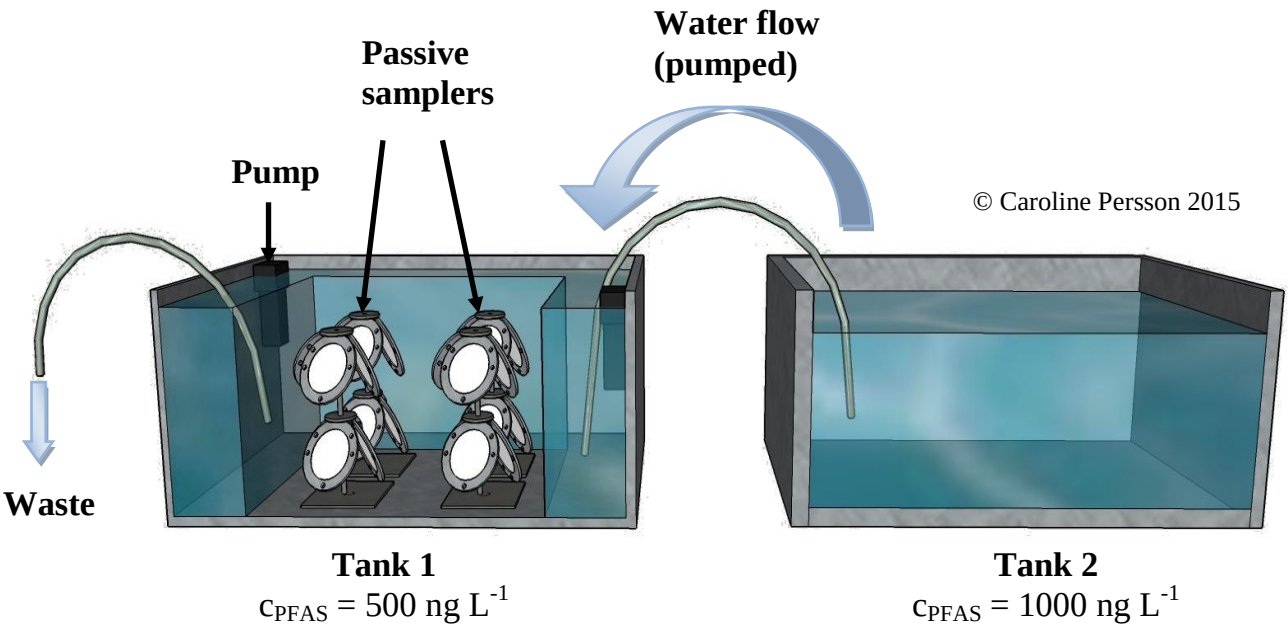


Figure 3. *A schematic of the laboratory calibration study set up. In tank 1, the passive samplers were deployed and the water was spiked to a PFAS concentration of 500 ng L^{-1}. Tank 2 was used as a reservoir and was spiked to a PFAS concentration of 1000 ng L^{-1}. In tank 1 two pumps were placed in the water to create a water circulation within the tank.*

3.4 APPLICATION OF PASSIVE SAMPLERS IN DWTP

For the deployment at the DWTP both types, POCIS WAX and POCIS HLB, were deployed for two weeks, the study site was Görvälnverket, situated in Järfälla in the northern part of Stockholm, Sweden. Lake Görväln is the watershed that provides water for Görvälnverket, which produced 43.4 billion liters of drinking water in 2010 and supplied half a million of people in and around Stockholm with drinking water (Norrvatten, no date a)

The sampling points at the DWTP were chosen to include the full-scale treatment plant and a pilot treatment plant. In the full-scale plant, the sampling points were i) raw water, ii) after the sand filtrate, iii) after the GAC filtrate and iv) drinking water (Figure 4) After the intake of raw water, aluminum sulphate is added to the water in order to flocculate soil particles, microorganisms, and humic substances and remove them by sedimentation. After the sand filtrate, the water is directly pumped into the GAC filtrate. After the GAC filtrate the water is cleaned by UV-light and pH adjusted with chlorine to obtain the finished drinking water (Norrvatten, no date b). In the pilot plant, the passive samplers were deployed at the sampling points v) after a GAC filtrate, vi) after nanofiltration and vii) after nanofiltration and a GAC filtrate (Figure 4). The water in the pilot plant was taken from the sand filtration in the full-scale DWTP.

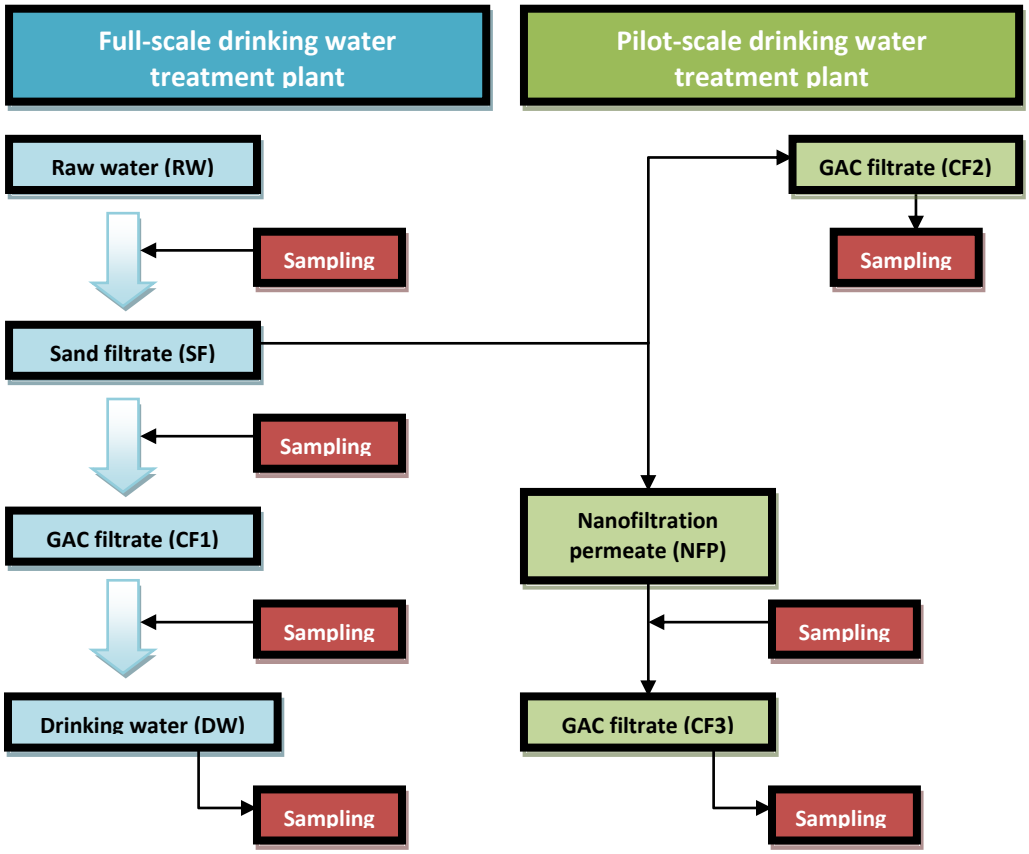


Figure 4. *Sampling points for the application of passive samplers in the DWTP. The blue color represents the full-scale plant while the green represent the pilot plant.*

In total, 21 POCIS (14 POCIS WAX and 7 POCIS HLB) were deployed at the DWTP for 14 days. At each of the sampling sites, the setup was three passive samplers (two POCIS WAX and one POCIS HLB), which were mounted together and put in a stain-less steel cage (Figure 5). The steel cage with the passive samplers was placed in a stain-less steel bucket. Water was transferred into the bucket through a plastic tube. The bucket had an outlet built into it close to the rim. From the outlet, another plastic tube transported the overflow water into waste. The water flow rate was measured at the inlet of the bucket and was assumed representative for the flow rate of the whole water body. The water flow rate along with pH and temperature was measured the first day of the calibration for all sampling sites. Water samples from each sampling site were collected at the beginning of the sampling, after one week and at the end of the sampling after two weeks. Additional water parameters were obtained from water analysis made by chemists at Görvälnverket.

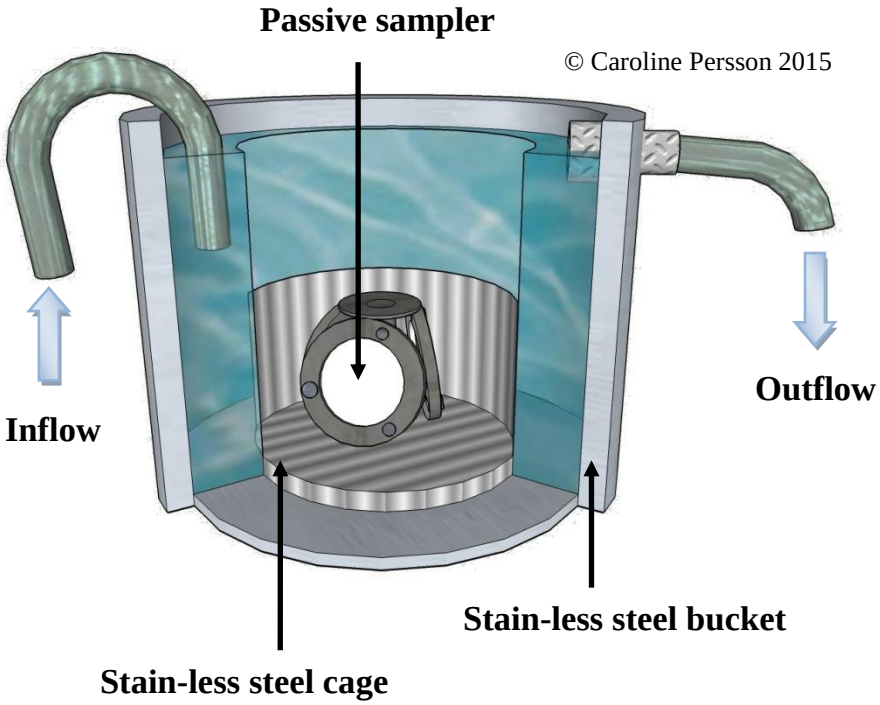


Figure 5. *A schematic of the application of the passive samplers at the DWTP.*

3.5 ANALYSIS OF PFASs IN PASSIVE SAMPLERS AND WATER SAMPLES

3.5.1 Extraction of passive samplers

The extraction of PFASs from the passive samples can be seen as a three-step process. The first step was to prepare the solid phase extraction (SPE) cartridges, followed by an elution of the deployed sampler using a SPE manifold and lastly a concentration of the samples.

The preparation of the SPE cartridges was carried out by rinsing all the equipment three times with methanol. A clean frit was then inserted into a clean cartridge and pushed to the bottom. The adsorbent from one passive sampler was transferred from the PES-membranes into the cartridge through a glass funnel and was washed down with Millipore water. The PES-membranes were dried by nitrogen gas and stored in 15 mL PP-tubes. The excess water was dried out of the cartridge by vacuum for about half an hour. When the cartridge was dried, another frit was added on top of the adsorbent.

The cartridges were spiked with 100 µL of PFAS IS (20 pg μL^{-1}). This was done to correct for any potential losses of PFASs during the extraction and the following concentration of the samples. The cartridges with Oasis WAX adsorbent were eluted with 4 mL of methanol followed by 4 mL of 0.1% ammonium hydroxide in methanol. The cartridges with Oasis HLB adsorbent were eluted with 8 mL of methanol. The elution for both the Oasis WAX and the Oasis HLB were collected into 15 mL PP-tubes. When all the elution had been added, the cartridges were dried by vacuum. To concentrate the samples to 1 mL, a nitrogen evaporation system (N-EVAP$_{TM}$112) was used. The samples were then spiked with 10 µL of an injection standard (200 pg μL^{-1}) and analyzed for PFASs using a liquid chromatography-mass-spectrometry (HPLC-MS/MS).

3.5.2 Extraction of water samples

The water samples from the laboratory calibration study were not filtrated or changed in any way before the extraction. However, the water samples from the DWTP were filtrated and mixed before the extraction. At the DWTP, a 1 L grab sample was taken using PP-bottles from each sampling site. The grab samples were collected at the first day, after one week and after two weeks at the end of the deployment. All the samples were stored at a +4 - +8^{o}C temperature until extraction. The three water samples from the same sampling site were mixed in order to make one water sample that would roughly reflect the whole deployment time. An amount of 0.330 g were weighted from each water sample and then mixed with the same amount from other water samples from the same site. This mixture of the three water samples were then filtrated using a glass microfiber filter (GF/C, Whatman), Werner Glass Filtration equipment and vacuum. After the filtration, the water samples were ready to be extracted.

The extraction of PFASs from the water samples was done according to Ahrens et al. (2009) using SPE. The SPE was conducted using Oasis WAX cartridges (Waters, 6 cc, 150 mg, 20 µm, Ireland) and a SPE workstation. Before the extraction, the samples were spiked with 100 µL of PFAS IS (20 pg µL^{-1}). The SPE-setup with the Oasis WAX cartridges was preconditioned before the extraction by 4 mL of ammonium hydroxide in methanol followed by 4 mL of methanol and finally 4 mL of Millipore water. After the preconditioning, the cartridges were loaded with the whole water sample of approximately 100 mL for the calibration study and 1 L for the application study. The flow of water through the cartridges was regulated by a vacuum pump to approximately one drop per second. After the water samples had passed through the cartridges, 4 mL of a buffer containing 25 mM of ammonium acetate buffer in Millipore water was used to rinse the cartridges. The remaining water in the cartridges was removed from the cartridges by using a centrifuge for 2 min at 3000 rpm.

The elution of PFASs in the cartridges was done using 4 mL of methanol and 4 mL of 0.1% ammonium hydroxide in methanol, which was eluted into 15 mL PP-tubes. To concentrate the samples to 1 mL, a nitrogen evaporat (N-EVAP$_{TM}$112) was used. The final step of the extraction of the water samples was to add 10 µL of an injection standard (200 pg µL^{-1}) into the samples before the instrumental analysis of PFASs using a liquid chromatography-mass-spectrometry (HPLC-MS/MS).

3.5.3 Instrument analysis

The 1 mL sample extracts from both water and passive samplers were analyzed according to the method described by Ahrens et al. (2009). For the analysis of PFASs a high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS) was used.

4 RESULTS

4.1 LABORATORY CALIBRATION OF PASSIVE SAMPLERS

The two passive sampler types, POCIS WAX and POCIS HLB, were characterized for 14 PFASs in a laboratory calibration study over 28 days. The calibration study showed that for POCIS WAX, only two PFASs (PFBA and PFTeDA) had reached equilibrium after 28 days (Figure 6). PFBA and PFTeDA were also the two compounds that were taken up the least by the passive samplers. All other PFASs appeared to be in the linear uptake phase after 28 days. The standard deviation of the duplicate samples was generally low with an average standard deviation for all PFASs of 15%, 15%, 11%, 38%, 10%, 22% and 16% for the days 0, 2, 4, 7, 14, 21 and 28, respectively. For PFBA, FOSA, PFBS, PFHxS and PFOS the accumulated amount had a dip at day 21 (6%, 2%, 9%, 3% and 9% less, compared to day 14), but the standard deviation of the accumulated amount was within the normal range of analytical error. The standard deviation for sampling day 7 were the highest (20–51%).

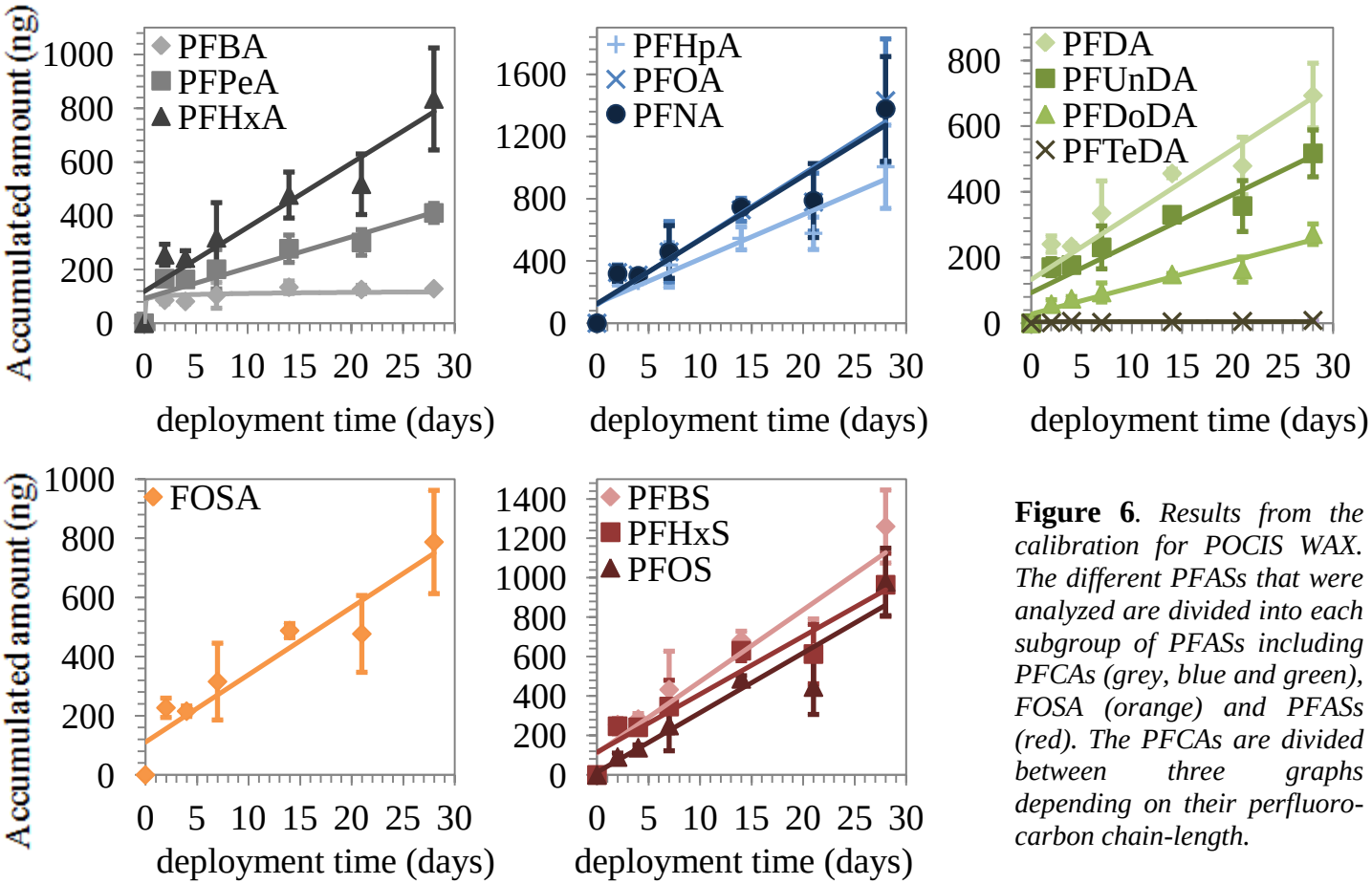


Figure 6. *Results from the calibration for POCIS WAX. The different PFASs that were analyzed are divided into each subgroup of PFASs including PFCAs (grey, blue and green), FOSA (orange) and PFASs (red). The PFCAs are divided between three graphs depending on their perfluoro-carbon chain-length.*

The calibration study showed that for POCIS HLB only three PFASs (PFBA, PFPeA and PFTeDA) had reached equilibrium after 28 days (Figure 7). All other PFASs appeared to be in the linear uptake phase after 28 days. The standard deviation of the duplicate samples was generally low with an average standard deviation for all PFASs of 16%, 12%, 25%, 22%, 25%, 42% and 12% for the days 0, 2, 4, 7, 14, 21 and 28, respectively. For PFPeA and PFHxA the accumulated amount had a dip at day 21 (35% and <1% less, compared to day 14), but the standard deviation of the accumulated

amount was, despite being the highest (3-66%), within the normal range of analytical error.

For the short-chained PFASs (PFBA, PFPeA and PFHxA) the accumulated amount in the POCIS HLB was much less (up to 0.5, 58, and 373 ng absolute, respectively after 28 days) compared to the accumulated amount in the POCIS WAX (up to 134, 410 respectively 834 ng absolute, respectively). For all the other compounds, the accumulated amount in the POCIS HLB was in the same range as for the POCIS WAX.

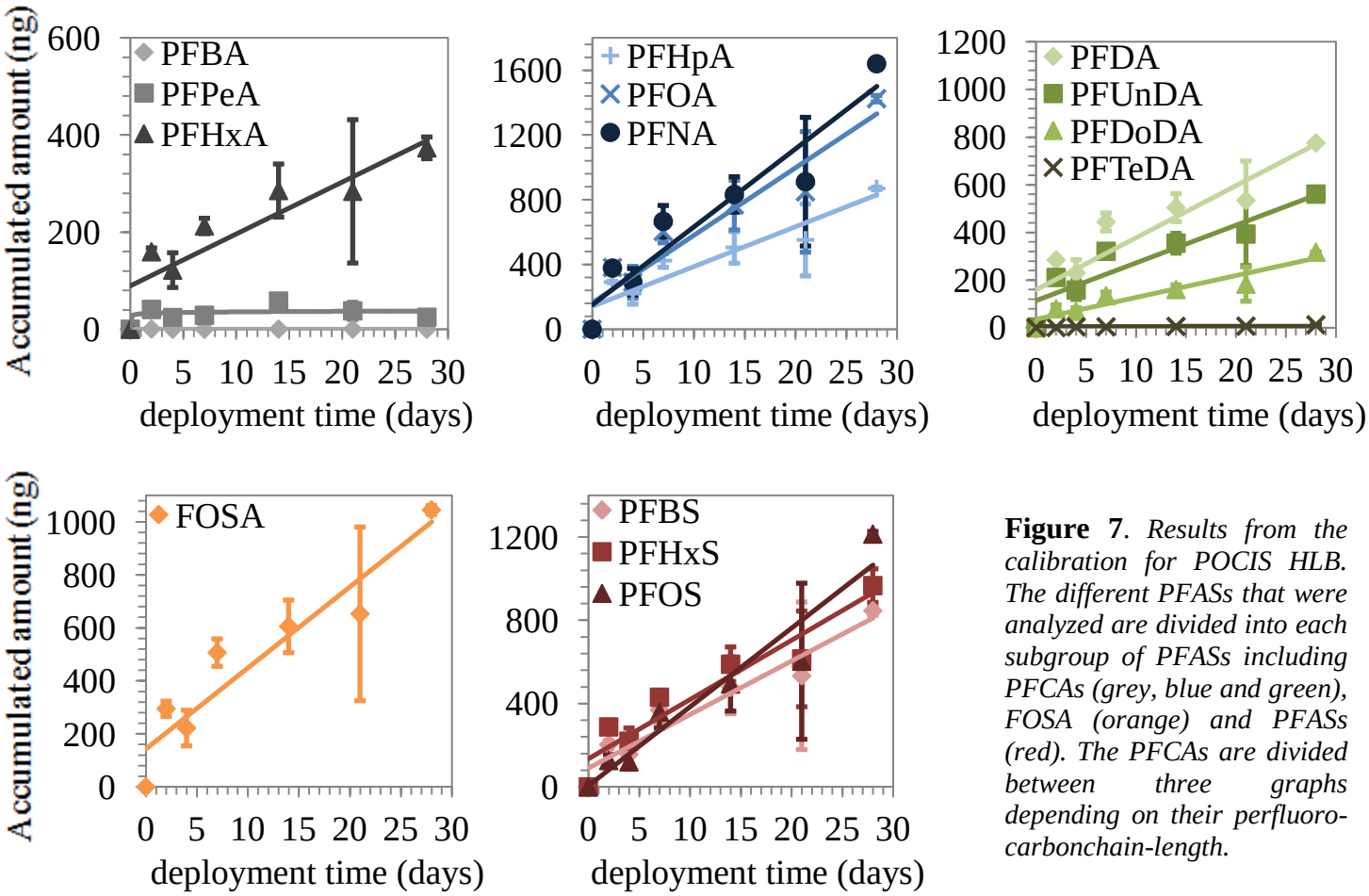


Figure 7. *Results from the calibration for POCIS HLB. The different PFASs that were analyzed are divided into each subgroup of PFASs including PFCAs (grey, blue and green), FOSA (orange) and PFASs (red). The PFCAs are divided between three graphs depending on their perfluoro-carbonchain-length.*

The concentration in tank 1 (c_{water}), the volume of water taken up by the passive sampler (V_{Eq}), the amount of PFAS collected in the passive sampler (m_p) and the ratio of amount of PFAS in the water over in the passive sampler (m_{wp}) are summarized in (Table 2). The average concentration for individual PFASs in tank 1 (with the passive samplers) ranged between 60–648 ng L^{-1} (Table 2). The average concentration for all PFASs in tank 1 was 425 ng L^{-1}, which was close to the concentration the calibration was aimed for (i.e. 500 ng L^{-1}). During the whole calibration study, the concentration for all PFASs was kept close constant, with a slight increase of concentration during the last days of the calibration study (average of 425 ng L^{-1} for the ∑PFASs with an average standard deviation of 17%) (Appendix B, Figure B1). The concentration for individual PFASs in tank 2 was close to the expected value of 1000 ng L^{-1} (Appendix B, Figure B2). The exception was for the long-chained PFASs (PFUnDA, PFDoDA and PFTeDA and FOSA) where the concentration was about 500, 200, 60 respectively 300 ng L^{-1}. The

concentration for PFBS exceeded the expected concentration and was as high as 1300 ng L^{-1}.

The R_s-values for POCIS WAX ranged between 0.003 and 0.10 L day^{-1} (Table 2). An increasing trend (0.003–0.070 L day^{-1}) for R_s could be seen with increasing perfluorocarbon chain length for the short-chained PFCAs (C_3–C_8). Similar R_s-values could be seen for the long-chained PFCAs (C_9–C_{11}, mean R_s-value of 0.034 L day^{-1}) with the exception of PFTeDA (C_{13}) that had a much lower R_s-value (0.0066 L day^{-1}). For the PFSAs, an increasing trend (0.040–0.071 L day^{-1}) could be seen with increasing perfluorocarbon chain length (C_4–C_8). For the PFASs with the same perfluorocarbon chain length of 8 (PFNA, PFOS and FOSA), FOSA had the highest R_s-value followed by PFOS and PFNA (0.1, 0.071, and 0.070 L day^{-1}, respectively). For the PFASs with the perfluorocarbon chain length of 4 (PFPeA and PFBS), PFBS (0.04 L day^{-1}) had the higher R_s-value compared to PFPeA (0.01 L day^{-1}). For the PFASs with the same perfluorocarbon chain length of 5 (PFHxA and PFHxS), PFHxS (0.05 L day^{-1}) had the higher R_s-value compared to PFHxA (0.03 L day^{-1}).

For POCIS HLB, the R_s-values ranged between 0.00052 and 0.13 L day^{-1} (Table 2). Similar to POCIS WAX, an increasing trend (0.00052–0.077 L day^{-1}) for R_s could be seen with increasing perfluorocarbon chain length for the short-chained PFCAs (C_3–C_8). Similar R_s-values could be seen for the long-chained PFCAs (C_9–C_{11}, mean value of 0.038 L day^{-1}), with the exception of PFTeDA (C_{13}) that had a much lower R_s-value (0.010 L day^{-1}). For the PFSAs, an increasing trend (0.028–0.088 L day^{-1}) could be seen with an increasing perfluorocarbon chain length (C_4–C_8). For the PFASs with the same perfluorocarbon chain length of 8 (PFNA, PFOS and FOSA), FOSA had the highest R_s-value followed by PFOS and PFNA (0.13, 0.088, and 0.077 L day^{-1}, respectively). For the PFASs with the perfluorocarbon chain length of 4 (PFPeA and PFBS), PFBS (0.03 L day^{-1}) had the higher R_s-value compared to PFPeA (0.0003 L day^{-1}). For the PFASs with the same perfluorocarbon chain length of 5 (PFHxA and PFHxS), PFHxS (0.05 L day^{-1}) had the higher R_s-value compared to PFHxA (0.01 L day^{-1}).

The K_{pw}-values for POCIS WAX ranged between 661 and 12 540 L kg^{-1} (Table 2). An increasing trend (926–7193 L kg^{-1}) for K_{pw} could be seen for the short-chained PFCAs with increasing perfluorocarbon chain length (C_3–C_8). An increasing trend (4232–6235 L kg^{-1}) could also be seen for long-chained PFCAs (C_9–C_{11}) with the exception of PFTeDA (C_{13}) that had a much lower K_{pw}-value (661 L kg^{-1}). For the PFSAs an increasing trend (4899–6315 L kg^{-1}) could be seen with an increasing perfluorocarbon chain length (C_4–C_8). For the PFASs with the same perfluorocarbon chain length of 8 (PFNA, PFOS and FOSA), FOSA had the highest K_{pw}-value followed by PFNA and then PFOS (12 540, 7193, and 6315 L kg^{-1}, respectively). For the PFASs with the perfluorocarbon chain length of 4 (PFPeA and PFBS), PFBS (4866 L kg^{-1}) had the higher K_{pw}-value compared to PFPeA (2318 L kg^{-1}). For the PFASs with the same perfluorocarbon chain length of 5 (PFHxA and PFHxS), PFHxS (5523 L kg^{-1}) had the higher K_{pw}-value compared to PFHxA (4607 L kg^{-1}).

For POCIS HLB the K_{pw}-values ranged between 0.42 and 22 240 L kg^{-1} (Table 2). Similar to POCIS WAX, an increasing trend (0.42-13 982 L kg^{-1}) for K_{pw} could be seen for the short-chained PFCAs with increasing perfluorocarbon chain length (C_3–C_8). A decreasing trend (7424-1789 L kg^{-1}) could be seen for long-chained PFCAs (C_9–C_{11}). For the PFSAs, an increasing trend (4953-14 278 L kg^{-1}) could be seen with increasing

perfluorocarbon chain length (C_4–C_8). For the PFASs with the same perfluorocarbon chain length of 8 (PFNA, PFOS and FOSA), FOSA had the highest K_{pw}-value followed by PFOS and then PFNA (22 204, 14 278 and 13 982 L kg^{-1}, respectively). For the PFASs with the perfluorocarbon chain length of 4 (PFPeA and PFBS), PFBS (4953 L kg^{-1}) had the higher K_{pw}-value compared to PFPeA (171 L kg^{-1}). For the PFASs with the same perfluorocarbon chain length of 5 (PFHxA and PFHxS), PFHxS (8524 L kg^{-1}) had the higher K_{pw}-value compared to PFHxA (2766 L kg^{-1}).

A comparison between the values for R_s and for K_{pw} showed a positive linear relation for POCIS WAX (R^2 = 0.89) and POCIS HLB (R^2 = 0.99) (Figure 8). A positive relation between R_s and K_{pw} indicates that the uptake is sorbent-phased controlled (Kaserzon et al., 2012). The uptake is therefore not as affected by environmental conditions as a sampler with a membrane-controlled uptake.

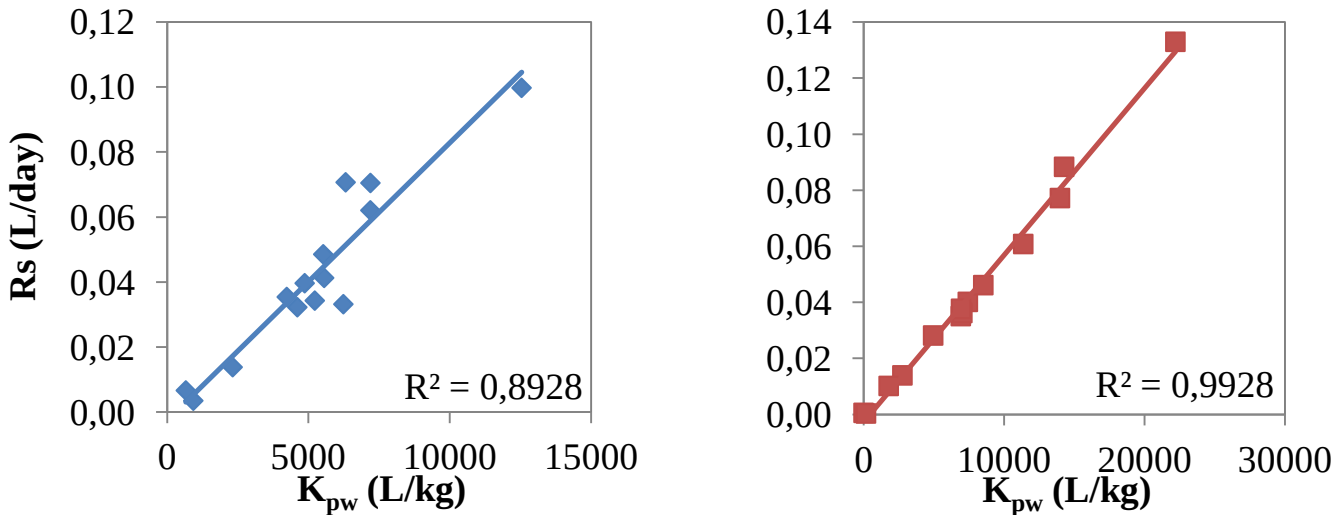


Figure 8. *Plot of sampling rate (R_s in L day^{-1}) versus adsorbent-water sorption coefficient (K_{pw} in L kg^{-1}) for POCIS WAX (left, blue) and POCIS HLB (right, red).*

Table 2. Summary of results for the calibration study including concentration in tank 1 (c_{water}), volume of water taken up by the passive sampler (V_{Eq}), amount of PFAS collected in the passive sampler (m_p), the ratio of amount of PFAS in water over amount of PFAS in passive sampler (m_{wp}), the sampling rate (R_s), the adsorbent water sorption coefficient (K_{pw}) and the half-life time ($t_{1/2}$).

Compound	c_{water}[a] (ng L^{-1})	V_{Eq}[b] (L)	m_p[c] (ng)	m_{wp}[d] (ng ng^{-1})	R_s[e] (L $days^{-1}$)	K_{pw}[f] (L kg^{-1})	log K_{pw} (L kg^{-1})	$t_{1/2}$[g] (days)
POCIS WAX								
PFBA	552	0.19	128	$0.64 \cdot 10^{-6}$	0.003	926	2.97	37
PFPeA	586	0.57	410	$2.05 \cdot 10^{-6}$	0.01	>2318	>3.37	23
PFHxA	548	1.24	834	$4.17 \cdot 10^{-6}$	0.03	>4607	>3.66	20
PFHpA	513	1.60	1005	$5.03 \cdot 10^{-6}$	0.041	>5555	>3.74	19
PFOA	501	2.28	1430	$7.15 \cdot 10^{-6}$	0.062	>7191	>3.86	16
PFNA	483	2.35	1377	$6.88 \cdot 10^{-6}$	0.070	>7193	>3.86	14
PFDA	403	1.33	693	$3.46 \cdot 10^{-6}$	0.035	>4232	>3.63	17
PFUnDA	357	1.30	517	$2.58 \cdot 10^{-6}$	0.034	>5223	>3.72	21
PFDoDA	249	1.19	271	$1.36 \cdot 10^{-6}$	0.033	>6235	>3.79	26
PFTeDA	60.0	0.25	8.36	$0.04 \cdot 10^{-6}$	0.0066	661	2.82	14
FOSA	283	3.35	788	$3.94 \cdot 10^{-6}$	0.10	>12540	>4.10	17
PFBS	648	1.48	1260	$6.30 \cdot 10^{-6}$	0.040	>4866	>3.69	17
PFHxS	439	1.70	965	$4.82 \cdot 10^{-6}$	0.049	>5523	>3.74	16
PFOS	324	2.30	979	$4.90 \cdot 10^{-6}$	0.071	>6315	>3.80	12
POCIS HLB								
PFBA	552	0.00008	0.12	$0.0003 \cdot 10^{-6}$	0.00052	0.42	-0.37	0.11
PFPeA	586	0.034	24.3	$0.22 \cdot 10^{-6}$	0.0003	171	2.23	78
PFHxA	548	0.55	389	$1.87 \cdot 10^{-6}$	0.014	>2766	>3.44	28
PFHpA	513	1.38	875	$4.35 \cdot 10^{-6}$	0.035	>6923	>3.84	27
PFOA	501	2.27	1438	$7.12 \cdot 10^{-6}$	0.061	>11368	>4.06	26
PFNA	483	2.80	1634	$8.20 \cdot 10^{-6}$	0.077	>13982	>4.15	25
PFDA	403	1.48	773	$3.88 \cdot 10^{-6}$	0.040	>7424	>3.87	26
PFUnDA	357	1.41	557	$2.80 \cdot 10^{-6}$	0.036	>7032	>3.85	27
PFDoDA	249	1.39	316	$1.59 \cdot 10^{-6}$	0.038	>6941	>3.84	25
PFTeDA	60.0	0.36	12.2	$0.06 \cdot 10^{-6}$	0.010	1789	3.25	24
FOSA	283	4.44	1057	$5.23 \cdot 10^{-6}$	0.13	>22204	>4.35	23
PFBS	648	0.99	862	$4.23 \cdot 10^{-6}$	0.028	>4953	>3.69	24
PFHxS	439	1.70	1024	$4.83 \cdot 10^{-6}$	0.046	>8524	>3.93	26
PFOS	324	2.86	1205	$6.07 \cdot 10^{-6}$	0.088	>14278	>4.15	22

[a]amount of PFAS over volume water that was analyzed
[b]amount of PFAS in passive samplers over concentration of PFAS in water
[c]average amount of PFAS in passive sampler at the end of the calibration
[d]amount of PFAS over amount of adsorbent (200 mg) in passive sampler
[e]see equation 3
[f]see equation 1
> indicates that equilibrium has not been reached
[g]see equation 2

4.2 APPLICATION OF PASSIVE SAMPLERS IN DWTP

At the DWTP, the passive samplers POCIS WAX and POCIS HLB were deployed for two weeks. The average flow rate at the sampling sites was 21 mL s^{-1}, the average pH was 6.7 and the average temperature was 9.6 ^{o}C (Appendix E, table E). The average color was of the water was 6.63 mg L^{-1}, average UV 254 was 0.42 and average total organic carbon (TOC) was 4.42 mg L^{-1} (Appendix E, table E). The POCIS WAX detected 10 out of the 26 analyzed PFASs (PFBA, PFHxA, PFHpA, PFOA, PFDA, PFDoDA, PFTeDA, PFBS, PFHxS and PFOS) throughout the DWTP, both full-scale plant and pilot plant (Figure 9). The POCIS HLB also detected 10 out of 26 analyzed PFASs (PFHxA, PFHpA, PFOA, PFDA, PFUnDA, PFDoDA, PFTeDA, PFBS, PFHxS and PFOS). The grab samples detected 13 out of 26 analyzed PFASs (PFBA, PFHxA, PFHpA, PFOA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, FOSA, PFBS, PFHxS and PFOS).

For the POCIS WAX, the ∑PFAS concentrations ranged between 11 and 17 ng L^{-1} at sampling sites RW, SF, GAC 1 and DW in the full-scale DWTP and at NFP in the pilot plant, whereas no PFASs were detected at sampling sites GAC 2 and GAC 3 in the pilot plant (Figure 9). For the POCIS HLB, the ∑PFAS concentrations ranged between 0.11 and 8.1 ng L^{-1} at sampling sites RW, SF, GAC 1 and DW in the full-scale DWTP as well as at GAC 2 in the pilot plant, whereas no PFASs were detected at site NFP and GAC 3 in the pilot plant. For the grab samples, the ∑PFAS concentrations ranged between 4.8 and 8.7 ng L^{-1} at sampling site RW, SF, GAC 1 and DW in the full-scale DWTP and at NFP and GAC 3 in the pilot plant, whereas no PFASs were detected at site GAC 1 in the pilot plant.

For the POCIS WAX, the PFAS that was detected at the highest concentration was PFBS (average of 34% of the ∑PFASs in both DWTP and pilot plant), followed by PFHxA (23%), PFHxS (14%), PFOA (10%), PFBA (8%), PFHpA (4%), PFOS (4%), PFDA (2%), PFDoDA (<1%) and PFTeDA (<1%) (Appendix C, Table C1). For the POCIS HLB the PFAS that was detected at the highest concentrations in the DWTP was PFHxA (average of 25% of the ∑PFASs in the DWTP) followed by PFHxS (19%), PFBS (18%), PFOA (6%), PFOS (5%), PFDA (4%), PFDoDA (2%), PFTeDA (1%), PFHpA (<1%), PFUnDA (<1%). For the pilot-plant only PFTeDA was detected by the POCIS HLB. For the grab samples the PFAS that was detected at the highest concentrations was PFBS (35% of the ∑PFASs in both DWTP and pilot plant), followed by PFBA (19%), PFOS (16%), PFHxA (6%), PFHxS (6%), PFHpA (<1%), PFUnDA (<1%), PFOA (<1%), PFDA (<1%), PFDoDA (1%), PFTriDA (<1%), PFTeDA (<1%) and FOSA (<1%).

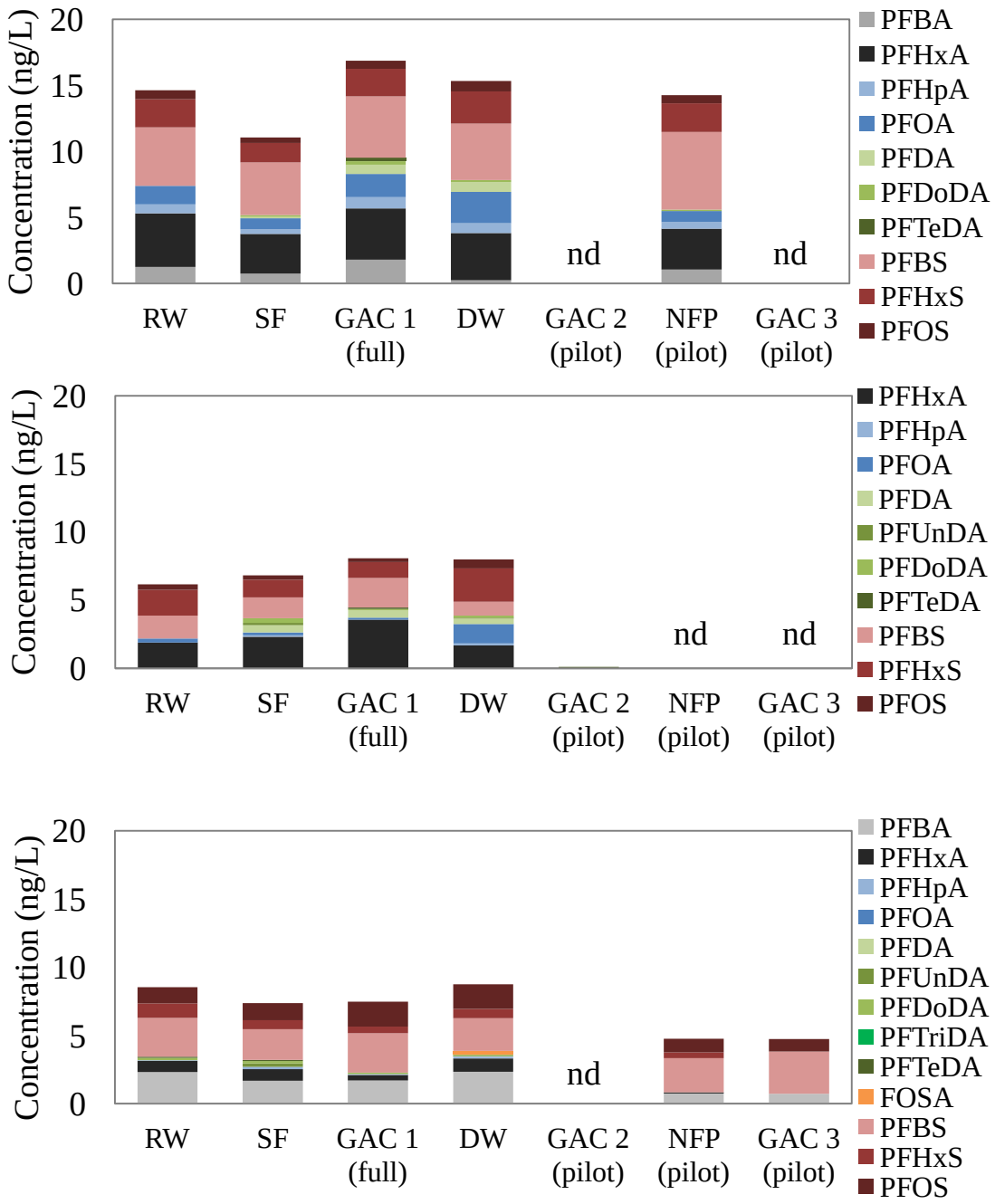


Figure 9. *Amount of PFASs detected by POCIS WAX (top), POCIS HLB (middle) and grab samples (bottom) at the DWTP. RW = raw water, SF = after sand filtrate, GAC 1 (full) = after GAC filtrate in the full-scale DWTP, DW = drinking water, GAC 2 (pilot) = after GAC filtrate in pilot plant, NFP (pilot) = after nanofiltration in pilot plant, GAC 3 (pilot) = after both nanofiltration and GAC filtrate in pilot plant (see Figure 4) and nd = not detected*

4.2.1 Comparison between passive samplers and between passive and grab sampling

A comparison was made between the TWA concentrations of POCIS WAX and POCIS HLB as well as the passive samplers and grab samples (Figure 10). Overall, the ∑PFAS concentrations in POCIS WAX were approximately 40% higher (11-15 ng L^{-1}) compared to POCIS HLB (0.11-8.1 ng L^{-1}) and approximately 60% higher compared to the grab samples (4.8-8.8 ng L^{-1}).

Both passive samplers detected 10 out of 26 PFASs during the application. However, POCIS WAX did not detect PFUnDA while POCIS HLB detected levels of PFUnDA in the SF and in the drinking water. Further, POCIS HLB did not detect PFBA anywhere in the DWTP or in the pilot plant while POCIS WAX detected PFBA in raw water, SF, GAC 1 and drinking water in the DWTP as well as in the NFP in the pilot plant. The grab samples detected 13 out of 26 PFASs during the application. Compared with the passive samplers the grab samples detected PFOA, PFTriDA and FOSA in addition at the DWTP. The number of detected PFASs also differed between the different sampling sites. The POCIS WAX did not detect PFASs at GAC 2 and GAC 3 in the pilot plant while at the NFP, 8 out of 26 PFASs (PFBA, PFHxA, PFHpA, PFOA, PFDoDA, PFBS, PFHxA and PFOS) were detected. The POCIS HLB did not detect PFASs at the NFP or at GAC 3 in the pilot plant while in the GAC 2 levels of PFTeDA were detected in the pilot plant. For the grab samples, levels of PFAS were detected at all sampling sites except GAC 2 and compared to the passive samplers the grab samples detected levels of PFBA, PFBS and PFOS in GAC 3.

From the total concentration of PFASs a comparison was made between the TWA concentration in the passive samplers and the grab samples at the DWTP (Figure 10). The comparison did not show any trend for the PFAS concentration in the grab samples compared to POCIS WAX (R^2 = 0.24) and POCIS HLB (R^2 = 0.10) (Figure 10). Furthermore, a comparison was made between the TWA concentrations of the two passive samplers from all the sampling sites and a good correlation (R^2 = 0.63) was found (Figure 10).

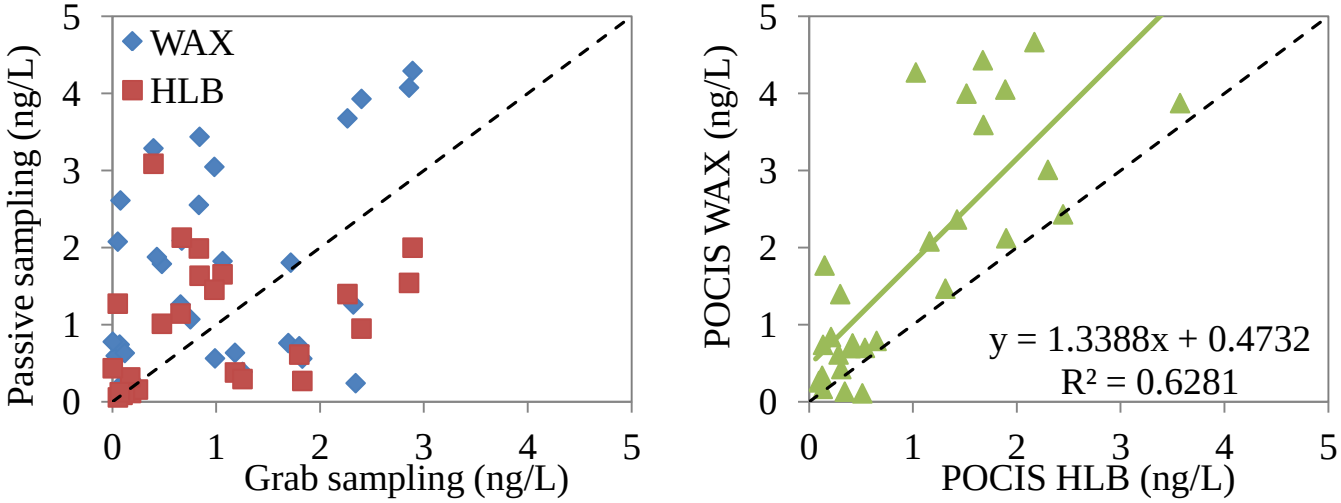


Figure 10. *Comparison between total concentration in water (ng L^{-1}) for passive sampling and grab sampling for drinking water at the DWTP (left) and for the two passive samplers and all sampling sites (right). The dotted 1:1 line represents a perfect agreement.*

4.2.2 Removal efficiency of PFASs in the DWTP

The removal efficiency was calculated in the DWTP using POCIS WAX (Table 3), POCIS HLB (Appendix D, Table D1) and grab samples (Appendix D, Table D2). In the full-scale DWTP (RW to DW), the average removal efficiency of all analyzed PFASs was 32%. High removal efficiency was observed for PFBA (81%), whereas the removal efficiency was lower for PFHxA (11%) and PFBS (4%). PFHpA, PFOA, PFHxS and PFOS were not removed in the full-scale DWTP. For the pilot plant, the removal efficiency was 100% removal for all the detected compounds in the raw water (PFBA, PFHxA, PFHpA, PFOA, PFBS, PFHxA and PFOS).

Table 3. Removal efficiency (%) at the DWTP for the PFASs that were detected by the POCIS WAX.

Compound	RW to DW (full-scale DWTP)[a]	RW to GAC 2 (pilot plant)[a]	RW to GAC 3 (pilot plant)[a]
PFBA	81	100	100
PFHxA	11	100	100
PFHpA	NR[b]	100	100
PFOA	NR[b]	100	100
PFDA	NC[c]	NC[c]	NC[c]
PFDoDA	NC[c]	NC[c]	NC[c]
PFTeDA	NC[c]	NC[c]	NC[c]
PFBS	4	100	100
PFHxS	NR[b]	100	100
PFOS	NR[b]	100	100

[a]RW = raw water; DW = drinking water, GAC = granulated activated carbon (see Figure 4).
[b]NR = no removal.
[c]NC = not able to calculate because PFASs were not detected in raw water but detected at other sampling sites.

5 DISCUSSION

5.1 LABORATORY CALIBRATION OF PASSIVE SAMPLERS

In the current study, only two PFASs for the POCIS WAX (PFBA and PFTeDA) and three PFASs for the POCIS HLB (PFBA, PFPeA and PFTeDA) reached equilibrium during the calibration. All other PFASs were still in the linear uptake phase. The PFASs that reached equilibrium (PFBA and PFTeDA for POCIS WAX and PFBA, PFPeA and PFTeDA for POCIS HLB) had low accumulated amounts after 28 days (134 and 8.4 ng absolute, respectively and 0.35, 387 and 12 ng absolute, respectively) compared to the other studied PFASs (average of 877 for POCIS WAX and 921 ng absolute for POCIS HLB, respectively).

Kaserzon et al. (2012) performed a calibration study for 7 different PFASs (PFHxA, PFHpA, PFOA, PFDA, PFBS and PFOS) using POCIS with 600 mg using Strata XAW (Phenomenex, Sydney, Australia). Strata XAW is a weak anion exchange sorbent with similar characteristics compared to WAX and found trends for the uptake which were similar to the POCIS WAX and POCIS HLB in this study. Kaserzon et al. (2012) found that the short-chained PFASs (C_4 to C_6) reached their half-life/equilibrium faster by a factor of 1.2-1.8 compared to the long-chained PFASs (C_7 to C_{10}). This trend was also observed by a later study by Kaserzon et al. (2013) where nine PFASs (PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFHxS, and PFOS) were studied. For the short-chained PFCAs (PFPeA, PFHxA and PFHpA) equilibrium was reached after 15 days, while for the long-chained PFCAs (PFOA to PFUnDA) were still in the linear uptake phase as well as were the PFSAs after 15 days (Kaserzon et al., 2013).

In this study, the trends for the R_s-values were similar for both passive samplers in the calibration study. For the short-chained PFCAs there was an increasing trend with increasing perfluorocarbon chain length (C_3-C_8). For the long-chained PFCAs (C_9-C_{11}) the R_s-values were similar (in average 0.036 L day^{-1}), and for PFTeDA (C_{13}) the R_s-value was very low (in average 0.0084 L day^{-1}). For the PFSAs there was an increasing trend with increasing perfluorocarbon chain length (C_4-C_8). For the PFASs with a carbon-chain length of 8 (i.e. PFNA, PFOS, FOSA), FOSA had the highest R_s (0.10 and 0.13 L day^{-1} for POCIS WAX and POCIS HLB). A similar trend for R_s (with the flow rate of 0.06 m s^{-1}) and the short-chained PFCAs could be seen by Kaserzon et al. (2013). For PFCAs with a perfluorocarbon chain length of C_4-C_6 the R_s-values ranged from 0.11-0.20 (Kaserzon et al., 2013). No trend was seen for the long-chained PFCAs (C_7-C_9) (average R_s-value 0.18 L day^{-1}), with the exception of PFUnDA where the R_s-value was the highest (0.22 L day^{-1}). The increasing trend for the PFSAs was not confirmed, but there was an indication of a decreasing trend with increasing perfluorocarbon chain (C_4-C_8) and (C_6-C_8) with 0.37-0.36 and 0.21-0.17, respectively (Kaserzon et al., 2012; Kaserzon et al., 2013).

The trends that could be seen from the calibration study for K_{pw} were similar as was seen by Kaserzon et al. (2012) with one exception. For the short-chained PFCAs there was an increasing trend with increasing perfluorocarbon chain length (C_5-C_7) from 2036 to 5106 L kg^{-1} (Kaserzon et al., 2012) similar to this study (4607-7191 L kg^{-1} for POCIS WAX and 2766-11 368 L kg^{-1} for POCIS HLB). For the long-chained PFCAs (C_8-C_9) there was an decreasing trend of the K_{pw} with increasing perfluorocarbon chain length for the POCIS WAX (7193-4232 L kg^{-1}) and for the POCIS HLB (13 982-7424 L kg^{-1}). The decreasing trend was also observed by Kaserzon et al. (2012) for PFCAs (C_8-C_9)

and the POCIS Strata XAW (2986-2139 L kg^{-1}). For the PFSAs, there was an increasing trend (1909-2034 L kg^{-1}) with increasing perfluorocarbon chain length (C_4-C_8) observed by Kaserzon et al., 2012, which was also seen by the POCIS WAX (4866-6315 L kg^{-1}) and the POCIS HLB (4953-14 248 L kg^{-1}) in this study. For the PFASs with a perfluorocarbon-chain length of 8, Kaserzon et al. (2012) had a higher K_{pw} for PFNA compared to PFOS (2968 and 2064 L kg^{-1}) which was also seen in this study for the POCIS WAX (6315 and 7193 L kg^{-1}). However, for the POCIS HLB, PFOS had a higher K_{pw} compared to PFNA (14 278 and 13 982 L kg^{-1}).

5.1.1 Uptake of PFASs influenced by the functional group and perfluorocarbon chain length

The uptake of PFASs compared to their functional group and perfluorocarbon chain length is shown in Figure 11. For the POCIS WAX, the accumulated amount for the PFCAs against their perfluorocarbon chain length showed an increasing trend until PFOA with a perfluorocarbon chain length of 7 after which it decreased (Figure 11). For the PFSAs the uptake decreased with an increase of the perfluorocarbon chain length. In comparison between PFSAs and PFCAs, PFBS (C_4) had by a factor of 3 higher uptake compared to PFPeA (C_4) whereas PFHpA (C_6) had a similar uptake compared to PFHxS (C_6) (1005 and 965 ng, respectively). However, a comparison between PFNA (C_8), PFOS (C_8) and FOSA (C_8) showed by a factor of 1.4 and 1.7 higher uptake for PFNA compared to PFOS and FOSA, respectively. In its turn, PFOS had by a factor of 1.2 higher uptake than FOSA. This indicates that the chain length and functional group have an influence on the uptake of PFASs. However, Kaserzon et al. (2013) found no significant relationship between the response ratio (i.e. divided accumulated amount in POCIS at 0.34 m s^{-1} by accumulated amount in POCIS at 0.02 m s^{-1}) and the molar mass (i.e. perfluorocarbon chain length).

For the POCIS HLB the accumulated amount for the PFCAs against their perfluorocarbon chain length showed an increasing trend up until PFNA with a perfluorocarbon chain length of 8 after which it decreased (Figure 11). For the PFSAs the uptake increased with an increase of the perfluorocarbon chain length. In comparison between PFSAs and PFCAs, PFBS (C_4) had by a factor of 34 higher uptake compared to PFPeA (C_4). This is an indication that for short-chained PFASs the POCIS HLB adsorbs sulfunic groups to a much greater extent than carboxylic groups. However, a comparison between PFHpA (C_6) and PFHxS (C_6) showed a similar uptake (870 and 967 ng, respectively) and a comparison between PFNA (C_8), PFOS (C_8) and FOSA (C_8) showed a higher uptake by a factor of 1.4 and 1.6 for PFNA compared to PFOS and FOSA, respectively. In its turn, PFOS had a higher uptake by a factor of 1.2 than FOSA. This indicates that the chain length and functional group have an influence on the uptake of PFASs.

For the POCIS WAX and the POCIS HLB, the overall uptake was comparable for the same compound in both of the passive samplers, with some exceptions. For the short-chained PFCAs (C_3 to C_6), POCIS WAX had by a factor of 1.9 higher (128-1005 ng absolute after 28 days) uptake compared to the POCIS HLB (0.06-870 ng absolute) (Figure 11). This indicates that the POCIS WAX adsorbs the short-chained PFCAs to a greater extent than the POCIS HLB. For the long-chained PFCAs (C_7 to C_{11}), both adsorbents (WAX and HLB) showed similar values for the uptake and both had very low uptake for PFTeDA (C_{13}, 8.4 ng and 12 ng absolute, respectively). It could be an indication that both adsorbents have a low capacity to collect compounds with a chain-

length longer than 13 perfluorocarbons. For the PFSAs, the two passive samplers showed opposite trends. For POCIS WAX the uptake decreased slightly with an increase of the carbon chain length while for POCIS HLB it increased slightly with an increasing carbon chain length. The POCIS WAX had by a factor of 1.5 higher uptake for PFBS (C_4) but by a factor of 1.2 lower uptake of PFOS (C_8) compared to the POCIS HLB. For FOSA, the POCIS HLB had a higher uptake by a factor of 1.3 than the POCIS WAX. Kaserzon et al. (2012) came to the conclusion that the POCIS HLB might be suitable for sampling long-chained PFASs but not for short-chained PFASs. The POCIS HLB has therefore a disadvantage in comparison with a modified POCIS (600 mg Strata XAW) (Kaserzon et al., 2012). This is in agreement with this study showing higher uptake for the long-chained PFASs for the POCIS HLB compared to the POCIS WAX, but a lower uptake for the short-chained PFAS.

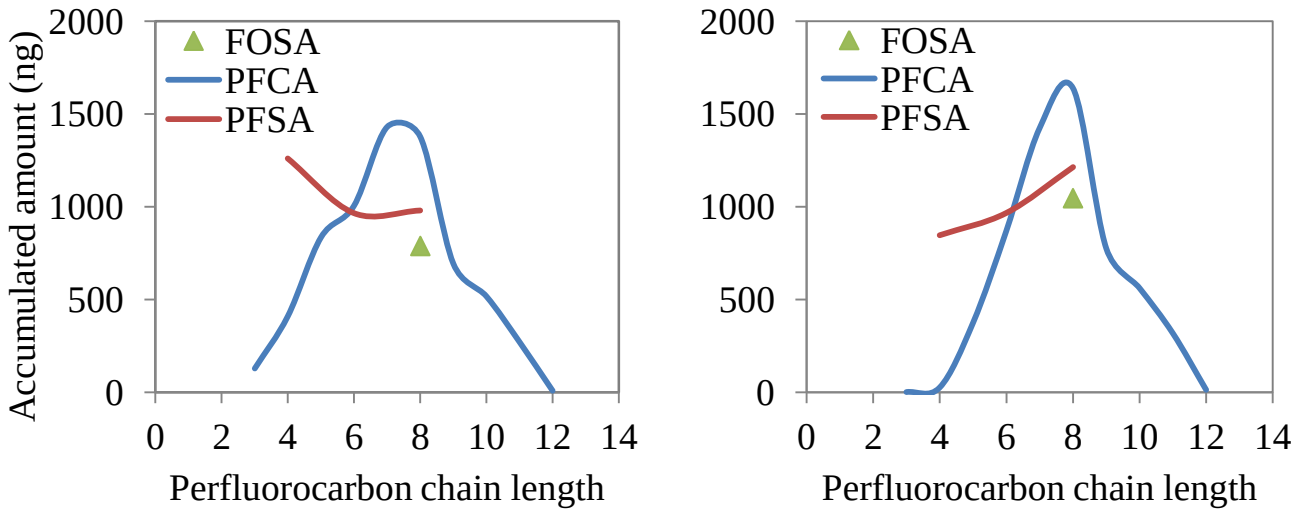


Figure 11. *Comparison of uptake at the last day of the calibration against the perfluorocarbon chain length for POCIS WAX (left) and for POCIS HLB (right). The results are divided between the different subgroups of PFASs, PFCAs (blue), PFSAs (red) and FOSA (green).*

5.1.2 Uptake of PFASs influenced by the log K_{ow}

Along with the functional group and the perfluorocarbon chain length, the log K_{ow} may also affect the uptake in the passive samplers. Overall, the log K_{ow} values for PFASs increase with an increasing perfluorocarbon chain length (Table 1). A comparison with log K_{ow} and the accumulated amount as well as with the perfluorocarbon chain-length showed similar results for the uptake (Figure 12). However, the log K_{ow} values can clarify why the long-chained PFASs have low uptakes. The higher the value of the log K_{ow}, the more hydrophobic the compound is. This can explain why PFTeDA (C_{13} and a log K_{ow} value of 7.05) had a very low uptake, since POCIS WAX nor POCIS HLB had the capacity to absorb hydrophobic compounds to a great extent. The observation of that the longer-chained PFASs have lower uptakes compared to the short-chained is in line with the restrictions of the POCIS in general with an operating interval for log K_{ow}-values between 0 and 4 (Alvarez et al., 2004; Fauvelle et al., 2012). In this study it can be argued the operational interval for POCIS WAX is for log K_{ow}-values between 0 and 7, and for POCIS HLB between 2 and 6. However, the uncertainty in the values for the log K_{ow} values needs to be taken into account when comparing with the uptake (Du et al., 2014; Kim et al., 2014). Further, Li et al. (2010b) did not find a relationship between the response ratios and log K_{ow} values for pesticides, pharmaceuticals and personal care

products. Kaserzon et al. (2013) did not find a correlation between log K_{ow} and uptake of PFASs.

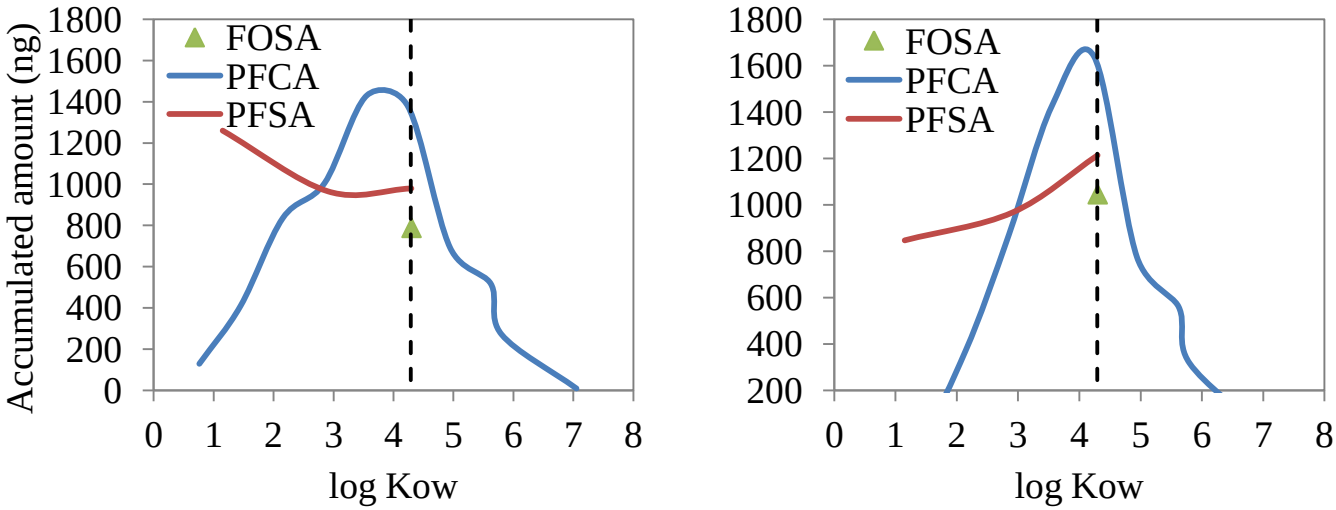


Figure 12. *Comparison between uptake at the last day for the calibration study against log K_{ow} values for POCIS WAX (left) and POCIS HLB (right). The results are divided between the different subgroups of PFASs, PFCAs (blue), PFSAs (red) and FOSA (green). The dashed black line in both graphs represents the mean log K_{ow} value for PFNA, PFOS and FOSA (all with a perfluorocarbon chain length of 8).*

5.2 APPLICATION OF PASSIVE SAMPLERS IN A DWTP

The application of the passive samplers in the DWTP showed that both POCIS WAX and POCIS HLB could detect ultra-trace levels of PFASs. However, the results differed between the two passive samplers and with the corresponding grab samples. In general, the POCIS WAX showed a TWA concentration twice as high as both the POCIS HLB and grab sample (Figure 13). The passive samplers and grab samples also detected different PFASs at the different sampling sites. FOSA and PFTriDA were only found in the grab samples from the drinking water. The comparison between conventional grab samples and passive sampling showed no linear correlation (R^2 = 0.24 for POCIS WAX and R^2 = 0.10 for POCIS HLB). However, the true concentration of PFASs is unknown. Kaserzon et al. (2012) had a field deployment (in Homebush Bay, Sidney, Australia) with a good agreement between grab samples (0.25 ng L^{-1}) and passive sampling (0.1-12 ng L^{-1}) for a 7 day exposure time. Further Kaserzon et al. (2012) had no significant difference between their POCIS with 600 mg Strata XAW and a standard POCIS with 200 mg HLB.

The difference in concentration between the passive samplers and the grab samples should not be disconcerting for the applicability of the samplers in the future. Other studies have used passive sampling and the POCIS successfully in field application. Bailly et al. (2013) successfully deployed the POCIS to monitor pharmaceuticals in hospital wastewater and found a good correlation with 24 hour composite samples. Fedorova et al. (2012) deployed both the POCIS HLB and a pesticide POCIS in a WWTP for monitoring levels of PFASs and detected 10 out 15 PFASs. Harman et al. (2011) deployed successfully the POCIS to monitor levels of illicit drugs in wastewater. Li et al (2010a) found good correlation between deployed POCIS HLB and grab samples for a field deployment in Lake Ontario, Canada for phamaceuticals and personal care products and edocrine-disrupting substances. These are just a few

examples of where the POCIS have been successfully used for monitoring levels of contaminants in water. Further, Metcalfe et al. (2014) did a similar field deployment of POCIS in a DWTP as in this study. Metcalfe et al. (2014) had sampling sites in the raw water and in the finished drinking water and found seven out of seven indicator compounds (carbamazepine, trimethoprim, sulfamethoxazole, ibuprofen, gemfibrozil, estrone and sucralose) in the raw water and six out of seven in the drinking water. Metcalfe et al. (2014) found a good correlation between the TWA concentrations from the passive samplers and grab samples. Metcalfe et al. (2014) conclude that the POCIS is a useful technique for monitoring contaminants in water and that concentration in grab samples typically were below the detection level whilst the POCIS showed TWA concentration above the detection limit. With this in mind, the POCIS can be applicable for monitoring levels of contaminants in a DWTP, but further studies are needed to understand how the uptake mechanisms work between the POCIS and the contaminant.

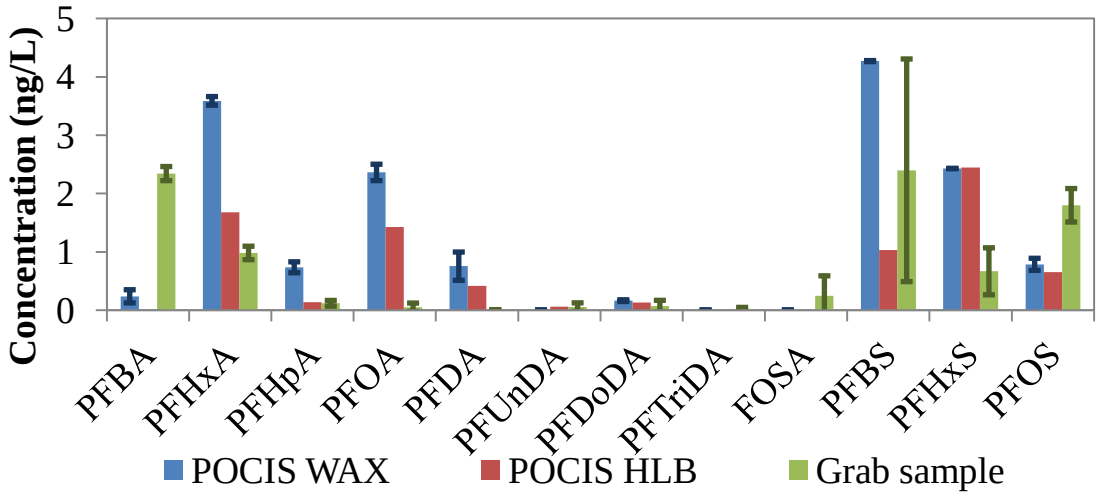


Figure 13. *Comparison between TWA concentrations of detected PFASs for POCIS WAX and POCIS HLB as well as concentrations from corresponding grab sample from drinking water at the DWTP.*

The removal efficiency calculated from the TWA concentrations of the POCIS WAX showed that for all the detected PFASs in the raw water a 100% removal was seen in the pilot plant after GAC. This is in line with what other researchers have detected for pilot scale treatments and for new and unused GAC (Eschauzier et al., 2012; Rahman et al., 2014). Takagi et al. (2011) used reactivated GAC and had a removal efficiency for PFOS (close to 90%) and for PFOA (78-85%) in a full-scale DWTP.

In the full-scale DWTP, the removal efficiency (calculated based on the TWA concentrations of the POCIS WAX) was as follows for the PFASs detected in the raw water, PFBS (81%), PFHxA (11%), PFBS (4%), PFHpA (no removal), PFOA (no removal), PFHxA (no removal) and PFOS (no removal). The concentrations of the other PFASs were too low in the raw water to calculate removal efficiencies. This could be because of biofouling of the passive samplers in the raw water after two weeks deployment. Biofouling was only obvious for the passive samplers deployed in the raw water and could also be the reason for why no levels of PFDA, PFDoDA and PFTeDA were detected in the raw water, whilst they were at other sampling sites. Biofouling could also be the cause for the higher levels in the drinking water for PFHpA, PFOA, PFHxS and PFOS compared to the raw water. Takagi et al. (2011) found that for other

DWTPs with the same treatment steps as Gövälnverket had a removal efficiency as follows for PFOS (from no removal up to 60%) and for PFOA (from no removal up to 4%). Eschauzier et al. (2012) had almost the same treatment steps obtained a removal efficiency as follows for PFHxA (70%) and PFBA (9%).

The ∑PFAS concentrations, in drinking water found by using POCIS WAX (15.3 ng L^{-1}), POCIS HLB (7.1 ng L^{-1}) and the grab sampling (7.4 ng L^{-1}) are all well below guidelines from The Swedish National Food Agency of 90 ng L^{-1} for drinking water. The drinking water therefore generates no probable health risk for the consumer. The drinking water concentrations are comparable with other concentrations found in studies around the world, where concentrations of PFOA and PFOS was below 5 ng L^{-1} in most cases (Rahman et al., 2014). However, if the concentration of PFOS in the raw water can be assumed to represent the PFOS concentration in the lake it is well above the EQS of 0.65 ng L^{-1} for surface water set by the European Parliament (Flores et al., 2013).

5.3 FUTURE PERSPECTIVES

During the calibration, the concentration in tank 1 was kept close to the theoretical value of 500 ng L^{-1} with the exception of a slight increase towards the end of the calibration study (Appendix B, Figure B1). A near-constant concentration in the water ensures fewer errors in the calculation of R_s and K_{pw} (Kot-Wasik et al., 2007; Li et al., 2010a). Thus, this calibration set up and method was successful and can be applied for future calibration studies of passive samplers. However, the calibration study showed that for most of the PFASs the passive samplers were still in the linear phase for the uptake. To reach the equilibrium phase in future calibration studies it could be beneficial to let the calibration study go on for longer than 28 days.

Another improvement to be made for the calibration study concerns the extraction of the adsorbent in the passive sampler. The problem that occurred during the disablement of the passive sampler was that the adsorbent powder was still wet and more or less dissolved in water. The wetness of the adsorbent made it hard to transfer it to the cartridge without any loss. If the disablement had been done over a small piece of aluminum foil, the loss of adsorbent could then have been easily collected and transferred to the cartridge if the piece of aluminum had been replaced for every new passive sampler.

Lastly, the grab samples from the calibration study were not filtered before the extraction of PFASs. In retrospect, this should have been done since it is possible that microalgae had grown in the water even though the tanks being covered in aluminum foil to prevent light exposure.

6 CONCLUSIONS

The overall aim was to calibrate and investigate the applicability of the POCIS WAX and POCIS HLB, both with 200 mg of adsorbent, as a sampling method for PFASs in drinking water. In total, 14 different PFASs were used in the calibration study, and it lasted for 28 days. All 14 PFASs had been taken up by the two different passive samplers. However, at the end of the calibration, only PFBA and PFTeDA had reached equilibrium for the POCIS WAX, and only PFBA, PFPeA and PFTeDA had reached equilibrium for the POCIS HLB. The rest of the PFASs were still in the linear uptake phase. The calibration study for the purpose of this study was successful. However, for future studies with an application of more than two weeks it is advised to have a longer time interval for calibration study so that all studied contaminants reach equilibrium.

R_s ranged from 0.003 to 0.1 L day^{-1} for the POCIS WAX and from 0.00052 to 0.13 L day^{-1} for the POCIS HLB. For the PFCAs, R_s increased with increasing perfluorocarbon chain length up until C_8, after which it decreased for both passive samplers. An increasing trend with increasing perfluorocarbon chain length could also be seen for the PFSAs. FOSA showed the highest R_s followed by PFOS and PFNA for the PFASs with the perfluorocarbon chain length of 8. Along with the perfluorocarbon chain length and functional group, the log K_{ow} also affected the uptake in the passive samplers. Overall, the log K_{ow}-values for PFASs increases with an increasing perfluorocarbon chain length. A comparison between the accumulated amount and log K_{ow} showed a prominent decrease of the accumulated amount after the value of 4 for log K_{ow} which represents PFASs with a perfluorocarbon chain length >8. However, the operational interval for log K_{ow} is between 0 and 7 for POCIS WAX and between 2 and 6 for POCIS HLB. For both of the passive samplers, the accumulated amount was similar with the exception of the short-chained PFCAs (C_3-C_5), where POCIS WAX had a much higher uptake (up to 134, 410 and 834 ng, respectively) compared to the POCIS HLB (up to 0.5, 58 and 373 ng, respectively).

The application of the passive samplers at the DWTP showed that both passive samplers could detect ultra-trace levels of PFASs. A comparison of the TWA concentration showed that the two passive samplers were linear correlated (R^2 = 0.63), and that the TWA concentrations derived by POCIS WAX was generally 40% higher compared to POCIS HLB. For the comparison between concentrations in the passive samplers and the grab samples, no correlation could be seen (R^2 = 0.24 for POCIS WAX and R^2 = 0.10 for POCIS HLB). The ∑PFAS concentration throughout the DWTP and pilot plant ranged between 11-15 ng L^{-1} for POCIS WAX, between 0.11-8.1 ng L^{-1} for POCIS HLB. For the grab samples, the ∑PFAS concentration throughout the DWTP and pilot plant ranged between 0 and 8.7 ng L^{-1}. The high concentrations of PFAS in the POCIS WAX for the drinking water (∑PFAS concentration of 15.3 ng L^{-1}) in this study do not exceed the guidelines from The Swedish National Food Agency of 90 ng L^{-1} for the sum of 7 PFASs in drinking water, and the intake of drinking water is most likely no risk for human health.

The application also included a comparison of the removal efficiency in the conventional DWTP and a pilot plant with additional treatments steps of GAC and NF. For the full-scale DWTP the average removal efficiency was 32% and high removal efficiency was observed for PFBA (81%). For the pilot plant, the removal efficiency was 100% removal for all the detected PFASs in the raw water (PFBA, PFHxA, PFHpA, PFBS, PFHxS and PFOS).

More research is needed to understand the uptake mechanisms for both passive samplers and PFASs, in order to understand the uncertainties that come with passive sampling and monitoring levels of PFASs in drinking water. Future studies should let the calibration study go on for longer than 28 days so that equilibrium is reached for all PFASs. Future studies should also focus on the impact of water flow rate and biofouling on the uptake of PFASs. However, the POCIS passive sampler show promise for future applications at DWTPs for monitoring of PFASs.

7 REFERENCES

Ahrens, L., (2011) Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. *Journal of Environmental Monitoring* 13(1), pp. 20-31.

Ahrens, L., Barber, J. L., Xie, Z. and Ebinghaus, R., (2009). Longitudinal and latitudinal distribution of perfluoroalkyl compounds in the surface water of the Atlantic Ocean. *Environmental science & technology*, 43(9), pp. 3122-3127.

Alvarez, D., Petty, J. D., Huckins, J. N., Jones-Lepp, T. L., Getting, D., Goddard, J. P. and Manahan, S. E., (2004). Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. *Environmental Toxicology and Chemistry* 23(7), pp. 1640-1648.

Bailly E., Levi, Y. and Karolak, S., (2013). Calibration and filed evaluation of polar organic compound integrative sampler (POCIS) for monitoring pharmaceuticals in hospital wastewater. *Environmental Pollution* 174, pp. 100-105.

Belles, A., Tapie, N. and Pardon, P., (2014). Development of the performance reference compound approach for the calibration of "polar organic integrative sampler" (POCIS). *Analytical and Bioanalytical Chemistry* 406(4), pp. 1131-1140.

Buck, R. C., Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., de Voogt, P., Jensen, A. A., Kannan, K., Mabury, S. A., and van Leeuween, S. P., Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification and origins. *Integrated environmental assessment and management*, 7(4), pp. 513-541.

Charlestra, L., Amirbahman, A., Countemanch, D. L., Alvarez, D. A. and Patterson, H., (2012). Estimating pesticide sampling rate by the polar organic integrative sampler (POCIS) in the presence of natural organic matter and varying hydrodynamic conditions. *Environmental Pollution* 169, pp. 98-104.

Eschauzier, C., Beerendonk, E., Scholte-Vreenendaal, P. and De Voogt, P., (2012). Impact of treatment processes on the removal of perfluoroalkyl acids from the drinking water production chain. *Environmental science & technology* 46(3), pp. 1708-1715.

Fauvelle, V., Mazzella, N., Delmas, F., Madarassou, K, Eon, M. and Budzinski, H., (2012). Use of mixed-mode ion exchange adsorbent for the passive sampling of organic acids by polar organic compound integrative sampler (POCIS). *Environmental Toxicology and Chemistry* 46(24), pp. 13344-13353

Fedorova, G., Golovko, O., Randak, T. and Garbic, R., (2012). Passive sampling of perfluorinated acids and sulfonates using polar organic compound integrative samplers. *Environmental Science and Pollution Research* 20(3), pp. 1344-1351

Flores, C., Ventura, F., Martin-Alonso, J. and Caixach, J. (2013). Occurrence of perfluorooctane sulfonate (PFOS) and perfluorooctanote (POFA) in NE Spanish surface waters and their removal in a drinking water treatment plant that combines conventional and advanced treatments in parallel lines. *Science of The Total Environment* 461, pp. 618-626.

Glynn, A., Berger, U., Bignert, A., Ullah, S., Aune, M., Lignell, S. and Darnerud, P. O., (2012). Perfluorinated alkyl acids in blood serum from primiparous women in Sweden: serial sampling during pregnancy and nursing and temporal trends 1996-2010. *Environmental science & technology* 46(16), pp. 9071-9079

Górecki, T. and Namiésnik, J., (2002). Passive sampling. *Trends in Analytical Chemestry* 21(4), pp. 276-291.

Harman, C., Reid, M. and Thomas, K. V., (2011). In situ calibration of a passive sampling device for selected illicit drugs and their metabolites in wastewater, and subsequent year-long assessment of community drug usage. *Environmental Science and Technology* 45(13), pp. 5675-5682.

Harman, C., Allan, I. J. and Vermeirssen, E. L. M., (2012). Calibration and use of the polar organic compound integrative sampler – a critical review. *Environemntal Toxicology and Chemistry* 31(12), pp. 2724-2738.

Huckins, J. N., Petty, J. D., Lebo, J. A., Lebo, J. A., Orazio, C. E., Clark, R. C. and Gibson, V. L., (2002). *SPMD Technology Tutorial (3rd Edition).* Available from: http://wwwaux.cerc.cr.usgs.gov/spmd/SPMD-Tech_Tutorial.htm [30 December 2014]

Kaserzon, S. L., Kennedy, K., Hawker, D. W., Thompson, J., Carter, S., Roach, A. C., Booij, K. and Mueller, J. F., (2012). Development and calibration of a passvie sampler for carboxylates and sulfonates in water. *Environmental science & Technology* 46(9), pp. 4985-4993.

Kaserzon, S. L., Vermeirssen, E. L. M., Hawker, D. W, Kennedy, K., Bentley, C., Thompson, J., Booih, K. and Mueller, J. F., (2013). Passive sampling of perfluorinated compounds in water: Flow rate effects on compound uptake. *Environmental Pollution* 177, pp. 58-63.

Kim, M., Li, L., Grace, J. R. and Yue, C., (2014). Selecting reliable physicochemical properties of perfluoroalkyl and polyfluoroalkyl substances (PFASs) based on molecular descriptors. *Environmental Pollution* 196, pp. 462-472.

Kot-Wasik, A., Zabiegala, B., Urbanowicz, M., Dominiak, A. W. and Namisnik, J., (2007). Advances in passive sampling in environmental studies. *Analytica Chemica Acta* 602(2), pp. 141-163.

Li, H., Helm, P. A. and Metcalfe, C. D., (2010a). Sampling in the Great Lakes for pharmaceuticals, personal care products and endocrine-disrupting substances using the passive polar organic compound integrative sampler. *Environmental Toxicology and Chemistry*, 29(4), pp. 751-762.

Li, H., Vermeirssien, E. L. M., Helm, P. A. and Metcalfe, C. D., (2010b). Controlled field evaluation of water flow rate effects on sampling polar organic compounds using polar organic chemical integrative samplers. *Environmental Toxicology and Chemistry*, 29(11), pp. 2461-2469.

Livsmedelsverket, (2013). Riskvärdering av perfluorerande alkylsyror i livsmedel och dricksvatten. *National Food Agency, Sweden* Report 11-2013

Livsmedelsverket, (2014). Riskhantering av PFAA i dricksvatten. Available from: http://www.slv.se/sv/grupp1/Dricksvatten/Dricksvattenkvalitet/Perfluorerade-alkylsyror/Riskhanteringsatgard-PFAA/ [3 December 2014]

Mak. Y. L., Taniyasu, S., Yeung, L. W., Lu, G., Jin, L., Yang, Y., Lam., P. KS., Kannan, K., and Yamashita, N., (2009). Perfluorinated compounds in tap water from China and several other countries. *Environmental science & technology*, 43(13), pp. 4824-4829.

Mazzella, N., Lissalde, S., Moreira, S., Delmas, F., Mazellier, P. and Huckins, J. N., (2010). Evaluation of the use of performance reference compounds in an Oasis-HLB adadsorbent based passive sampler for improving water concentration estimates of polar herbicides in freshwater. *Environmental sciences & technology* 44(5), pp. 1713-1719.

Metcalfe, C., Hoque, M. E., Sultana, T., Murray, C., Helm, P. and Kleywgt, S., (2014). Monitoring for contaminants of emerging concern in drinking water using POCIS passive samplers. *Environmental Science: Processes & Impacts* 16(3), pp. 473-481.

Naturvårdsverket, (2008). Förslag till gränsvärden för särskilda förorenade ämnen – Stöd till vattenmyndigheterna vid statusklassificering och fastställande av MKN.

Swedish Environmental Protection Agency Report 5799, ISBN 978-91-620-5799-2

Naturvårdsverket, (2012). Environmental and Health Risk Assessment of Perfluoroalkylated and Polufluoroalkylated Substances (PFASs) in Sweden. *Swedish Environmental Protection Agency* Report 6513, ISBN 978-91-620-6513-3.

Norrvatten no date a,. *Produktion av dricksvatten.* Available from: http://www.norrvatten.se/Dricksvatten/Produktion-av-vatten/ [2 December 2014]

Norrvatten no date b,. *Reningsprocessen.* Available from: http://www.norrvatten.se/Dricksvatten/Produktion-av-vatten/Reningsprocessen/ [2 December 2014]

Post, G. B., Louis, J. B., Lippincott, R. L., and Procopio, N. A., (2013) Occurrence of Perfluorinated Compounds in Raw Water from New Jersey Public Drinking Water Systems. *Environmental science & technology,* 47(23), pp. 13266-13275

Rahman, M. F., peldszus, S., and Anderson, W. B., (2014) Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: a review. *Water research,* 50, pp. 318-340.

Seethapthy, S., Górecki, T. and Li, X., (2008). Passive sampling in environmental analysis. *Journal of Chromatography A* 1184 (1), pp. 234-253.

Takagi, S., Adachi, F., Miyano, K., Koizumi, Y., Tanaka, H., Mimura, M., Watanabe, I., Tanabe, S., Kannan, K., (2011). Fate of perfluorooctanesulfonate and perfluorooctanoate in drinking water treatment processes. *Water research* 45(13), pp. 3925-3932.

Vrana, B., Allan, I. J., Greenwood, R., Millis, G. A., Dominiak, E., Svensson, K., Knutsson, J. and Morrison, G., (2005). Passive sampling techniques for monitoring pollutants in water. *TrAC Trends in Analytical Chemistry* 24(10), pp. 845-868.

Wang Z., MacLeod, M., Cousins, I. T., Scheringer, M. and Hungerbühler, K., (2011). Using COSMOtherm to predict physicochemical properties of poly- and perfluorinated alkyl substances (PFASs). *Environmental Chemistry* 8 pp. 389-398

Zushi, Y., Hogarth, J. N., and Masunaga, S., (2012). Progress and perspective of perfluorinated compound risk assessment and management in various countries and institutes. *Clean Technologies and Environmental Policy*, 14(1), pp. 9-20.

8 APPENDIX

APPENDIX A –SUPPLEMENT INFORMATION FOR PASSIVE SAMPLING

R_s can be calculated using the fact that it is directly proportional to the exposure of the effective membrane surface area to the surrounding water (Alvarez et al., 2004), and can be calculated by equation 4:

$$R_s = k_o \cdot A \tag{4}$$

where k_o (in L days^{-1} dm$^{2^{-1}}$) is the overall mass transfer coefficient and A (in dm^2) is the water-sampler interfacial area. To determine k_o the accumulation can be seen as a three-stage process through the water boundary layer (WBL), the membrane and into the sorption phase (equation 5) (Kaserzon et al., 2012):

$$\frac{1}{k_o} = \frac{1}{k_w} + \frac{1}{k_m \cdot \rho_m \cdot K_{mw}} + \frac{1}{k_s \cdot \rho_s \cdot K_{pw}} \tag{5}$$

where k_w (in L days^{-1} dm$^{2^{-1}}$) is the mass transfer coefficient of the WBL, k_m (in L days^{-1} dm$^{2^{-1}}$) is the mass transfer coefficient of the membrane, ρ_m (in g L^{-1}) is the density of the membrane, K_{mw} (in L g^{-1}) is the membrane-water sorption coefficient, k_s (in L days^{-1} dm$^{2^{-1}}$) is the mass transfer coefficient of the sorption phase and ρ_s (in g L^{-1}) is the density of the adsorbent (Kaserzon et al., 2012).

The dissipation rate for PRCs is determined by (equation 6):

$$c_{PCR} = c_{PRC}^0 \cdot e^{-k_e \cdot t} \tag{6}$$

where c_{PRC} (in ng g^{-1}) is the concentration of PRC in the receiving phase after exposure and c_{PRC}^0 (in ng g^{-1}) is the initial concentration of PRC in the receiving phase and k_e (in days^{-1}) is the elimination rate constant or the term $\frac{R_s}{m_s K_{pw}}$ in equation 1 (Belles et al., 2014).

APPENDIX B – WATER SAMPELS FROM THE CALIBRATION STUDY

At every sampling date (0, 2, 4, 7, 14, 21, 28 days) during the calibration study a grab sample was taken from tank 1. The grab samples were analyzed in the same way as the grab samples from the DWTP except that the samples from the calibration study were not filtered before the SPE extraction. The result from the analysis was that the concentration was almost constant during the calibration study (Figure B1). The concentration was close to the estimated 500 ng L^{-1} for each PFAS. However, the concentration of PFTeDA was at its highest at day 0 with a concentration close to 120 ng L^{-1} and went as low as 30 ng L^{-1} at day 28. For all the other PFASs the concentration varied between 200 to 700 ng L^{-1} during the calibration study.

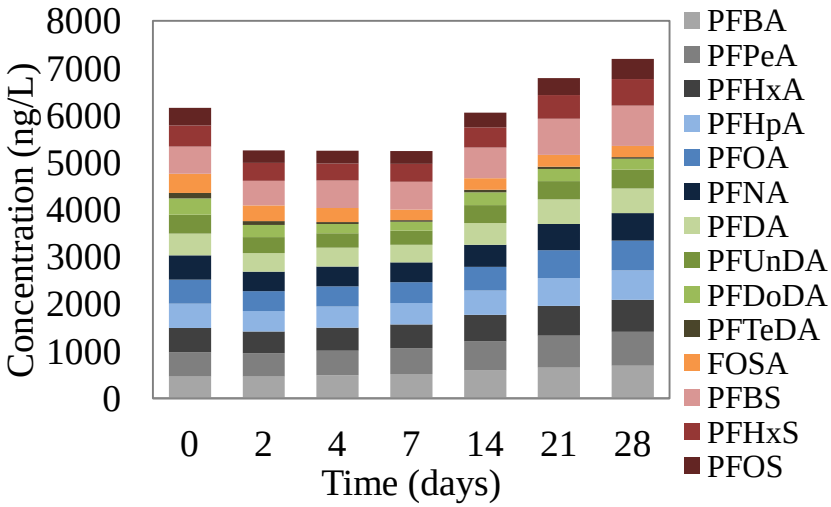


Figure B1. *Concentration of PFASs in Tank 1 during the calibration study.*

At the last day of the calibration study a grab sample was also taken from tank 2. In tank 2 the concentration of PFASs was close to the expected value of 1000 ng L^{-1} (Figure A2). The exception was for the long-chained PFASs, PFUnDA, PFDoDA and PFTeDA as well as for FOSA were the concentration was around 500, 200, 60 respectively 300 ng L^{-1}. The concentration for PFBS exceeded the expected concentration and was as high as 1300 ng L^{-1}.

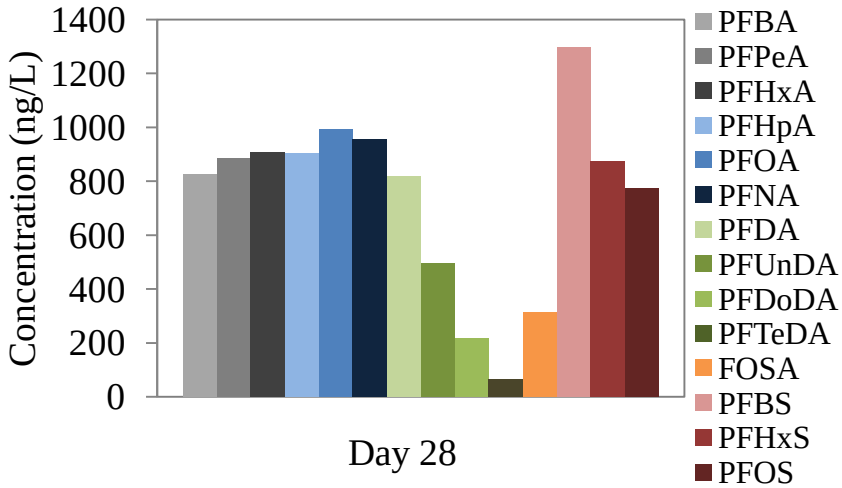


Figure B2. *Concentration of PFASs in tank 2 at the last day of the calibration study.*

APPENDIX C – DETECTED PFASs DURING APPLICATION

For the application of passive samplers and from the grab samples from drinking water the average percent of a specific compound was calculated from the total sum of PFASs detected.

Table C1. The average percent of a specific PFASs detected during the application from the total sum of PFASs for each sampling technique.

Compound	POCIS WAX (% of ∑PFAS in DWTP and pilot plant)	POCIS HLB (% of ∑PFAS in DWTP)	Grab samples (% of ∑PFAS)
PFBA	8	ND[a]	33
PFHxA	23	25	12
PFHpA	4	<1	1
PFOA	10	6	ND[a]
PFDA	2	4	<1
PFUnDA	ND[a]	<1	1
PFDoDA	<1	2	ND[a]
PFTriDA	ND[a]	1	<1
PFTeDA	<1	ND[a]	ND[a]
FOSA	ND[a]	ND[a]	7
PFBS	34	18	14
PFHxS	14	19	10
PFOS	4	5	21

[a] not detected in the sample

APPENDIX D – REMOVAL EFFICIENCY AT THE DWTP

For the TWA concentrations from the POCIS HLB and from the grab samples the removal efficiency was calculated throughout the DWTP (Table D1 and Table D2). For the POCIS HLB the removal efficiency showed that for the pilot plant a 100% removal was achieved for all the detected compounds in the raw water and in the full-scale plant levels of PFHxA were reduced by 11% and 39% for PFBS. For the grab samples the removal efficiency ranged between 16% and 100% in the full-scale plant and between 22% and 100% in the pilot plant.

Table D1. Removal efficiency (%) at the DWTP for the PFASs that were detected by the POCIS HLB.

Compound	DWTP[a]	Pilot plant[b]	Pilot plant[c]
PFHxA	11	100	100
PFHpA	NR[d]	NR[d]	NR[d]
PFOA	NR[d]	100	100
PFDA	NR[d]	NR[d]	NR[d]
PFUnDA	NR[d]	NR[d]	NR[d]
PFDoDA	NR[d]	NR[d]	NR[d]
PFTeDA	NR[d]	NR[d]	NR[d]
PFBS	39	100	100
PFHxS	NR[d]	100	100
PFOS	NR[d]	100	100

[a]RW to DW, [b]RW to GAC 2, [c]RW to GAC 3, [c]NR = no removal

Table D2. Removal efficiency (%) at the DWTP for the PFASs that were detected in the grab samples.

Compound	DWTP[a]	Pilot plant[b]	Pilot plant[c]
PFBA	NR[d]	100	68
PFHxA	NR[d]	100	100
PFHpA	NR[d]	100	100
PFOA	NR[d]	100	100
PFDoDA	60	100	100
PFTeDA	100	100	100
PFBS	16	100	NR[d]
PFHxS	37	100	100
PFOS	NR[d]	100	22

APPENDIX E – MEASURED WATER PARAMETERS AT DWTP

The water parameters, temperature, water flow rate and pH, were measured the first day of the application at the DWTP for each of the sampling sites (Table E1). The temperature ranged from 8.8 to 10.6 ^{o}C and the pH ranged from 6.4 to 7.3. The water flow rate was measured at the inlet of the bucket at the sampling site. The large variety of 7.6-36 mL s^{-1} for the flow rate was dependent on how well the water drained out of the bucket so that the water did not overflow the rim. Color, UV 254 and TOC was obtained from chemists at Görvälnverket. The average color was 6.63 mg L^{-1}, average UV 254 was 0.42 and average TOC was 4.42 mg L^{-1}.

Table E1. Measured water parameters for temperature (^{o}C), water flow rate at the inlet of the bucket (mL s^{-1}) and pH for all the sampling sites at the DWTP at the first day of the application.

Sampling location	Temperature (^{o}C)	Flow rate (mL s^{-1})	pH	Color (mg L^{-1})	UV 254 (5 cm)	TOC (mg L^{-1})
RW	9.2	7.6	7.3	23.12[a]	7.67 [a]	7.67 [a]
SF	8.8	36	6.5	4.77 [a]	0.42 [a]	4.53 [a]
GAC 1 (full scale)	8.4	20	6.6	6.44[b]	0.44 [b]	n.a.
DW	10.3	14	7.1	n.a.	n.a.	n.a.
GAC 2 (pilot)	10.6	16	6.5	4.17 [b]	0.30 [b]	n.a.
NF (pilot)	10	36	6.4	1.28 [a]	0.11 [a]	1.14 [a]
GAC 3 (pilot)	9.7	16	6.5	0.032 [b]	0.007 [b]	n.a.

[a] = average of measurements taken every 5 min and for the dates November 26, December 2, 5, 8, 11 and 15.

[b] = average of a single measurement taken November 26 and December 2, 5, 8, 11 and 15.

n.a. = not available