Transport of per- and polyfluoroalkyl substances in soil and groundwater in Uppsala, Sweden

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Acknowledgements

Abstract

In recent years, per- and polyfluoroalkyl substances (PFASs) have received increasing public attention due to their persistence, bioaccumulation potential and toxicity to humans and wildlife. PFASs are widely used in various products including surfactants in paper, textiles, and aqueous film forming foams (AFFFs). The application of PFAS-containing AFFFs has been linked to the contamination of the aqueous environment with PFASs. The leaching of PFASs from PFAS contaminated soil to groundwater may also affect drinking water quality, which in turn may be a possible exposure source for humans. This study focused on *i)* the occurence of 26 individual PFASs in soil and groundwater, *ii)* their mobility and transport in different compartments including soil, sediment, groundwater, surface water and drinking water, and *iii)* identification of their source by comparing their composition profiles. Samples were collected in soil (*n=12*), sediment (*n=2*), groundwater (*n=28*), surface water (*n=6*) and drinking water (*n=4*) in Uppsala and in the nearby area in May/June 2014. The sampling sites included three fire fighting training sites, the first was located in the north part of Uppsala (Fire fighting facility 1), the second was located in the east part of Uppsala (Fire fighting facility 2), and the third was located close to the city centre of Uppsala (Fire fighting facility 3). In the soil and sediment, the dominant PFASs were perfluorooctane sulfonate (PFOS; 81% of the ∑PFASs) and perfluorooctanesulfonamide (FOSA; 5%), and the highest concentrations were detected at Fire fighting facility 2 (∑PFASs = 608 ng g^{-1} dry weight (dw)), while the maximum ∑PFAS concentrations at Fire fighting facility 1 and 3 were 139 ng g^{-1} dw and 3 ng g^{-1} dw, respectively. In groundwater along Uppsalaåsen (i.e. groundwater flow from north to south in Uppsala), were the dominant PFASs perfluorohexane sulfonate (PFHxS; 54%), PFOS (13%) and perfluorobutane sulfonate (PFBS; 11%) while at Fire fighting facility 2, located on the east side of Uppsalaåsen, the dominant PFASs were 6:2 fluorotelomer sulfonate (6:2 FTSA; 51%), PFOS (20%) and perfluorohexanoate (PFHxA; 8%). Fire fighting facility 2 had the highest detected concentrations in groundwater (∑PFASs = 8015 ng L^{-1}) and groundwater near Fire fighting facility 1 had the second highest (∑PFASs = 1000 ng L^{-1}). The concentration along the groundwater flow decreases towards the south of Uppsala. In the river water samples, PFOS (47%), PFHxS (41%), PFHxA (7%) and PFPeA (3%) has been detected with ∑PFASs ranging between below the detection limit and 15 ng L^{-1}. In contrast, much higher ∑PFAS concentrations were found in surface water at a pond at Fire fighting facility 2 with 3026 ng L^{-1}. The ∑PFAS concentrations in drinking water in Uppsala were generally low ranging between 1 ng L^{-1} and 8 ng L^{-1}. The dominant PFASs in drinking water were PFHxS (73%) and PFBS (17%). A Principal Component Analysis (PCA) was performed for the PFAS pattern in the groundwater samples. The PCA showed that the PFAS pattern at Fire fighting facility 2 did not correspond with the PFAS pattern at Uppsalaåsen (the groundwater flow from north to south) which indicates that Fire fighting facility 2 is not connected to Uppsalaåsen. It is important to note that this study was a one-time grab sampling campaign and all values should be interpreted with care. More detailed studies are needed to verify the spatial distribution of PFASs in soil and groundwater, vertical and horizontal transport of PFASs in soil and groundwater, and seasonal and long-term changes of the PFAS contamination in the environment.

Key words: PFASs, PFOS, fire fighting foams, aqueous film forming foams, AFFF, groundwater, soil, surface water, river water, drinking water, drinking water quality, Uppsala.

Sammanfattning

Under de senaste åren har uppmärksamheten för per- och polyfluoralkylerade ämnen (PFASs) ökat på grund av dess persistens, bioackumulering och toxicitet för människor och djur. PFASs används i olika produkter, bland annat som tensider i papper, textiler och filmbildande skum (AFFFs). Användning av AFFFs innehållande PFASs har kopplats till PFAS föroreningar i vattenmiljöer. Utlakningen av PFASs från PFASs förorenad mark till grundvatten kan också påverka dricksvattenkvalitéten, vilket i sin tur kan vara en exponeringskälla för människor. Denna studie fokuserar på i) förekomst av 26 individuella PFASs i jord och grundvatten, ii) deras rörlighet och transport i olika faser, inklusive mark, sediment, grundvatten, ytvatten och dricksvatten, och iii) att spåra källan genom att jämföra deras föroreningssammansättning. Prover samlades in i jord (n=12), sediment (n=2), grundvatten (n=28), ytvatten (n=6) och dricksvatten (n=4) i Uppsala och i närheten av Uppsala i maj/juni 2014. Provtagning utfördes på tre brandövningsplatser, den första belägen i norra delen av Uppsala (Brandövningsanläggning 1), den andra belägen i den östra delen av Uppsala (Brandövningsanläggning 2), och den tredje belägen nära Uppsala centrum (Brandövningsanläggning 3). I jord och sediment var perfluorooktansulfonat (PFOS) det dominerande ämnet (81% av ΣPFASs) tillsammans med perfluoroktansulfonamid (FOSA; 5%), och de högsta halterna påträffades vid Brandövningsanläggning 2 (ΣPFASs 608 ng g^{-1} torrvikt (dw)), medan ΣPFAS-koncentrationerna vid Brandövningsanläggning 1 och 3 var 139 ng g^{-1} dw respektive 3 ng g^{-1} dw. I grundvattnet i Uppsalaåsen (dvs grundvattenflödet från norr till söder) dominerade perfluorhexansulfonat (PFHxS; 54%), PFOS (13%) och perfluorbutansulfonat (PFBS; 11%), medan de dominerande PFASs på Brandövningsanläggning 2, (beläget på östra sidan av Uppsalaåsen) var 6:2 fluortelomer sulfonat (6:2 FTSA; 51%), PFOS (20%) och perfluorhexanoat (PFHxA; 7%). Brandövningsanläggning 2 hade de högsta halterna i grundvattnet (ΣPFASs = 8015 ng L^{-1}) följt av grundvattnet nära Brandövningsanläggning 1 (ΣPFASs = 1000 ng L^{-1}). Koncentrationen längs Uppsalaåsen minskade mot södra Uppsala. I å vattenproverna i Uppsala detekterades PFOS (47%), PFHxS (41%), PFHxA (7%) och PFPeA (3%), där ΣPFASs varierade från under detektionsgränsen upp till 15 ng L^{-1}. Däremot detekterades högre ΣPFAS-halter i ytvattnet i en damm vid Brandövningsanläggning 2 med 3026 ng L^{-1}. ΣPFAS-halterna i dricksvatten i Uppsala var låga mellan 1 ng L^{-1} och 8 ng L^{-1}. De dominerande PFASs i dricksvatten var PFHxS (73%) och PFBS (17%). En prinipalkomponentanalys (PCA) utfördes för grundvattenprovernas föroreningssammansättning. Den visade att PFAS-mönstret vid Brandövningsanläggning 2 inte överensstämde med PFAS-mönstret vid Uppsalaåsen längs grundvattenflödet, vilket tyder på att Brandövningsanläggning 2 är inte ansluten till Uppsalas grundvattenflöde från norr till söder. Det är viktigt att notera att denna studie grundas på s.k. momentanprovtagning (eng. grab sampling), och alla värden bör tolkas med försiktighet. Det behövs mer detaljerade studier för att kontrollera den spatiella fördelningen av PFASs i mark och grundvatten, vertikal och horisontell transport av PFASs i mark och grundvatten, samt säsongs- och långsiktiga förändringar av PFAS förorening i miljön.

Nyckelord: PFASs, PFOS, brandskum, filmbildande skum, AFFF, grundvatten, mark, ytvatten, dricksvatten, dricksvattenkvalité, Uppsala.

Populärvetenskaplig sammanfattning

Transport av per- och polyfluorerade ämnen i mark och grundvatten i Uppsala, Sverige

Sofia Bergström

Per- och polyfluorerade ämnen (PFASs) har fått stor uppmärksamhet under senaste åren eftersom de upptäckts i drickvatten på ett flertal platser i Sverige. Många av dessa ämnen är kända för att vara toxiska, bioaccumulerande och persistenta, dvs. de är giftiga för människor och djur, ansamlas i levande organismer och är mycket svårnedbrytbara. PFASs har använts i många produkter och varor, så som textiler, matförpackningar och brandskum på grund av deras fett-, olje- och vattenavvisande egenskaper. Perfluoroktansulfonat (PFOS) är det ämne som har uppmärksammats mest. PFOS är inkluderat i Stockholmskonventionen som en persitent, organisk miljöförorening (POP) och är förbjudet att använda och producera sedan 2009. Det finns dock undantag. Brandskum som innehåller detta ämne fick användas enda fram till 2011 om skummet var inköpt före 2006. Dessutom produceras PFOS fortfarande i länder som inte skrivit under Stockholmskonventionen.

Brandskum har använts på brandövningsanläggningar på flera olika områden i Uppsala. Detta har lett till att relativt stora markytor är förorenade med dessa hälso- och miljöfarliga ämnen. PFASs i mark kan läcka ned till grundvattnet eller transporteras till närmaste vattendrag. Uppsala tätort har grundvattnet under staden som försörjningskälla för dricksvatten. Det finns starka indicier för att användning av PFASs vid brandövningsanläggningar och efterföljande infiltration till grundvattnet har förorenat Uppsalas dricksvattenakvifär, Uppsalaåsen, och därmed några av dricksvattenbrunnarna. Syftet med denna studie var provta jord, sediment, grundvatten, ytvatten och dricksvatten och sedan mäta innehållet av 26 olika PFASs i dessa matriser för att få en bättre förståelse för hur PFASs beter sig i miljön, dvs. hur PFASs transporteras från jord till vatten, vilka fraktioner som når grundvatten, ytvatten och dricksvatten, hur sammansättningen förändras vid vertikal och horisontell transport och hur kan man använda sådan information för att spåra källor. Den här typen av information är viktig att ta fram för att kunna förutspå framtida förorening. PFASs beteende i miljön är beroende av ämnernas fysikaliska-kemiska egenskaper och då framförallt deras tendens att adsorberas i mark, dvs. bindas till partiklar. PFASs består av en flourerad kolkedja (svansen) och en hydrofil funktionell grupp (huvudet). Svansen på molekylen är hydrofob, den ogillar vatten. Ju längre denna kolkedja, desto mer tenderar den att binda till partiklar för att undvika vatten. PFASs med kortare kolkedjor är mindre hydrofoba och löser sig lättare i vatten. Dessa skillnader i egenskaper avspeglades i studiens resultat. PFASs med långa kolkedjor utgjorde en relativt hög fraktion i jord och sediment, medan PFASs med korta kolkedjor hade en högre fraktion i vatten.

I vår studie ingick tre brandövningsanläggningar (1, 2 och 3). De högsta halterna av PFASs uppmättes nära Brandövningsanläggning 1 och 2 (jord: ΣPFASs upp till 608 ng g^{-1} torrvikt (dw), grundvatten: upp till 8015 ng L^{-1}), vilket är en stark indikation på att att dessa brandövningsanläggningar utgör källan till grundvattenföroreningen. Vid Brandövningplats 3 detekterades låga halter i jord (ΣPFASs upp till 3 ng g^{-1} dw). En kraftig påverkan på grundvattnet från denna plats är mindre tänkbart. Vattendragen i Uppsala, dvs. Fyrisån och Sävjaån, var också påverkade av PFASs (ΣPFASs upp till 15 ng L^{-1}) med något högre halter nedströms det kommunala reningsverket. Högre halter av PFASs i ytvattenprover belägna nedströms reningsverk stämmer väl överens med tidigare studier. I dricksvattnet i Uppsala uppmättes låga halter (ΣPFASs upp till 8 ng L^{-1}), vilket överensstämde med halterna i grundvattenrören.

De tre olika brandövningsplatserna i Uppsala, har använt olika sorters brandskum som innehåller olika blandningar av PFASs. Detta resulterar i att föroreningssammansättningen i marken varierar mellan olika brandövningsplatser, vilket ger dem karakteristiska "fingeravtryck". Efter infiltration erhålls ett nytt karakteriskist fingeravtryck i grundvattnet. Genom att använda sig av dessa fingeravtryck kan man spåra likheter och olikheter mellan olika matriser och provtagningsplatser. Denna typ av information kan användas för att spåra källor. PFASs fingeravtrycken i grundvattnet nära Brandövningsanläggning 1 liknade grundvattnet längs med Uppsalaåsen, medan fingeravtrycken i grundvattnet vid Brandövningsanläggning 2 skilde sig åt från de i Uppsalaåsen.

PFASs är realtivt starkt bundet till partiklar i jorden och kommer med tiden att sakta desorberas från partiklarna, dvs. avlägsnas från ytan som de är bundna till. Kontamineringen av grundvattnet kommer därför inte att upphöra inom överskådlig framtid. Dessutom finns en risk för att de föroreningar som nu påträffas i Uppsalaåsens grundvatten får ytterligare horisontal utbredning.

Contents

Abbreviations

Abbreviation	Explanation	Abbreviation	Explanation
PFASs	per- and polyfluoroakyl substances	AFFF	aqeuous film forming foam
PFSAs	perfluoroalkane sulfonic acids	bw	body weigth
PFCAs	perfluoroalkyl carboxylic acids	dw	dry weigth
FOSAs	perfluorooctanesulfonamide	f_{oc}	organic carbon fraction
FOSEs	perfluorooctane sulfonamidoethanols	g	gram
FOSAAs	perfluorooctyl sulfonamide acetic acids	GFF	glass fibre filter
PFOA	perfluorooctanoate	HPLC-MS/MS	high-performance liquid chromatography coupled with tandem mass spectrometry
PFOS	perfluorooctane sulfonate	K_d	soil-water partitioning coefficient
FTOH	fluortelomeralcohol	K_{OC}	organic carbon normalised partition coefficient
6:2 FTSA	6:2 fluorotelomer sulfonate	K_{OW}	partitioning coefficient between water and octanol
PFBS	perfluorobutane sulfonate	L	liter
PFHxS	perfluorohexane sulfonate	MDL	method detection limit
PFDS	perfluorodecane sulfonate	MQL	method quantitation limit
PFBA	perfluorobutanoate	n	number of samples
PFPeA	perfluoropentanoate	n.a.	not available
PFHxA	perfluorohexanoate	ND	not detected
PFHpA	perfluoroheptanoate	PP	polypropylen
PFNA	perfluorononanoate	REACH	regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals
PFDA	perfluorodecanoate	TC	total carbon
PFUnDA	perfluoroundecanoate	TIC	total inorganic carbon
PFDoDA	perfluorododecanoate	TOC	total organic carbon
PFTriDA	perfluorotridecanoate		
PFTeDA	perfluorotetradecanoate		
PFHxDA	perfluorohexadecanoate		
PFOcDA	perfluorooctadecanoate		
FOSA	perfluorooctanesulfonamide		
N-MeFOSA	*N*-methylperfluorooctansulfonamide		
N-EtFOSA	*N*-ethylperfluorooctanesulfonamide		
N-MeFOSE	*N*-methylperfluorooctanesulfonamido-ethanol		
N-EtFOSE	*N*-ethylperfluorooctanesulfonamido-ethanol		
FOSAA	perfluorooctanesulfonamidoacetic acid		
N-MeFOSAA	*N*-methylperfluorooctanesulfonamidoacetic acid		
N-EtFOSAA	*N*-ethylperfluorooctanesulfonamido acid		

1. Introduction

1.1 Per- and polyfluoroakyl substances (PFASs)

Per- and polyfluoroalkyl substances (PFASs) are highly fluorinated organic chemicals which were created for surface protection due to their resistance against water, dirt and oil. PFASs have been used since the 1950's but not until the last decade has the environmental and human risk of these chemicals been discovered (Borg and Håkansson, 2012). The most discussed PFASs are perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) which have been ubiquitously detected in soil, sediment, water and biota (Ahrens et al, 2010; Newsted et al, 2007). PFASs have been found to be persistent, bioaccumulative and toxic. PFASs are among other used in aqueous film forming foams (AFFFs), which are mixes of perfluorocarbon and hydrocarbon surfactants with different percentage of perfluorosubstances (Hagenaarsa et al, 2011). Fire fighting foams, in other word AFFFs, has been used by military, at airports, in industrial settings and for fire fighting training for several decades. In the past, AFFFs was not collected by any drainage so contaminants was instead leaching down or flowing to nearby surface water. PFASs contamination in soil will start a slow process of leaching down to the groundwater and high concentrations of PFAS in groundwater and contaminated drinking water are now problems we are facing.

1.2 Physical and chemical properties of PFASs

PFASs are a large group of highly fluorinated organic compounds with a fluorinated carbon chain and a functional group in the end of the chain. The carbon chain of PFASs is hydrophobic, while the functional group is hydrophilic which gives them surfactant characteristics (Bjermo et al, 2013). Studies show that the number of carbon atoms is significant for adsorption to particles. A long chain length (> 7 carbon atoms) will have a higher adsorption capacity than a shorter chain length (< 7 carbon atoms) (Gellrich et al, 2011). For PFASs, the hydrogen atoms in the carbon chain are exchanged by fluor atoms. If all hydrogen atoms have been fully exchange to fluor atoms, the substances are called perfluoroakyl substances. If only some hydrogen atoms are exchanged to fluorine they are called polyfluoroakyl substances (Järnberg et al, 2007; Glynn and Sand, 2014). The strong carbon-fluorine bond makes PFASs very resistant against any sort of degradation, chemical degradation, biological degradation and thermal degradation (Borg and Håkansson, 2012).

The chemical properties for each PFASs is varying and much is dependent of the carbon chain length (Forest and Rayne, 2009). Longer chained PFASs are less soluble in water because they are more hydrophobic. Studies have shown that also the functional groups of PFASs are affecting the water solubility which decrease for perfluorinated carboxylate acids for (PFCAs) (COOH-group) > perfluorinated sulfonic acids (PFSAs) (SO$_3$H-group) > perfluorinated alkyl sulphonamides (FOSAs) > fluorotelomer alcohols (FTOHs) (Wang et al, 2011). Some PFASs that have an acidic functional group is ionized, including PFSAs and PFCAs. The acid dissociation constant (pK_a) is describing the strength of an acid in solution. pK_a for PFASs is relatively small; PFOS is ~0 and perfluorobutanoate (PFBA) ~1.8 which means that PFCAs and PFSAs is mostly ionized at pH prevailing in nature. Ionized PFASs (PFSAs and PFCAs) are more water soluble than natural (FTOHs, FOSAs and perfluorooctane sulfonamidoethanols; FOSEs) (Wang et al, 2011; Jahnke, 2007). Several classes of PFASs can also degrade to more toxic PFCAs and PFSAs, called precursors (Houtz et al, 2013). Fluortelomer sulfonate (6:2 FTSA) can slowly degrade to PFBA, perfluoropentanoate (PFPeA), and perfluorohexanoate (PFHxA) via oxidation, while perfluorooctanesulfonamide (FOSA) can degrade to PFOS and FTOHs can degrade to PFCAs though oxidation and metabolism (Ellis et al, 2004;

Nordström och Viktor, 2012; Xu et al, 2004). Some of these precursors are present in AFFFs which can lead to higher concentrations of the more longer chained persistent PFSAs and PFCAs in soil and groundwater.

1.3 Uses and restrictions

Due to their properties, PFASs have been used and are still in use in many products (Bjermo et al, 2013). PFASs is mainly used for impregnated textiles, leather and carpets, surface treatments for food packaging, detergents and fire fighting foams (AFFFs) (Hovgard et al, 2009). AFFF is a synthetic film forming foam of fluorotensides used among others for extinguish hydrocarbon-fuel based fires (Holm and Solyom, 1995; Houtz et al, 2013). AFFFs have been used by the military, at airports and for fire fighting practise since 1960 (Hagenaarsa et al, 2011). The main producer of PFASs was 3M until 2000 when they stopped their production (3M, 2014-06-05). PFOS and PFOS related substances were included as a persistent organic pollutant (POP) in the Stockholm Convention in 2009 (Stockholm Convention, 2009). AFFFs were an exception; it could still be used until June 2011 if the AFFFs were brought before December 2006 (Swedish Chemical Agency, 2013). PFOS is still produced in Asia and in various industries due to the difficulties to find replacement chemicals (European Union, 2006; Bjermo et al, 2013).

1.4 Exposure and toxicity

PFASs have been detected worldwide in humans and wildlife, including biota in the Arctic. It is known to be toxic, bioaccumulative and biomagnified and it accumulate in the body and binds covalently to proteins (Järnberg et al, 2007, Peterson et al, 1992). The bioaccumulation of PFASs is affected by the strong binding capacity of longer chained PFASs; the longer chain length, the stronger bioaccumulation potential. This leads to a risk for biomagnification in the food chain, and studies have shown that predators have higher concentration of PFASs than consumers in the base of the food web (Butt et al, 2009).

Intake of drinking water and food are the main exposure pathways but exposure through inhalation of dust is also possible (Herzke et al, 2012; Shoeib et al, 2005). Reports show that PFASs distributes to the liver- and blood proteins but the knowledge of the toxicity of PFASs is still limited. Experiments on pregnant animals which were exposed to PFOS and PFOA showed weight reduction of the baby and reduced number of live birth (Stahl et al, 2001). Also other reports documented effects on the endocrine system and immunotoxicity.

To reduce the harm from PFASs for human and biota, the European Food Safety Authority (EFSA) investigated the Tolerable Daily Intake (TDI) of PFOS and PFOA. The TDI for PFOS is 150 ng kg^{-1} bodyweight (bw) day^{-1} and for PFOA 1500 ng kg^{-1} bw day^{-1} (European Food Safety Authority, 2008). The limit for PFOS in drinking water in Sweden is 350–1000 ng L^{-1} and in limnic waters 30 000 ng L^{-1} (Swedish Enviromental Protection Agency, 2008). Due to the lack of studies of human toxicity, it is difficult to set an exposure limit for PFASs (Bjermo et al, 2013).

1.5 PFASs in soil

Direct emission of PFASs occurs via usage and manufacturing. Especially usage of AFFFs which is directly sprayed on the soil or leaching from industries is the major emission source (Eschauzier et al, 2010). Indirect sources can be from leaching from sludge from waste water treatment plants (WWTPs) or landfills with impregnated textiles (Sepulvado et al, 2011; Oliaei et al, 2013). In the environment,

leaching from soil to groundwater is a fact. There are many parameters that affect leaching from soil to groundwater, such as soil permeability, soil composition and binding capacity of the compound (Higgins and Luthy, 2006; Ahrens et al, 2010). The different PFASs bind differently strong to soil depending on the chain length and functional group. Longer chain length PFASs bind stronger to soil particles so the leaching though the soil takes longer time (Gellrich et al, 2011). Instead shorter chained PFASs have a lower binding capacity which makes the transport down to groundwater faster. This makes the concentration of longer chained PFASs higher in soils and sediment and the concentration of shorter chained PFASs is instead lower because it is transported faster through the soil. The functional group is also affecting the sorption to soils (Ahrens et al, 2010; Higgins and Luthy, 2006). A PFAS with the same perfluorocarbon chain length but different functional groups adsorbs differently. Adsorption is higher for PFSAs (SO_3H-group) than for PFCAs (COOH-group). The soil composition can also affect the mobility of PFASs, especially pH, organic carbon (f_{oc}, TOC) and calcium ions (Ca^{2+}). Higgins and Luthy (2006) investigated the sorption mechanism of PFCAs, PFSAs and perfluorooctyl sulfonamide acetic acids (FOSAAs). These compound groups showed tendencies to sorb more to soils with high organic carbon content, low pH and high [Ca^{2+}] (Higgins and Luthy, 2006). Ahrens et al, 2009[b] did a similar study showing that PFOS, FOSA, perfluoroundecanoate (PFUnDA), N-ethylperfluorooctanesulfonamidoacid (N-EtFOSAA), perfluorononanoate (PFNA) and perfluorododecanoate (PFDoDA) had a higher concentration in soils when the organic matter (OM) content was high (Ahrens et al, 2009[b]). This is explained by the tendency of PFASs to sorb more to surfaces with more lipid character, like organic carbon (Forest and Rayne, 2009). The study of Ahrens et al, 2009[b] also showed that decreasing pH increased the concentration of sorbed PFOS, PFNA and PFDoDA because of the affect pH have on the charge of OM.

The partitioning of PFASs between soil, pore water and groundwater is a complex process (Ahrens et al, 2011[b]). The soil-water partitioning coefficient (K_d) (L kg^{-1}) can be used to estimate concentrations of sorbed and dissolved contaminants in the solid and water phase. The soil organic carbon-water partitioning coefficient (K_{oc}) (L kg$_{OC}$$^{-1}$) can be calculated by dividing the K_d by the fraction of organic carbon (f_{oc}) (Schwarzenbach et al, 2003). The K_{oc} depends on the functional group and perfluorocarbon chain length (C_n), K_{oc} increases with perfluorocarbon chain length in PFCAs, PFSAs and FOSAAs. PFOS (C_8) has in contrast a higher Log K_{oc} (4.8±0.1 L kg$_{OC}$$^{-1}$) than perfluorodecane sulfonate (PFDS, C_{10}) (3.5±0.1 L kg$_{OC}$$^{-1}$). PFSAs has also a higher K_{oc} than PFCAs. PFSAs with a carbon chain length of C_8 have a higher Log K_{oc} (4.8±0.1 L kg$_{OC}$$^{-1}$) than PFCAs with the same carbon chain length (C_8 4.0±0.1 L kg$_{OC}$$^{-1}$) and longer carbon chain length (C_9 4.6±0.1 L kg$_{OC}$$^{-1}$, C_{11} 3.3±0.1 L kg$_{OC}$$^{-1}$). The octanol-water partitioning coefficient (K_{ow}) can also be used for determination of the ratio between water and octanol (solids). This coefficient is as hard to determine because PFASs partition in both phases.

Since PFOS and PFOS related substances have been banned in counties all over the world, the distribution of these chemicals has decreased (Bjermo et al, 2013; Borg and Håkansson, 2012). But once PFASs are released into the enviroment, they will stay there for several hundreds of years because of the non-degradable properties.

1.6 PFASs in water

1.6.1 PFASs in surface water

Surface runoff, rainfall and waste water treatment plants is a potential source of PFASs to surface water (Ahrens et al, 2009[a]; Eschauzier et al, 2010; Hagenaarsa et al, 2011). Surface runoff from locations where AFFFs has been used intense can give high concentrations of PFASs in nearby surface waters. The water solubility, binding capacity and sediment-water partitioning will affect the occurrence in surface water (Krusic et al, 2005; Pan and You, 2010). If the binding capacity to particles is high it will bind to the sediments while more water soluble PFASs will occur in the surface water (Ahrens, 2011). But sorbed PFASs in sediment can also be readmitted to water again and affect the water concentration.

1.6.2 PFASs in groundwater

Leaching from contaminated soils to groundwater is a known source for PFASs in groundwater, with partitioning between pore water and soil particles as the main reason for the efficient vertical transport (Ahrens et al, 2009[b]). Shorter chained PFASs have a lower sorption potential to particles, the mobility is higher, and the transport through soil to groundwater is faster. The longer chained PFASs are commonly observed in low concentrations in ground- and surface water, and the shorter chained PFASs are more likely to be observed in the ground- and surface water (Gellrich et al, 2011). Shorter chained PFCAs (< 7 carbon atoms) were mostly found in the pore water, while longer chained PFCAs (>7) were found in sediment. Most of the PFASs are still bound in the environment and can later contaminate groundwater additionally.

1.6.3 PFASs in drinking water

Drinking water has been shown to be an important exposure factor of PFASs to humans (Ahrens, 2011; Skutlarek et al, 2006). PFASs in soils will leach to groundwater and in turn contaminate the tap water and the conventional cleaning techniques are not effective for the removal of PFASs in the drinking water. Research to find methods to clean the drinking water from PFASs is ongoing. For example, carbon filter are effective in the removal of PFASs in the drinking water (Gellrich, 2014; Cirkulation, 2014).

1.7 Aims

Recently, increasing levels of PFASs have been reported in inhabitants of Uppsala, and the drinking water was suspected to be the main source (Glynn et al, 2012). Groundwater samples of the drinking water source (i.e. Uppsalaåsen) showed high levels of especially perfluorohexane sulfonate (PFHxS) and PFOS (Uppsala Vatten, 2013). It is assumed that that the contamination originates from fire fighting facilities which have used PFAS-containing AFFFs which eventually leached into the groundwater. In this thesis, transport and mobility of PFASs in soil and groundwater in Uppsala is investigated. Groundwater, soil, sediment, surface water and drinking water samples have been collected in Uppsala and its surrounding area with the following objectives:

- ✖ Examine the occurence of PFASs in soil and groundwater.
- ✖ Investigate the transport of PFASs in different compartments including soil, sediment, groundwater, surface water and drinking water.
- ✖ Comparison of the composition profile of PFASs to identify sources of PFASs.

2. Method

2.1 Sample locations

Soil (*n*=12), sediment (*n*=2), groundwater (*n*=28), surface water (*n*=6) and drinking water (*n*=4) samples were collected in Uppsala and in the north part of Uppsala municipality, Sweden (Figure 1), between May 22, 2014 and June 27, 2014.

Uppsala is Sweden's fourth largest city with 206 000 inhabitants (Uppsala Kommun, 2014-07-07). The drinking water source in Uppsala is the esker, Uppsalaåsen. Uppsalaåsen is flowing from north to south with groundwater flowing into Uppsalaåsen from north-west, Jumkilsåsen and from south-east, Sävjaån. The river in Uppsala, Fyrisån, is flowing from north to south though the city, passing a waste water treatment plant, the tributary Sävjaån and end in Lake Ekoln, which continues to Lake Mälaren. To avoid reduction of the amount of water in the esker, it is continuously refilled with water from the north part of Fyrisån in Uppsala, called artificial infiltration. The surface water is pumped to infiltration plants, and leaching through the sand in the plants the natural way down to Uppsalaåsen. The soil in Uppsala is dominating of postglacial and glacial clay. The thick layer of clay in Uppsala is protecting the aquifer from contaminants in most cases, but some areas the clay layer is thin or no overlaying clay layer exist (Swedish Geological Survey, 1993).

The Fire fighting facility 1 (F1, F2, Figure 1) is a military facility and airport, which is located in the north part of Uppsala between the two eskers, Jumkilsåsen and Uppsalaåsen. Fire fighting practice has been performed there at two places, in the west and east side of the area (F1-F2). The PFOS-containing AFFF Uniform was used from 1985 to 2005. After 2005, the PFOS free Sthamex AFFF was used. The AFFFs usage today has stopped and no information exists about the amount of AFFFs used at the two fire training grounds. The fire fighting field is located over a groundwater shed, which makes the groundwater flow west into Jumkilsåsen and away from Uppsalaåsen (Niras, 2013). The soil at the sampled area is mostly fine grained sediments, silt and clay. Four soil samples were collected at the two fire training grounds, So1-So2 and So3-So4 and one control sample 300 m away from the fire fighting grounds (F1-F2), So5.

The Fire fighting facility 2 (F3, F4) is located 4 km south-east of Uppsala city and is still used for fire fighting practice. The fire fighting practice started in 1990 and the AFFFs used were 3M AFFF 3% and 6%, which contained 3% and 6%, respectively, fluorinated surfactants. Large amounts were used between 1990 and 1996, however, it is not known the exact amount of AFFFs used. Since 1996 until now, AFFF MB5 (PFASs free) is used and ARC-miljö (containing fluortensides) purchased from Dafo Brand (Dafo Brand AB 2014-07-29). Two locations at the area were used for fire fighting practice (F3-F4) and both are still used today. Today is the AFFFs and water collected in a drain where the water is transported to a pond (W6) which it was not in the past. After the pond the water flows to Sävjaån south of the area (Bjerking, 2014). The area has earlier been a clay source until 1950 when it was filled with 1-4 m depth filling material (Structor, 2013). The area is dominated by glacial clay and under layered by stony moraine and bedrock (Geological survey of Sweden, 2014). The clay thickness at the area is varying with the deepest layers in the north, where G20 had a clay layer of nine meters. In total 15 samples were collected at the area including four soil samples, So6-So9, two sediment samples from the pond, Se1-Se2, eight groundwater samples, G16-23 and one surface water sample at the pond, W6.

The Fire fighting facility 3 (F5) is located south of Uppsala center close to Fyrisån. The area is located approximately 100 m from Uppsalaåsen which is protected by a thick layer of clay with a thickness of 10 m with sand and gravel located under the clay (Geological survey of Sweden, 2014). At the area fire fighting practice has been conducted since the 1990s until ~1996 but it is unknown which type of AFFFs or how much AFFFs was used. Three soil samples, So10-So12 and one groundwater sample, G15 were collected at the area.

Different amounts and different brands of AFFFs which contains different PFASs were used at the fire fighting facilities. Furthermore, the content of the AFFFs differed of the AFFF produced before and after the ban of PFOS in 2009. Before the ban of PFOS the AFFFs mainly contained PFSAs (perfluorobutane sulfonate; PFBS, PFHxS, PFOS), shorter chained PFCAs (PFBA, PFPeA, PFHxA), FOSA and 6:2 FTSA (Herzke et al, 2012). In contrast, after the ban of PFOS, the PFASs-containing AFFFs mainly contain PFAS with $<C_8$ perfluorocarbon chain length (Place and Field, 2012). New AFFFs, mainly contained 6:2 FTSA, FTOHs, PFBA, PFPeA, PFHxA but also PFOA, FOSA, PFDoDA.
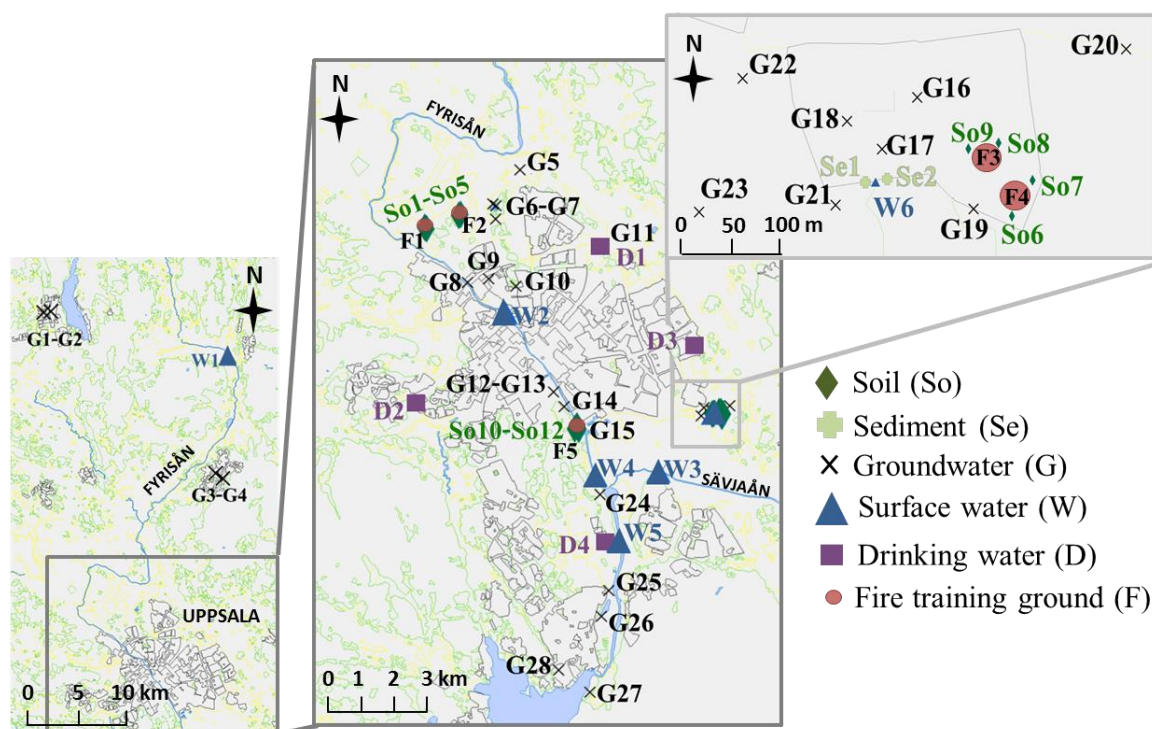
Figure 1: Sampling sites for PFASs in Uppsala. Soil samples in dark green (So), sediment samples in light green (Se), groundwater in black (G), surface water in blue (W) and drinking water in purple (D).

2.2 Sampling

To avoid contamination the water samples were collected in polypropylene (PP) bottles that were cleaned by rinsing with ethanol before dishwashing and later rinsed three times with methanol. In addition, at every sampling location the bottles were rinsed with the collected water to clean the bottle. The soil samples were collected in glass jars that were burned in 400°C and rinsed three times with methanol prior to use. Contamination were avoided with aluminum foil that were used under the lid.

2.2.1 Soil and sediment sampling

The soil samples were collected in the precleaned glass jars below the grass and root layers (10-30 cm). The jars were stored in a cooling box during the time in field and later stored in a fridge at 4°C

until analysis. In total, 12 soil samples (So1-So12) and two sediment samples (Se1-Se2) were collected at three different locations including Fire fighting facility 1 (So1-So5) on May 22, 2014, Fire fighting facility 2 (So6-So9, Se1-Se2) on May 29, 2014 and Fire fighting facility 3 (So10-So12) on June 11, 2014. At Fire training facility 1, two soil samples were collected from each fire training ground, F1 (So1-So2), F2 (So3-So4), and one control sample (So5) 300 m away from F1 and F2. At Fire fighting facility 2, six samples were collected (So6-So9, Se1-Se2). Two samples were collected at each fire training ground F3 (So8-So9) and F4 (So6-So7) and two sediment samples from a dried out pond (Se1-Se2). At Fire fighting facility 3, three samples were collected (So10-So12). The soil and sediment samples were characterized by organic matter (OM), total carbon (TC), total inorganic carbon (TIC), total organic carbon (TOC), and texture of the soil samples (see chapter '2.4 Soil characterization').

2.2.2 Groundwater sampling
For each groundwater sample, 1 L water was collected in precleaned PP bottles. For the water samples two different pumps were used. The first used were a suction pump, 12 V with a diameter of 46 mm which was driven by a car battery with capacity of 2-3 L s^{-1} for sampling sites G5-G9, G15-G18, G24-G27 and the second was a peristaltic pump with capacity of 0-2 L s^{-1} for sampling sites G19-23. The peristaltic pump was used at G19-G23 because the water flow into each well was too low for the suction pump. The samples G1-G4, G10-G14, G28 were collected by Uppsala Vatten. The groundwater was pumped ~one meter under the water level. The groundwater sample was collected when the temperature and pH was stable and the groundwater showed a clear color (usually after 15-30 minutes). The pH and water temperature, pumping level, water level, height above sea level and coordinates were recorded (Table A1 in the Appendix). The water bottles were stored in a cooling box during the time in field and later stored in a fridge room at 4°C. In total 28 groundwater samples were collected. Four reference points north of Uppsala in Björklinge (G1-G2) and Storvreta (G3-G4), three north of Fire fighting facility 1 (G5-G7), two near the Fire fighting facility 1 (G8-G9), eight at Fire fighting facility 2 (G16-G23) and one at Fire fighting facility 3 (G15). 16 samples were collected along Uppsalaåsen (G5-G15, G24-G28).

2.2.3 River and pond water sampling
For each river- and pond water sample, 1 L surface water samples was collected in precleaned PP bottles. The samples were collected with sampling equipment with adjustable length of the handle or with a stainless steel bucket with a long rope. The samples were all collected in the middle of the river or pond, either from a bridge or from the edge. The pH, water temperature and coordinates were recorded (Table A1 in the Appendix). In total, six surface water samples were collected (W1-W6), four samples along Fyrisån (W1-W2, W4-W5), one in Sävjaån (W3), the tributary to Fyrisån and one pond water sample from Fire fighting facility 2 (W6). The river water samples (W1-W5) were collected from north to south to see the change in PFASs composition. W3-W5 were distributed before and after the outflow of Sävjaån to see if it had any impact on Fyrisån.

2.2.4 Drinking water sampling
For each drinking water sample, 1 L surface water samples were collected in precleaned PP bottles. The samples were collected from the tap water which was spooled for 5 minutes before collecting the sample. pH and temperature was recorded (Table A1 in the Appendix). In total, four drinking water samples were collected. D1 was collected from the outgoing water at the drinking water treatment plant in Gränby and D2-D4 was tapwater in the west, east and south side of Uppsala.

2.3 Target compounds

The target compounds in this study consisted of 26 different PFASs: Four PFSAs (PFBS, PFHxS, PFOS, PFDS), thirteen PFCA (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA and PFOcDA), three FOSAs (FOSA, *N*-MeFOSA, *N*-EtFOSA), two FOSEs (*N*-MeFOSE, *N*-EtFOSE), three FOSAAs (FOSAA, *N*-MeFOSAA, *N*-EtFOSAA) and 6:2 FTSA (Table 1). The samples were all spiked with an internal standard mix (100 µL of an IS mixture, 20 pg µL^{-1}), including $^{13}C_8$-FOSA, d_3-*N*-MeFOSAA, d_5-*N*-EtFOSAA, d_3-*N*-MeFOSA, d_5-*N*-EtFOSA, d_7-*N*-MeFOSE, d_9-*N*-EtFOSE, $^{13}C_4$ 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. The IS were used to correct for variations in losses during sample preparation and instrumental analysis. The soil and sediment samples (So1-So12, Se1-Se2) were spiked directly before analyses with an injection standard (10 µL of an InjS mixture, 200 pg µL^{-1}) using $^{13}C_4$ PFOA to control matrix effects during instrumental analysis. No InjS was added for the water samples since the influence of matrix effects during instrumental analysis was minimal.

Table 1: Chemical properties of the PFASs analysed in this study.

Name	Abbreviation	Molecular formula	Log K_{OW} [b]	Log K_{OC} (L kg$_{OC}^{-1}$)	Log Sw [b] (mg L^{-1})
PFCAs					
perfluorobutanoate	PFBA	$C_3F_7CO_2^-$	2.82	n.a[a]	0.42
perfluoropentanoate	PFPeA	$C_4F_9CO_2^-$	3.43	n.a	-0.37
perfluorohexanoate	PFHxA	$C_5F_{11}CO_2^-$	4.06	n.a	-1.16
perfluoroheptanoate	PFHpA	$C_6F_{13}CO_2^-$	4.67	2.9±0.002[c]	-1.94
perfluorooctanoate	PFOA	$C_7F_{15}CO_2^-$	5.3	3.5±0.1[c]	-2.73
perfluorononanoate	PFNA	$C_8F_{17}CO_2^-$	5.92	4.0±0.1[c]	-3.55
perfluorodecanoate	PFDA	$C_9F_{19}CO_2^-$	6.5	4.6±0.1[c]	-4.31
perfluoroundecanoate	PFUnDA	$C_{10}F_{21}CO_2^-$	7.15	5.1±0.1[c]	-5.13
perfluorododecanoate	PFDoDA	$C_{11}F_{23}CO_2^-$	7.77	3.3±0.11[d]	-5.94
perfluorotridecanoate	PFTriDA	$C_{12}F_{25}CO_2^-$	8.25	n.a	-6.59
perfluorotetradecanoate	PFTeDA	$C_{13}F_{27}CO_2^-$	8.9	n.a	-7.42
perfluorohexadecanoate	PFHxDA	$C_{15}F_{31}CO_2^-$	n.a	n.a	n.a
perfluorooctadecanoate	PFOcDA	$C_{17}F_{35}CO_2^-$	n.a	n.a	n.a
PFSAs					
perfluorobutane sulfonate	PFBS	$C_4F_9SO_3^-$	6.49	n.a	-1.00
perfluorohexane sulfonate	PFHxS	$C_6F_{13}SO_3^-$	7.55	3.7±0.03[c]	-2.24
perfluorooctane sulfonate	PFOS	$C_8F_{17}SO_3^-$	8.07	4.8±0.1[c]	-3.92
perfluorodecane sulfonate	PFDS	$C_{10}F_{21}SO_3^-$	8.82	3.53±0.12[d]	-5.39
FTSAs					
6:2 fluorotelomer sulfonate	6:2 FTSA	$C_8H_4F_{13}SO_3^-$	4.44	n.a	-2.51
FOSAs					
perfluorooctanesulfonamide	FOSA	$C_8F_{17}SO_2NH_2$	5.62	4.5±0.1[c]	-5.05
N-methylperfluorooctansulfonamide	N-MeFOSA	$C_8F_{17}SO_2 N(CH_3)H$	6.07	n.a	-0.29
N-ethylperfluorooctanesulfonamide	N-EtFOSA	$C_8F_{17}SO_2(C_2H_5)H$	6.71	n.a	-0.26
FOSEs					
N-methylperfluorooctanesulfonamido-ethanol	N-MeFOSE	$C_8F_{17}SO_2(CH_3OH)H$	6.00	n.a	-6.22
N-ethylperfluorooctanesulfonamido-ethanol	N-EtFOSE	$C_8F_{17}SO_2(C_2H_5OH)H$	6.52	n.a	-6.73
FOSAAs					
perfluorooctanesulfonamidoacetic acid	FOSAA	$C_8F_{17}SO_2NH_3CH_2CO_2H$	n.a	n.a	n.a
N-methylperfluorooctanesulfonamidoacid	N-MeFOSAA	$C_8F_{17}SO_2NCH_3CH_2CO_2H$	n.a	3.11±0.16[d]	n.a
N-ethylperfluorooctanesulfonamidoacid	N-EtFOSAA	$C_8F_{17}SO_2N(CH_2)_3CH_3CO_2H$	n.a	3.23±0.18[d]	n.a

[a], not available. [b], (Wang et al, 2011). [c], (Ahrens et al, 2009[b]). [d], (Higgins and Luthy, 2006).

2.4 Soil characterization

2.4.1 Organic matter (OM) and total carbon (TC), total inorganic carbon (TIC), and total organic carbon (TOC)

For the determination of the OM content, approximately 5 g of each soil and sediment sample were burned in 450°C for 4 hours with a stepwise temperature increase and decrease (total time 24 h). The samples were weighted before and after burning. TC, TIC and TOC were determined by the Markfysiklab, Department of Soil and Environment, SLU, Uppsala (Table 2). Samples from the same location, which have a comparable texture were combined into 7 samples. The samples were i) So1-So2, ii): So3-So4, iii): So6-So7, iv): So8, v): So9, vi): So11-So12, and vii): Se1-Se2.

2.4.2 Texture

For the determination of the texture, the 14 and sediment soil samples were air dried for 72 h. Samples from the same location, which have a comparable texture, were combined into 7 samples. The samples were i) So1-So2, ii): So3-So4, iii): So6-So7, iv): So8, v): So9, vi): So11-So12, and vii): Se1-Se2. The texture was determined by the Marklab, Department of Soil and Environment, SLU, Uppsala, using pipette method according to ISO 11277 (sieving and sedimentation) (Table 2).

2.4.3 Moisture content

To determine the dry weight, approximately 5 g of soil was weighted and then burned at 105°C for 24 hours. The samples were then weighted again after drying (Table 2).

Table 2: Soil characterisation including moisture, organic matter (OM), total carbon (TC), total inorganic carbon (TIC), total organic carbon (TOC), and texture of the soil samples.

ID	Moisture content (%)	OM content (%)	TIC (%)	TOC (%)	TC (%)	Clay <0.002 mm (%)	Silt 0.002-0.05 mm (%)	Sand >0.05 mm (%)
So1	23	29	0.04[a]	2.37[a]	2.41[a]	33.7[a]	54.1[a]	12.2[a]
So2	23	27						
So3	18	23	0.06[b]	2.46[b]	2.52[b]	45.9[b]	42.1[b]	12.1[b]
So4	19	24						
So5	19	24	n.a[f]	n.a	n.a	n.a	n.a	n.a
So6	24	31	3.19[c]	2.55[c]	5.75[c]	11.6[c]	24.3[c]	64.0[c]
So7	7	9						
So8	18	24	0.28	1.98	2.26	58.7	26.6	14.6
So9	16	21	0.06	1.91	1.98	57.8	29.4	12.7
So10	10	17	n.a	n.a	n.a	n.a	n.a	n.a
So11	15	19	0.39[d]	1.79[d]	2.19[d]	29.4[d]	44.7[d]	10.0[d]
So12	13	20						
Se1	23	26	1.62[e]	1.12[e]	2.75[e]	58.1[e]	33.7[e]	8.2[e]
Se2	23	26						

[a], average of So1, So2. [b], average of So3, So4. [c], average of So6, So7. [d], average of So11, So12. [e], average of Se1, Se2. [f], not available.

2.5 Extraction

All samples were extracted and analysed in the POP laboratory of the Department of Aquatic Sciences and Assessment, SLU, Uppsala, Sweden.

To avoid contamination, all glassware were washed with distilled water, rinsed with ethanol three times, dish washed, burned at 400°C, and rinsed with methanol three times before use. The glass vials and glass fibre filters (GFFs) were burned at 400°C before use. Polypropylen (PP) tubes were rinsed with methanol three times before use. Five duplicates for water samples and one duplicate and three triplicates for soil were also analysed.

2.5.1 Extraction of soil and sediment

The soil and sediment samples were analysed according to Ahrens et al. (2009[b]). The soil were sieved though a 2 mm sieve, thus small stones, leaves and sticks were removed. The soil samples (10-15 g) were freeze-dried for 48 h. After freeze-drying, 5 g homogenized soil was weighted into clean PP tubes and stored in the freezer (-20°C) until analysis. For the solid-liquid extraction (SLE), 2 mL of 100 mM sodium hydroxide (NaOH in 80% methanol and 20% in Millipore water) was added into the PP tube and soaked for 30 min. Then, 20 mL methanol and 100 µL PFAS-IS standard mix (20 pg µL^{-1}) was added. The PP tubes were placed in a wrist shaker for 60 min at 200 rpm and afterwards centrifuged at 3000 rpm for 15 min. The samples were decanted into a new 50 mL PP tube. The procedure was repeated but only 1 mL NaOH and 10 mL methanol was added and the shaking time was reduced to 30 min (200 rpm). After centrifugation (3000 rpm for 15 minutes), the samples were decanted to the rest of the supernatant. 100 µL 4 M hydrochloric acid (HCl) was added to neutralize the sample and the sample was centrifuged for 5 min at 3000 rpm. A volume of 4.15 mL (1/8) of the sample was transferred into a 15 mL PP tubes and concentrated to 1 mL using a nitrogen evaporator. For the clean-up, 25 mg ENVI-carb and 50 µL glacial acetic acid was added into a 1.7 mL PP Eppendorf micro centrifuge tubes. The samples were added to the PP Eppendorf micro centrifuge tube and then vortexed for 30 sec and centrifuged at 4000 rpm for 10 min. A volume of 0.5 mL of the sample was transferred into a 2 mL glass vial. Finally, an 10 µL injection standard (200 pg µL^{-1}) was added. So2, So7 and S10 were analysed in triplicates and So1 was analysed in duplicate.

2.5.2 Extraction of groundwater, surface water and drinking water

The water samples were first filtrated using a filtration equipment and GFFs. The filtration unit was rinsed 3 times with methanol before use, and every second filtration the glassware was switched to clean equipment. After the filtration of one sample, the filtration unit and PP-bottles were rinsed with methanol and transferred to the filtrated water. The water was split into two bottles because only 0.5 L was used for the solid phase extraction (SPE). The empty and the full bottles were weighted to detemine the volume of the water.

For SPE, Oasis weak anion exchange (WAX) 6 cc cartridge 500 mg, 60 µm (Waters) and a SPE workstation was used (for details see Ahrens et al, 2009[c]). Before the SPE the water samples were spiked into the bottles with 100 µL IS mixture (20 pg µL^{-1}). The cartridges were preconditioned with 4 mL 0.1% ammonium hydroxide in methanol, 4 mL methanol, and 4 mL Millipore water. The SPE was then started with one drop per second adjusted by the stop cock and vacuum pressure. After the loading of the water, the cartridge was washed with 4 mL 25 mM ammonium acetate buffer with pH 4, and then the cartridge was dried using a centrifuge at 3000 rpm in 2 min. The samples were eluted into 15 mL PP tubes with 4 mL methanol and 4 mL 0.1% ammonium hydroxide in methanol. The samples were then concentrated using nitrogen evaporator to about 1 mL and transferred into 2 mL glass vials.

The PP tube was rinsed twice with methanol and also transferred to the 2 mL glass vial. Finally, the sample extract was concentrated to 1 mL. For each batch of 10 samples, one duplicate and two solvent blanks were used. The duplicates were W1, W6, G10, G12 and G20.

2.6 Instrumental analysis

All samples were analysed with high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS) (for details see Ahrens et al. 2009[c]). Concentrations in the samples were calculated from the concentrations of the injection standards. The analysis was done at the POPs laboratory, Department of Aquatic Sciences and Assessment, SLU.

2.7 Quality assurance and quality control

To avoid contamination of the samples, material and objects that could contain fluorinated compounds was avoided. In total 3 solvent blanks for soil and 10 solvent blanks for water were used. The blanks were used to calculate the method detection limit (MDL) and method quantitation limit (MQL) which was calculated by

$$MDL = \text{mean blanks} + (3 * SD \text{ blanks}) \quad MQL = {MDL}/{3} * 10$$ where SD is the standard deviation.

2.8 Data evaluation and statistical analysis

For sample relation and source tracing, uni- and multivariate statistical analyses were used. Pearson correlation was used for correlation between groundwater samples and soil samples using Excel (α=0.05). Principal Component Analysis (PCA) using normalized data was applied for fingerprinting analysis and source tracing (Canaco software). The normalization was done by dividing the concentration of the individual PFASs with the total PFAS concentration; thus each compound was characterized by the fraction in relation to ΣPFASs (ranging from 0 to 1). ArcGIS 10.2.2 was used for creating the maps.

3. Results

3.1 Quality assurance and quality control

For quality assurance and quality control, solvent blank controls, method detection limits (MDLs), method quantification limits (MQLs), recoveries and duplicate samples were evaluated (see Table 3 and 4). The MDLs for soil/sediment ranged from 0.01 ng g^{-1} dw (e.g. PFOA) to 1.15 ng g^{-1} dw (PFBA) (Table 4). The MDLs for water ranged from 0.1 ng L^{-1} (e.g. PFHxDA) to 14.4 ng L^{-1} (PFDoDA) (Table 4). The recoveries ranged from 88$\pm$11% (^{13}C$_5$ PFNA) to 128$\pm$13% (^{13}C$_4$ PFOA) for soil/sediment (n=14) and from 43$\pm$19% (d$_9$-N-EtFOSE) to 97$\pm$24% (d$_3$-N-MeFOSAA) for water samples (n=28) (Table 3). The differences in the duplicate and triplicate samples ranged between average 0% (e.g. 6:2 FTSA) and 52% (PFDoDA) for soil/sediment samples (n=4) and 0% (e.g. FOSA) and 8% (PFPeA) in the water samples (n=5).

Table 3: Recoveries (%) PFASs in soil and water samples.

Recovery (%)	Soil and sediment (*n*=14)		Water (*n*=28)	
	mean	SD	mean	SD
$^{13}C_4$ PFBA	97	12	55	27
$^{13}C_2$ PFHxA	90	9	81	16
$^{13}C_4$ PFOA	128	13	94	20
$^{13}C_5$ PFNA	88	11	96	23
$^{13}C_2$ PFUnDA	93	11	86	18
$^{13}C_2$ PFDoDA	93	11	79	19
$^{18}O_2$ PFHxS	115	11	90	18
$^{13}C_4$ PFOS	96	17	77	18
$^{13}C_8$-FOSA	105	7	77	17
d_5-*N*-EtFOSA	103	11	43	19
d_3-N-MeFOSA	97	12	47	17
d_7-*N*-MeFOSE	96	12	47	16
d_9-*N*-EtFOSE	98	9	45	17
d_3-*N*-MeFOSAA	109	16	97	24
d_3-*N*-MeFOSAA	110	18	92	21

Table 4: Concentration solvent blanks (ng g^{-1} dw/ng L^{-1}), MDL (ng g^{-1} dw/ng L^{-1}), MQL (ng g^{-1} dw/ng L^{-1}) for soil/sediment and water.

Soil and sediment (*n*=14)				Water (*n*=28)			
Compounds	Blanks (*n*=3) (ng g^{-1} dw)	MDL (ng g^{-1} dw)	MQL (ng g^{-1} dw)	Compounds	Blanks (*n*=10) (ng L^{-1})	MDL (ng L^{-1})	MQL (ng L^{-1})
PFBA	0.64	1.15	3.82	PFBA	1.33	6.04	20.1
PFPeA	0.39	0.40	1.33	PFPeA	0.06	0.34	1.15
PFHxA	0.05	0.08	0.28	PFHxA	0.09	0.55	1.82
PFHpA	ND[a]	0.01	0.03	PFHpA	0.10	1.59	1.96
PFOA	ND	0.01	0.03	PFOA	0.28	0.53	5.45
PFNA	ND	0.01	0.03	PFNA	0.85	4.96	16.5
PFDA	0.01	0.04	0.12	PFDA	0.20	1.27	4.22
PFUnDA	ND	0.03	0.10	PFUnDA	0.19	1.20	3.99
PFDoDA	0.04	0.05	0.16	PFDoDA	3.23	14.4	47.8
PFTriDA	ND	0.01	0.03	PFTriDA	ND	0.10	0.33
PFTeDA	0.03	0.04	0.15	PFTeDA	0.14	0.84	2.81
PFHxDA	ND	0.01	0.03	PFHxDA	ND	0.10	0.33
PFOcDA	ND	0.01	0.03	PFOcDA	ND	0.10	0.33
PFBS	ND	0.01	0.04	PFBS	0.17	1.08	3.59
PFHxS	0.28	0.31	1.04	PFHxS	0.08	0.50	1.65
PFOS	ND	0.01	0.03	PFOS	0.17	1.13	3.75
PFDS	ND	0.01	0.03	PFDS	ND	0.10	0.33
6:2 FTSA	ND	0.01	0.03	6:2 FTSA	ND	0.10	0.33
FOSA	ND	0.01	0.03	FOSA	0.50	2.61	8.69
MeFOSA	ND	0.01	0.03	MeFOSA	ND	0.10	0.33
EtFOSA	ND	0.01	0.03	EtFOSA	ND	0.10	0.33
MeFOSE	ND	0.01	0.03	MeFOSE	ND	0.10	0.33
EtFOSE	ND	0.01	0.03	EtFOSE	ND	0.10	0.33
FOSAA	ND	0.01	0.03	FOSAA	ND	0.10	0.33
MeFOSAA	ND	0.01	0.03	MeFOSAA	ND	0.10	0.33
EtFOSAA	ND	0.01	0.03	EtFOSAA	ND	0.10	0.33

[a], not detected.

3.2 Soil and sediment
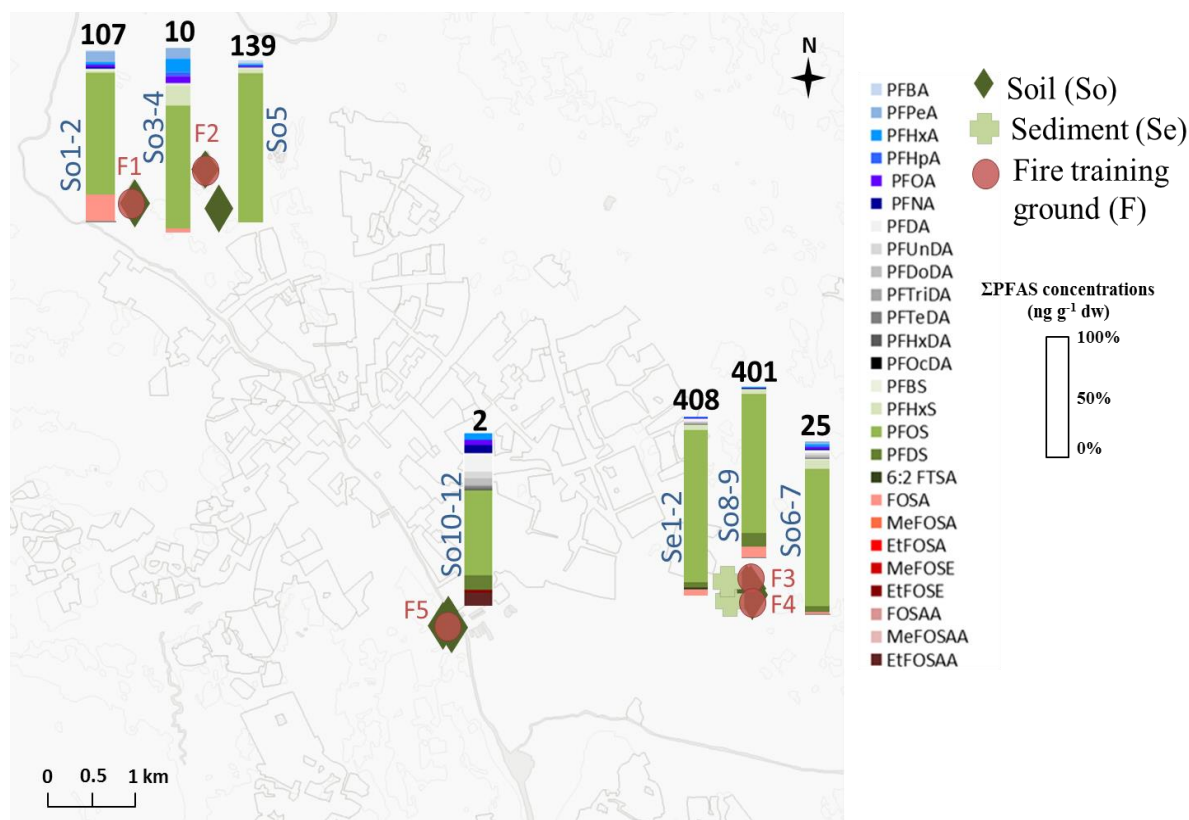
Figure 2: Composition profiles of detected PFASs in soil and sediment, and ΣPFASs concentrations in ng g^{-1} dw at the sampling sites. Average values are given for sites with >1 measurements.

In total, 25 out of 26 PFASs were detected in the soil samples (So1-So12); MeFOSE was the only PFAS not detected. The most frequently detected PFASs were PFOS (100%), PFHxA (83%), PFOA and FOSA (both 75%) and PFDA and PFHxS (both 67%). The ∑PFAS concentrations ranged from 0.2 ng g^{-1} dw (So11) to 608 ng g^{-1} dw (So8), with ∑PFSAs as the dominant PFAS class (average 91 ng g^{-1} dw, median 28 ng g^{-1} dw, 88%) followed by FOSAs (7 ng g^{-1} dw, 0.04 ng g^{-1} dw, 6%), PFCAs (5 ng g^{-1} dw, 4 ng g^{-1} dw, 5%), FOSAAs (0.5 ng g^{-1} dw, 0.01 ng g^{-1} dw, 0.5%), 6:2 FTSA (0.06 ng g^{-1} dw, <0.01 ng g^{-1} dw, 0.06%), and FOSEs (0.01 ng g^{-1} dw, <0.01 ng g^{-1} dw, 0.01%). The highest concentrations of individual PFASs had PFOS (on average 119 ng g^{-1} dw, median 55 ng g^{-1} dw), followed by PFDS (8 ng g^{-1} dw, 0.5 ng g^{-1} dw), FOSA (6 ng g^{-1} dw, 0.2 ng g^{-1} dw).

In the sediment samples (Se1-Se2), 22 out of 26 PFASs were detected; EtFOSA, MeFOSE, EtFOSE and PFBA were not detected. The detected PFASs were all detected in both samples (Se1-Se2). The ∑PFAS concentrations ranged from 349 ng g^{-1} dw (Se1) to 468 ng g^{-1} dw (Se2), with ∑PFSAs as the dominant PFAS class (on average 366 ng g^{-1} dw, 89%) followed by PFCAs (19 ng g^{-1} dw, 5%), FOSAs (17 ng g^{-1} dw, 4%), 6:2 FTSA (4 ng g^{-1} dw, 0.9%) and FOSAAs (2 ng g^{-1} dw, 0.6%). The highest concentrations of individual PFASs had PFOS (on average 343 ng g^{-1} dw, 84%), followed by FOSA (16 ng g^{-1} dw, 4%), PFHxS (12 ng g^{-1} dw, 3%).

The highest ΣPFAS concentrations was detected at the sediment samples of the pond (Se1-Se2) at Fire fighting facility 2 with average concentrations of 408 ng g^{-1} dw, followed by F3 (So8-So9) (401 ng g^{-1} dw), the reference site (So5) with 139 ng g^{-1} dw, F1 (So1-So2) with 107 ng g^{-1} dw, F2 (So3-So4) with 77 ng g^{-1} dw, F4 (So6-So7) with 25 ng g^{-1} dw and F5 (So10-So12) with 2 ng g^{-1} dw (Figure 2).

At Fire fighting facility 1 (F1, F2), was PFOS dominant at F1 (So1-So2) with an average of 75 ng g^{-1} dw (70% of the ∑PFASs) and at F2 (So3-So4) with an average of 7 ng g^{-1} dw, 67% of the ∑PFASs. The concentrations at F1 was about 10 times higher (∑PFAS concentrations 107 ng g^{-1} dw) than at F2 (∑PFAS concentrations 10 ng g^{-1} dw). At F1 and F2 (So1-So4), the dominant PFASs were PFOS (70%), FOSA (13%) and PFPeA (6%). Concentration of FOSA at F1 (average 15 ng g^{-1} dw) was 61 times higher than at F2 (average 0.2 g^{-1} dw). The reference soil sample at Fire fighting facility 1 (So5) had the highest ∑PFAS concentrations at the area (139 ng g^{-1} dw) and highest concentration of PFOS (average 127 ng g^{-1} dw, 91% of the ∑PFASs) compared to the other at the area (So1-So4) (average <79 ng g^{-1} dw, 70%). At the reference site, the dominant PFASs were PFOS (91%) and PFHxS (4%).

At Fire fighting facility 2 (F3, F4), the ∑PFAS concentration at F3 (So8-So9) was higher (on average 401 ng g^{-1} dw) compared to F4 (So6-So7) (25 ng g^{-1} dw). The dominating compound at F3 (So8-So9) and F4 (So6-So7) was PFOS (both 81%). Particular high concentrations of PFDS (8% of the ∑PFASs) and FOSA (5%) were detected at F3 compared to F4 (PFDS: 4% and FOSA: 1%). The sediment in the pond had the second and third highest ∑PFASs concentrations of all the sediment and soil samples (∑PFASs concentration of Se2: 468 ng g^{-1} dw and Se1: 349 ng g^{-1} dw).

The lowest ∑PFAS concentrations were found at Fire fighting facility 3 (F5, average 2 ng g^{-1} dw, median 1 ng g^{-1} dw) compared to the other facilities. The dominant PFASs at F5 (So10-S12) were PFOS (on average 1 ng g^{-1} dw, median 1 ng g^{-1} dw, 57% of the ∑PFASs), followed by PFDA (0.3 ng g^{-1} dw, median <0.04 ng g^{-1} dw, 12%). FOSA, which were detected at the other fire fighting facilities (F1-F4), were not detected at F5. PFDA, PFUnDA, PFDoDA, PFTriDA and PFTeDA were detected in higher concentrations at So10 (F5) compared the other fire fighting facilities (F1, F2, F3 and F4). Also the PFCAs (35% of the ∑PFASs) were higher at F5 especially PFNA, PFDA and PFHxA (5%, 12% and 3% of the ∑PFASs) compared to the other fire training grounds (F1 and F2: 0.6%, 0.6% and 2% of the ∑PFASs, F3 and F4: 0.2%, 0.2%, 0.4% of the ∑PFASs).

3.3 Groundwater

Figure 3: Composition profiles of detected PFASs in groundwater and ΣPFAS concentrations in ng L⁻¹ at the sampling sites. The black quadrat represents the reference points north of Uppsala, Björklinge (G1-G2) and Storvreta (G3-G4). Average values are given for sites with >1 measurements.

In total 18 out of 26 PFASs were detected in the groundwater samples G1-G28, where the dominant PFASs were PFHxS (71% of total ΣPFASs), PFPeA (68%), PFOS (61%), PFBS (61%), PFHxA (54%) and PFBAs (36%). PFDoDA, PFTriDA, PFHxDA, PFOcDA, PFDS, MeFOSA, EtFOSA, MeFOSE, EtFOSE, MeFOSAA and EtFOSAA were not detected. The dominant PFAS class was 6:2 FTSAs with an average of 192 ng L⁻¹ and median of <0.1 ng L⁻¹ which was only detected in three samples (G21, G19 and G17). The second most dominant PFAS class were PFSAs (160 ng L⁻¹, 11 ng L⁻¹) followed by PFCAs (94 ng L⁻¹, 3 ng L⁻¹), FOSAs (0.5 ng L⁻¹, <0.1 ng L⁻¹) and FOSAAs (0.004 ng L⁻¹, <0.1ng L⁻¹).

The sampling sites with high ΣPFAS concentrations were located near the fire fighting facilities (F1-F5) (Figure 3). The highest ΣPFAS concentrations were detected at Fire fighting facility 2 (F3-F4, G16-G23) where the dominating PFASs classes were 6:2 FTSAs (average 673 ng L⁻¹, median of <0.1 ng L⁻¹, 51% of ΣPFASs concentration), followed by PFSAs (average 362 ng L⁻¹, 18 ng L⁻¹, 27%) and PFCAs (average 272 ng L⁻¹, 6 ng L⁻¹, 21%). G21 had the highest ΣPFAS concentration (8015 ng L⁻¹) with 6:2 FTSA as the dominating compound (5360 ng L⁻¹, 61% of ΣPFASs concentration) followed by PFHxA (728 ng L⁻¹, 9%) and PFPeA (489 ng L⁻¹, 6%). G17 had also high ΣPFAS concentrations (2110 ng L⁻¹) with PFOS as the dominating compound (1680 ng L⁻¹, 80%). The concentrations were also

high near Fire fighting facility 1 (G8-G9), G9 had ΣPFAS concentration of 1000 ng L^{-1} and G8 had a ΣPFAS concentration of 279 ng L^{-1}. The dominating PFAS classes at G9 and G8 were PFSAs (average 539 ng L^{-1}, 84%) and PFCAs (100 ng L^{-1}, 16%) and the dominating compounds was PFHxS (G9: 62% and G8: 58% of the ΣPFASs), followed by PFOS (16% and 15%), PFHxA (8% and 12%) and PFBS (8% and 9%). PFOA was found at G9 (3% of the ΣPFASs) but not at G8. At Fire fighting facility 3 (F5, G15) the ΣPFAS concentrations were 61 ng L^{-1}. The dominant PFAS class were at G15, PFSAs with 44 ng L^{-1} (72% of the ΣPFASs) and PFCAs with 17 ng L^{-1} (28%). At G15, PFOS (21 ng L^{-1}, 34% of the ΣPFASs) and PFHxS (20 ng L^{-1}, 33%) had the highest concentrations. One of the highest percentages of PFBA was detected at G15 (9 ng L^{-1}, 14%) and PFTeDA was detected in small amount at G15 (1 ng L^{-1}, 2%).

Low concentrations or not detectable concentrations of PFASs were detected in the northern Uppsala (ΣPFASs <3 ng L^{-1}, G1-G4). Also samples north-west of Fire fighting facility 1 (G5-G7) was low contaminated (G5 and G6: no PFAS detected, G7: 2 ng L^{-1} for ΣPFASs). G10 and G11 had also low ΣPFAS concentrations (G10: 2 ng L^{-1}, G11: 1 ng L^{-1}) and the only PFASs detected at these two samples were PFHxS.

The southern samples, G12-G14 had a similar composition profile as G9 and G8. The ΣPFAS concentrations were 137 ng L^{-1} for G12, 207 ng L^{-1} for G13 and 83 ng L^{-1} for G14. PFSAs were the dominant PFAS class in these three samples (on average 247 ng L^{-1}, median 114 ng L^{-1}, 92% of ΣPFASs), followed by PFCAs (28 ng L^{-1}, 31 ng L^{-1}, 2%). The dominant compound in G12-G14 was PFHxS (G12: 71 ng L^{-1}, 49% of ΣPFASs G13: 91 ng L^{-1}, 41% G14: 61 ng L^{-1}, 54%). Other dominant PFASs were PFBS at G13 and G12 (G12: 27 ng L^{-1}, 18% G13: 64 ng L^{-1}, 29%), PFOS (G12: 16 ng L^{-1}, 11% G13: 24 ng L^{-1}, 11%) and PFBA (G12: 12 ng L^{-1}, 8% G13: 14 ng L^{-1}, 7%), whereas at G14 the dominant PFASs were PFOS (14 ng L^{-1}, 17%), PFBS (8 ng L^{-1}, 9%) and PFHxA (6 ng L^{-1}, 7%).

South of the Fire fighting facility 3 (G24-G28) the concentrations decreased (G24: ΣPFASs = 54 ng L^{-1} G25: 53 ng L^{-1} G26: 22 ng L^{-1} G27: 1 ng L^{-1} G28: no PFASs detected). The composition profiles were varying but PFHxS continued to dominate in these groundwater samples (G24: PFHxS = 36 ng L^{-1}, 66% of ΣPFASs G25: 21 ng L^{-1}, 36% G26: 15 ng L^{-1}, 63% and G27: 1 ng L^{-1}, 61%). G25 had higher levels of PFBA (10 ng L^{-1}, 18%) compared to G24, G26-G28, where no PFBA was detected. Furthermore, concentrations of PFPeA and PFHxA were higher in G24 (2 ng L^{-1} and 6 ng L^{-1}, respectively) and G25 (3 ng L^{-1} and 9 ng L^{-1}, respectively) than at G26-G28 (<0.5 ng L^{-1} and <0.55 ng L^{-1} respectively). G25 showed a slightly different composition profile with an increase of ΣPFCAs (31 ng L^{-1}, 52% of ΣPFASs) compare to G24 (11 ng L^{-1}, 20%), G26 (5 ng L^{-1}, 21%) and G27 (1 ng L^{-1}, 39%).
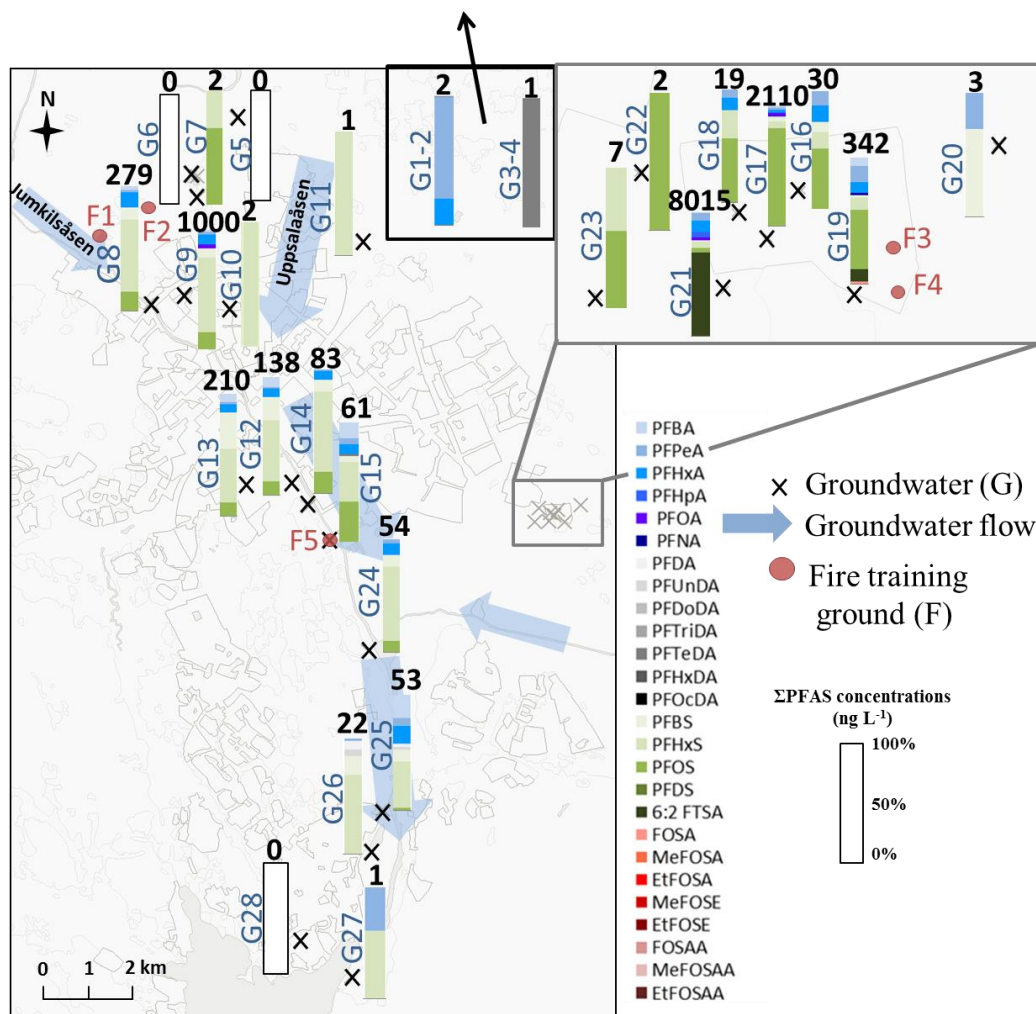
3.4 Surface water

Figure 4: Composition profiles of detected PFASs in surface water and ΣPFAS concentrations in ng L^{-1} at the sampling sites. The black quadrat represents the reference points north of Uppsala (W1).

In total 4 of 26 PFASs were found in the river water samples (W1-W5) including PFPeA, PFHxA, PFHxS and PFOS. At W1-W5, the most frequently detected PFASs were PFOS and PFHxS (both 80% of the ΣPFASs), PFHxA (60%), and PFPeA (40%). In contrast, 18 out of 26 PFASs were found in the surface water of the pond at Fire fighting facility 2 (W6). The PFASs not detected in the pond (W6) were PFDoDA, PFTeDA, PFHxDA PFOcDA, MeFOSA, EtFOSA, MeFOSE and EtFOSE.

The highest ΣPFAS concentration was found at the pond W6 with ΣPFASs concentration of 3026 ng L^{-1}, followed by Sävjaån (W3, 15 ng L^{-1}) and Fyrisån at W4 (13 ng L^{-1}), W5 (11 ng L^{-1}), W2 (8 ng L^{-1}) (Figure 4). The PFASs concentrations at W1, north of Uppsala, were below MDL. At W6, PFOS was the dominating compound with 43%, followed by 6:2 FTSA (25%), and the short chained PFHxS (10%), PFHxA (6%) and PFPeA (6%). At W2, W4-W5, PFHxS (on average 51%) was the dominating compound while the dominating compound at W3 was PFOS (62%). W3 had three times higher concentration of PFOS than PFHxS. PFPeA and PFHxA was also detected in small concentrations at W2-W5.

The fluxes of PFASs in the Fyrisån and Sävjaån were calculated using the following formula.

$$\text{Flux (g/day)} = \text{concentration (g/L)} * (\text{water flow (L/s)} * 86400)$$

Modeled water flow data (m^3 s^{-1}) for Fyrisån and measured water flow data (m^3 s^{-1}) for Sävjaån were collected from SMHI VattenWeb (SMHI 2014-07-30) (Table 5). The calculated flux has to be

considered as a rough estimation, since only modelled water flow data were used for the Fyrisån which have uncertainties. Furthermore only one grab sample was collected at each location.

The water flow was lowest at W3 with 1.57 m^3 s^{-1} and highest at W5 with 4.58 m^3 s^{-1}. The ∑PFAS flux in the Fyrisån and Sävjaån ranged from <0.1 g day^{-1} (W1) to 40 g day^{-1} (W5) with PFSAs as the dominant PFAS class (average 18 g day^{-1}, median 22 g day^{-1}, 61% of the ∑PFASs) followed by ∑PFCAs (5 g day^{-1}, 3 g day^{-1}, 16%), The highest concentrations of individual PFASs had PFOS (on average 8 g day^{-1}, median 9 g day^{-1}) followed by PFHxS (8 g day^{-1}, 8 g day^{-1}). Lowest concentrations were found for PFHxA (0.9 g day^{-1}) and PFPeA (average 0.2 g day^{-1}). The highest flux of PFASs was in W5 with ∑PFASs 40 g day^{-1} followed by W4 (25 g day^{-1}), W2 (24 g day^{-1}), W3 (14 g day^{-1}) and W1 (<0.1 g day^{-1}).

Table 5: Water flow (m^3 s^{-1}), flux (g day^{-1}) and percentage (%) of ΣPFAS for the four detected PFAS in river water.

Sample	Water flow (m^3 s^{-1})	Flux (g day^{-1})					Percentage of ΣPFAS (%)			
		PFPeA	PFHxA	PFHxS	PFOS	∑PFASs	PFPeA	PFHxA	PFHxS	PFOS
W1	1.86	ND[a]	ND	ND	ND	ND	0	0	0	0
W2	2.78	ND	ND	13.0	11.1	24.0	0	0	54	46
W3	1.57	0.95	1.26	2.93	8.43	13.6	7	9	22	62
W4	2.91	0.99	1.91	13.5	8.78	25.1	4	8	54	35
W5	4.58	ND	3.27	18.6	17.7	39.6	0	8	47	45

[a], not detected

3.5 Drinking water

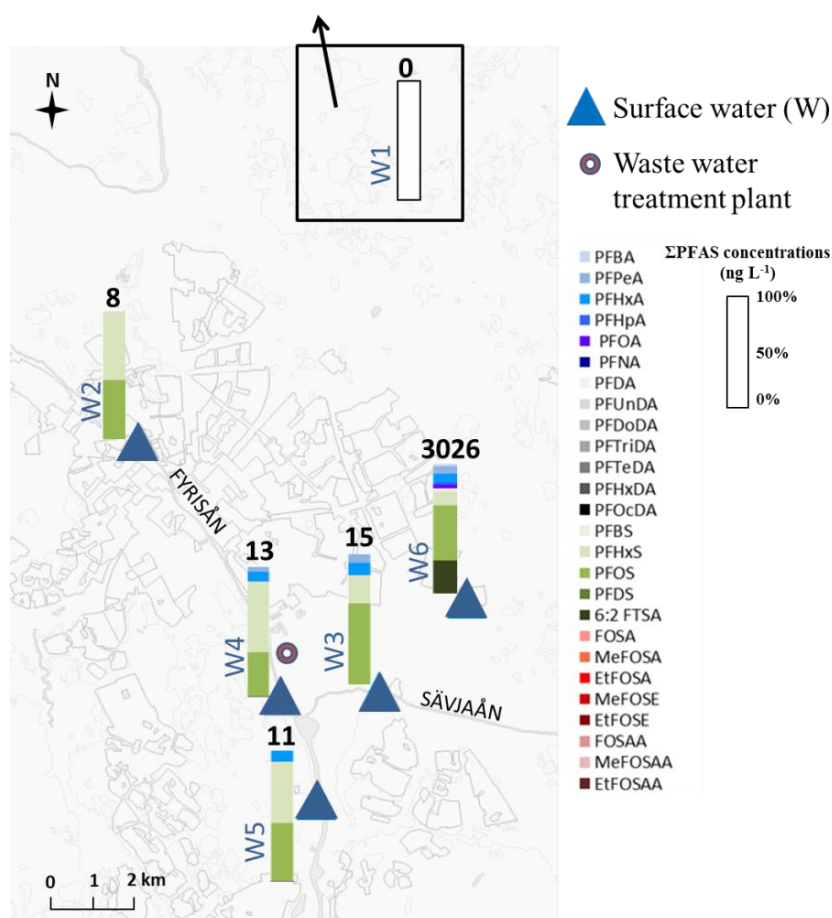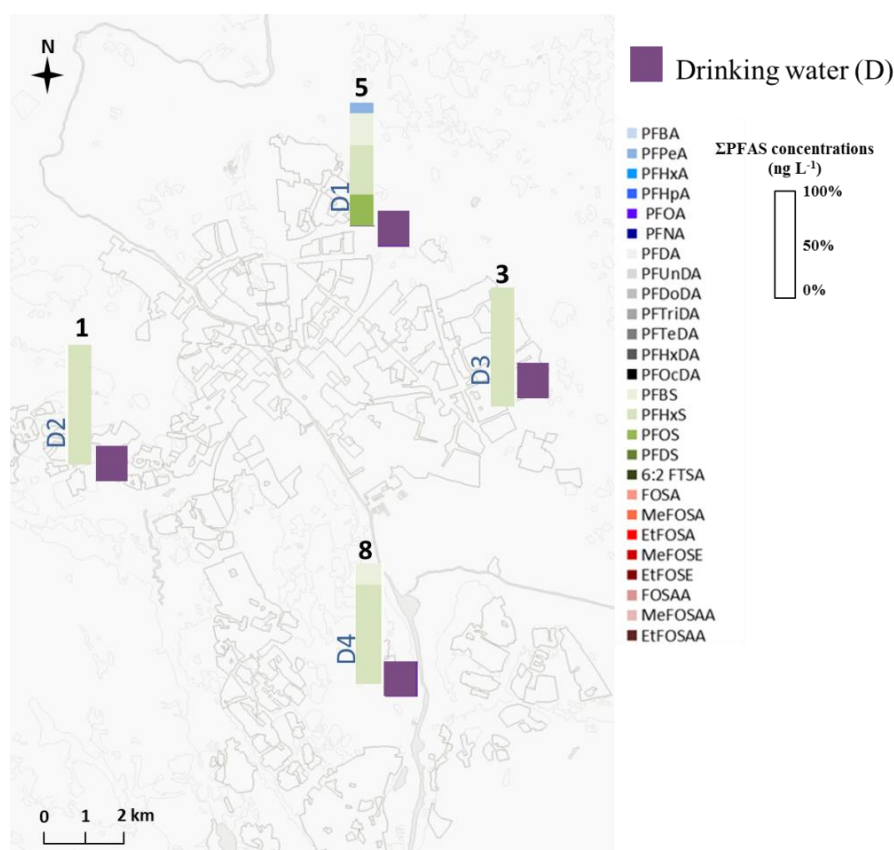**Figure 5:** Composition profiles of detected PFASs in drinking water and ΣPFAS concentrations in ng L^{-1} at the sampling sites.

In total 4 out of 26 PFASs were detected in the drinking water samples (D1-D4). PFHxS were the most frequently detected PFASs and found in each drinking water sample. The other dominating compounds were PFBS (50%), PFOS (25%) and PFPeA (25%). The ΣPFASs concentrations ranged from 1 ng L^{-1} (D2) to 8 ng L^{-1} (D4), with PFSAs as the dominating PFASs class (average 4 ng L^{-1}, median 4 ng L^{-1}) followed by PFCAs (0.1 ng L^{-1}, <0.1 ng L^{-1}). The drinking water sample with the highest concentration were D4 with 8 ng L^{-1}, followed by D1 (5 ng L^{-1}), D3 (3 ng L^{-1}), and D2 (1 ng L^{-1}) (Figure 5).

At the drinking water samples D1-D4 was the dominant PFAS class PFSAs (100% of total ΣPFASs concentration, D2-D4, 92%, D1). PFASs detected in D1 was PFHxS (2 ng L^{-1}, 40% of ΣPFASs concentration), PFBS (1.4 ng L^{-1}, 27%), PFOS (1.3 ng L^{-1}, 25%) and a small concentration of PFPeA (0.4 ng L^{-1}, 8%). D2, D3 and D4 had almost the same composition profiles, where PFHxS was the only detected compound at D2 (1 ng L^{-1}) and D3 (3 ng L^{-1}). At D4 both PFHxS (6 ng L^{-1}, 81% of ΣPFASs concentration) and PFBS (2 ng L^{-1}, 19%) were detected.

3.6 Comparison of PFASs in soil, sediment ground-, surface- and drinking water

3.6.1 Composition profiles
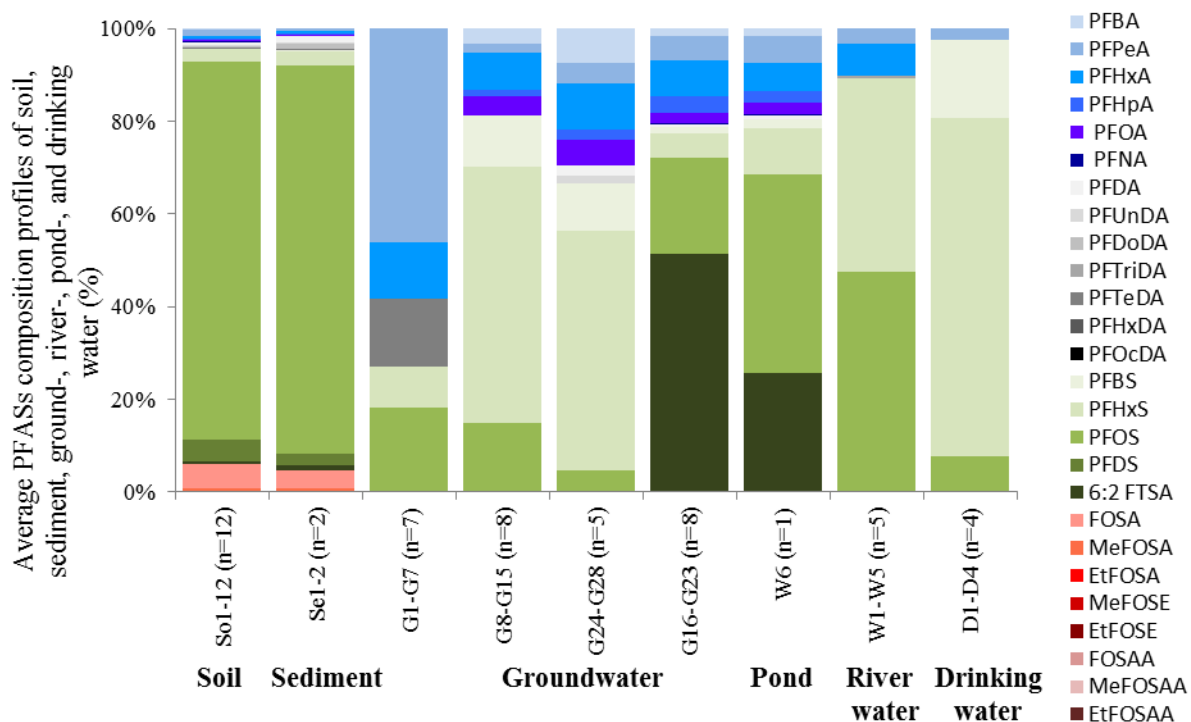
Figure 6: PFASs composition profile in procentage (%) in soil, sediment, groundwater, river water, pond water, and drinking water.

25 out of 26 PFASs were found, MeFOSE was the only compound not detected in any sample. The dominating PFASs in soil So1-So12 were PFOS (80%), FOSA (6%) and PFDS (6%). For the sediment samples (Se1-Se2) the dominant compounds were PFOS (84%), FOSA (4%), PFDS (3%) and PFHxS (3%). The composition of 6:2 FTSA and the longer chained PFCAs (PFDA, PFDoDA and PFTeDA) were higher at Se1-Se2 (0.9%, 1.5%, 0.9%, 0.2%, respectively) compare to So1-So12 (0.08%, 0.3%, 0.1%, 0.04% respectively) (Figure 6). The groundwater at G1-G7 was low contaminated (∑PFASs <3

ng L^{-1}) and these samples were also the only groundwater samples with a higher content of PFCAs (73%) compared to PFSAs (27%). At G8-G15 and G24-28, the dominant PFAS class was PFSAs (84% and 72%, respectively) and these groundwater samples had very similar composition profiles with PFHxS (57%/56%), PFOS (15%/5%), PFBS (11%/11%) and PFHxA (8%/11%) as dominant PFASs. South of Uppsala at G24-G28, PFOS had a lower composition (5%) and PFOA was not detected compared to G8-G15 in the north part of Uppsala (PFOS: 15%, PFOA: 2%). Furthermore, the composition of PFBA (8%), PFDA (2%), PFUnDA (2%), PFPeA (5%) was higher at G24-G28 compared to G8-G15 (PFBA 3%, PFDA 0%, PFUnDA 0%, PFPeA 2%).

The groundwater samples (G16-G23) and the pond (W6) at Fire fighting facility 2 had a similar composition profile. Percentage of ∑PFASs of the following PFASs were similar: PFBA (G16-G23: 2%, W6: 2%), PFPeA (5%/6%), PFHxA (8%/6%), PFHpA (3%/2%), PFOA (2%/2%), PFDA (0%/1%) and PFBS (1%/2%). The composition of PFHxS and PFOS were higher in the pond (PFHxS: 10%, PFOS: 43%) than in groundwater (5%, 21%) while 6:2 FTSA was two times higher in the groundwater (51%) than in the pond (21%). In the water samples, 6:2 FTSA were only detected at Fire fighting facility 2. Composition of river water and drinking water differed from the other samples. The river water samples had only four detected PFASs, PFOS (48%), PFHxS (42%) PFHxA (7%) and PFPeA (3%). The dominating PFASs in drinking water was PFHxS (73%), PFBS (17%) followed by PFOS (8%) and PFPeA (3%).

3.6.2 Concentration levels
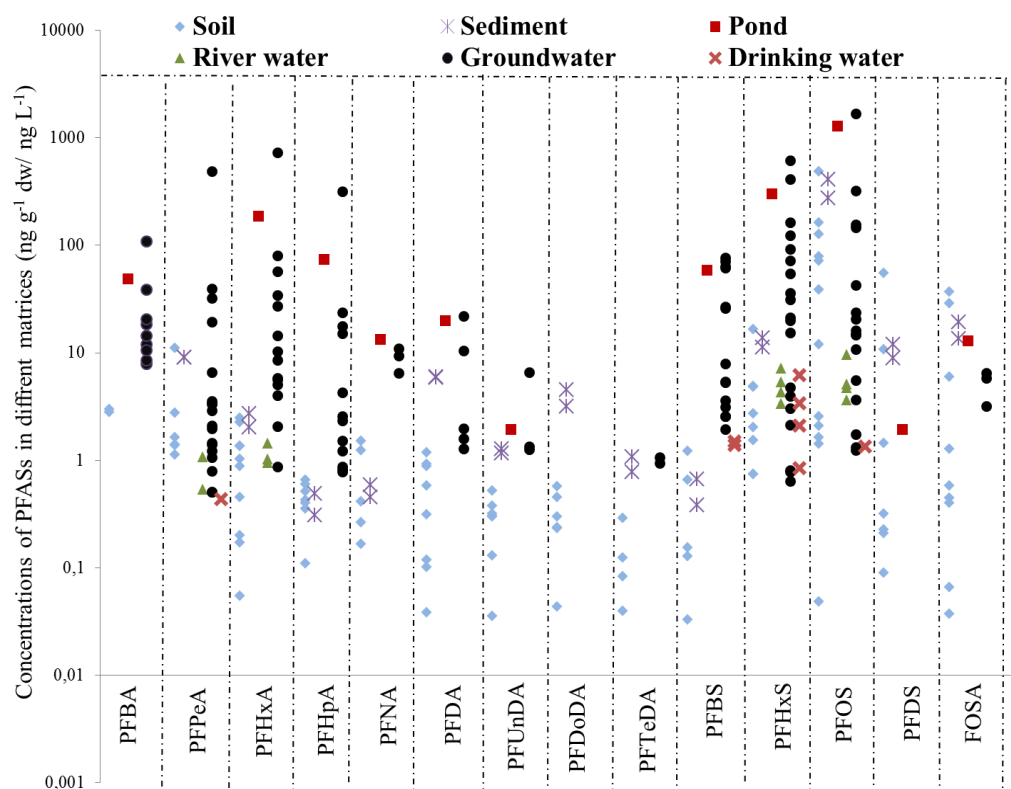
Figure 7: Composition diagram of PFASs showing which PFASs are dominant in different matrices; concentrations in soil (ng g^{-1} dw, n=12, blue diamond), sediment (ng g^{-1} dw, n=2, purple star), pond water (ng L^{-1}, n=1, red quadrat), river water (ng L^{-1}, n=5, green triangle), groundwater (ng L^{-1}, n=28, black circle) or drinking water (ng L^{-1}, n=4, red cross).

PFASs concentrations were compared between soil, sediment, pond water, river water, groundwater and drinking water (Figure 7). The selected PFASs are the 14 most frequently detected, namely

PFASs, PFBA, PFPeA, PFHxA, PFHpA, PFNA, PFDA, PFUnDA, PFDoDA, PFTeDA, PFBS, PFHxS, PFOS, PFDS and FOSA.

Figure 7 shows increasing concentrations of PFSAs in soil and sediment samples in the order; PFBS (average 0.2 ng g^{-1} dw, median 0.02 ng g^{-1} dw) < PFHxS (4.2 ng g^{-1} dw, 1.8 ng g^{-1} dw) < PFOS (119 ng g^{-1} dw, 55 ng g^{-1} dw). PFBS was barley detected in the soil samples (average 0.2 ng g^{-1} dw, median <0.01 ng g^{-1} dw) but had higher concentrations in the sediment samples (average 0.5 ng g^{-1} dw). For C$_3$-C$_{13}$ PFCAs the concentrations in soil and sediment samples were relatively similar ($\sum$PFCAs C$_3$-C$_{13}$ average 7 ng g^{-1} dw, median 4 ng g^{-1} dw). The sediment samples had a higher concentration of PFNA, PFDA, PFUnDA, PFDoDA and PFTeDA ($\sum$PFCAs C$_8$-C$_{13}$ average 12 ng g^{-1} dw) than the soil samples ($\sum$PFCAs C$_8$-C$_{13}$ average 7 ng g^{-1} dw, median 1 ng g^{-1} dw). The concentrations of FOSA was higher compared to PFCAs in sediment (average 16.4 ng g^{-1} dw) but not in soil (6 ng g^{-1} dw and median of 0.4 ng g^{-1} dw).

The groundwater samples were instead decreasing in amount and concentration from the shorter chained PFCAs to the longer chained PFCAs (C$_3$-C$_{13}$) in the order PFHxA (35 ng L^{-1}, 0.4 ng L^{-1}) $\approx$ PFPeA (22 ng L^{-1}, 1 ng L^{-1}) $\approx$ PFHpA (14 ng L^{-1}, <0.6 ng L^{-1}) $\approx$ PFBA (average 9 ng L^{-1}, median <6 ng L^{-1}) > PFNA (1 ng L^{-1}, <4.9 ng L^{-1}) > PFDA (1.3 ng L^{-1}, <1.3 ng L^{-1}) > PFUnDA (0.3 ng L^{-1}, <1.2 ng L^{-1}) > PFTeDA (0.07 ng L^{-1}, <0.8 ng L^{-1}) > PFDoDA (<14.4 ng L^{-1}, <14.4 ng L^{-1}). For the PFSAs in the groundwater, concentrations of PFBS (average 13 ng L^{-1}, median 1 ng L^{-1}) were lower compared to PFHxS (60 ng L^{-1}, 3 ng L^{-1}) and PFOS (88 ng L^{-1}, 2 ng L^{-1}), whereas PFDS was not detected in groundwater. PFBS had high concentrations in both pond water (59 ng L^{-1}) and groundwater but was not found in river water.

PFHxS and PFOS was found in all six phases, soil (PFHxS: average 3 ng g^{-1} dw, median 1 ng g^{-1} dw; PFOS: 82 ng g^{-1} dw, 25 ng g^{-1} dw), sediment (PFHxS: 13 ng g^{-1} dw, PFOS: 342 ng g^{-1} dw), pond water (PFHxS: 302 ng L^{-1}, PFOS: 1290 ng L^{-1}), river water (PFHxS: 4 ng L^{-1}, 4 ng L^{-1}, PFOS: 5 ng L^{-1}, 5 ng L^{-1}), groundwater (PFHxS: 60 ng L^{-1}, 4 ng L^{-1}, PFOS: 88 ng L^{-1}, 2 ng L^{-1}) and drinking water (PFHxS: 12 ng L^{-1}, 3 ng L^{-1}, PFOS: 1 ng L^{-1}, 0.3 ng L^{-1}). Concentration of FOSA in soil and sediment (average: 8 ng g^{-1} dw, median 0.5 ng g^{-1} dw) was lower compared to $\sum$PFSAs (136 ng g^{-1} dw, median 58 ng g^{-1} dw) and also in groundwater (FOSA: 0.5 ng L^{-1}, <2.61 ng L^{-1}, $\sum$PFSAs: 160 ng L^{-1}, 11 ng L^{-1}). $\sum$PFSAs were higher than $\sum$PFCAs in all matrices; soil (PFSAs: 91 ng g^{-1} dw, 28 ng g^{-1} dw, PFCAs: 5 ng g^{-1} dw, 4 ng g^{-1} dw), sediment (PFSAs: 408 ng g^{-1} dw, PFCAs: 19 ng g^{-1} dw), groundwater (PFSAs: 160 ng L^{-1}, 11 ng L^{-1}, PFCAs: 94 ng L^{-1}, 3 ng L^{-1}), pond water (PFSAs: 1650 ng L^{-1}, PFCAs: 592 ng L^{-1}, river water (PFSAs: 9 ng L^{-1}, 11 ng L^{-1}, PFCAs: 1 ng L^{-1}, 1 ng L^{-1}), and drinking water (PFSAs: 4 ng L^{-1}, 4 ng L^{-1}, PFCAs: 0.1 ng L^{-1}, <0.1 ng L^{-1}).

3.7 Correlation analysis
The statistical methods Pearson Correlation and Principal Component Analysis was used to evaluate the relation between samples.

3.7.1 Pearson Correlation
Pearson correlation was used for studying the relation between the soil and sediment samples and between groundwater samples. One Pearson correlation was made for soil and sediment and another for the groundwater samples. Samples with a PFASs detection frequency of <50% were excluded from the analysis.

3.7.1.1 Soil and sediment

Pearson correlation for soil and sediment (grouped together) showed a strong correlation between PFUnDA, PFDoDA and PFTeDA with a p-value <0.0001 (Table 6). PFOA had a correlation with the shorter chained PFPeA, PFHxA and PFHpA (p<0.001), while PFHxA correlated with PFHpA (p<0.01), could no correlation be detected between PFHpA and PFPeA (p>0.05). PFHxA were correlated with PFDA, PFUnDA, PFDoDA and PFTeDA (p<0.05) and PFHpA and PFOA were correlated with PFDA (p<0.05). There was also a correlation between the PFSAs (PFHxS, PFOS), FOSA and the PFCAs (PFHxA, PFHpA, PFOA, PFDA, PFUnDA, PFDoDA and PFTeDA). PFOS, PFHxS and FOSA correlated with PFHxA (p<0.01, p<0.01, p<0.001 respectively). The PFSAs (PFHxS, PFOS) and FOSA correlated with PFOA, PFDA, PFUnDA, PFDoDA and PFTeDA (p<0.05). But PFHxS correlated with more with PFOA and PFDoDA (p<0.01), and FOSA correlated with PFOA (p<0.001). PFOS and PFHxS had a strong correlation (p<0.0001), while FOSA correlated with PFOS and PFHxS (p<0.01).

Table 6: Pearson correlation for soil and sediment samples (α=0.05). Samples with a PFASs detection frequency of <50% were excluded from the analysis. For concentrations below the MDL, a value of 0.5 x MDL was used.

Soil/ sediment		PFHxA	PFHpA	PFOA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFHxS	PFOS	FOSA
PFPeA	R	0.57	0.52	0.81	0.17	0.29	0.07	0.02	0.12	0.12	0.60
	p	0.04	0.06	0.0005	0.55	0.32	0.81	0.94	0.67	0.67	0.02
PFHxA	R		0.72	0.85	0.59	0.66	0.61	0.56	0.77	0.77	0.83
	p		0.004	0.00012	0.03	0.011	0.02	0.04	0.0013	0.0014	0.0003
PFHpA	R			0.79	0.64	0.28	0.39	0.27	0.39	0.41	0.52
	p			0.0007	0.014	0.32	0.16	0.35	0.17	0.15	0.06
PFOA	R				0.48	0.61	0.44	0.50	0.46	0.49	0.78
	p				0.08	0.02	0.12	0.07	0.009	0.08	0.0009
PFDA	R					0.97	0.97	0.95	0.62	0.59	0.37
	p					1.0E-08	10.0E-09	1.0E-07	0.02	0.03	0.20
PFUnDA	R						0.94	0.95	0.66	0.63	0.51
	p						7.0E-07	5.0E-09	0.011	0.02	0.06
PFDoDA	R							0.99	0.68	0.59	0.37
	p							2.0E-11	0.007	0.03	0.20
PFTeDA	R								0.64	0.54	0.30
	p								0.014	0.05	0.30
PFHxS	R									0.96	0.67
	p									9.0E-08	0.009
PFOS	R										0.75
	p										0.002

Legend: p-value = Observed significance level; p>0.05; p<0.05; p<0.01; p<0.001; p<0.0001

3.7.1.2 Groundwater

In groundwater, all PFAS substances correlated with each other, except for PFOS which only correlated with PFBS (p<0.01). PFCAs in groundwater (PFPeA, PFHxA and PFHpA) correlated strongly (p<0.0001) (Table 7). PFSAs and PFCAs correlated with each other for PFBS, PFHxS, PFPeA, PFHxA and PFHpA (p<0.01). PFHxS correlated more with PFHxA than with PFPeA and PFHpA (p<0.001) and PFBS correlated less with PFHpA than with PFPeA and PFHxA (p<0.05). PFBS and PFHxS did correlate strongly (p<0.0001).

Groundwater		PFHxA	PFHpA	PFBS	PFHxS	PFOS
PFPeA	**R**	0.99	0.99	0.52	0.52	0.21
	p	2.0E-26	4.0E-26	0.005	0.003	0.24
PFHxA	**R**		0.99	0.57	0.60	0.22
	p		7.0E-23	0.002	0.0007	0.21
PFHpA	**R**			0.47	0.50	0.15
	p	p-value = Observed significance level p>0.05		0.011	0.006	0.42
PFBS	**R**	p<0.05			0.84	0.54
	p	p<0.01			2.0E-08	0.003
PFHxS	**R**	p<0.001				0.26
	p	p<0.0001				0.18

3.7.2 Principal Component Analysis (PCA)

The fingerprints are used to compare the composition profiles (pattern) of PFASs between different samples and can be helpful in tracking the source of the PFASs. Principal Component Analysis (PCA) was used to examine for correlations for the PFAS patterns and to see how samples were related to each other. Samples that have pattern (fingerprint) similarities are located near each other in the score plot, and samples that differ are further apart. The arrows in the loading plot represent the most varying direction of the data set and thereby which PFASs are mainly contributing to separation of the objects (samples) in the score plot (Swedish Environmental Protection Agency, 2014-08-04). The data were normalized before analyses by dividing each individual PFAS concentration with the ∑PFAS concentration for each sample.

3.7.2.1 Soil and sediment

The selected soil and sediments samples for analysis were So1-So5 from Fire fighting facility 1 in green and So6-So9, Se1-Se2 from Fire fighting facility 2 in red. Soil and sediment samples from Fire fighting facility 2 (So6, So8, So9, Se1-Se2) are located at the left side of the score plot and close to each other (Figure 8). Soil samples from Fire fighting facility 1 (So1-So5) is scattered over the score plot but also located next to soil samples at Fire fighting facility 2 (So5, So1). This shows that the contamination in the analysed soil samples, So1, So5-So6, So8-So9 and the sediment samples, Se1-Se2 have similar pattern. The arrows indicate that the variability in PFOS, PFHxS and PFHxA are the substances that are the most important for separate the samples.
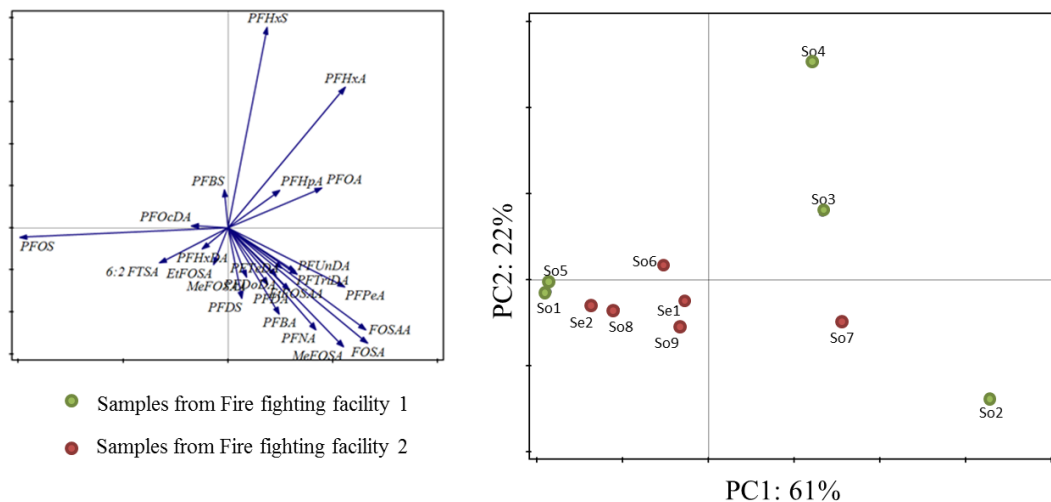
Figure 8: PCA of normalized PFAS concentrations in soil and sediment. Left: the loading plot and right: the score plot. Green dots in the score plot represent soil and sediment at Fire fighting facility 1 (So1-So5), and red dots represent Fire fighting facility 2 (So6-So9, Se1-Se2). PC1 and PC2 explained together 83% of the variance.

3.7.3.2 Groundwater

The groundwater samples in the PCA included groundwater near Fire fighting facility 1 (G8-G9) in green and Fire fighting facility 2 in red (G16-G23) and groundwater samples along the groundwater flow in blue (G7, G10-G15, G24-G27). Groundwater samples at Fire fighting facility 2 (in red) are all located on the right side of the score plot, while groundwater samples near Fire fighting facility 1 (in green) are located close together in the left corner of the score plot (Figure 9). Samples collected along the groundwater flow (in blue) are all gathered mainly in the left corner around the groundwater samples near Fire fighting facility 1 (in green). The arrows in this diagram show that PFOS, PFHxS and PFDS are the variables that explain the separation among the samples the most.
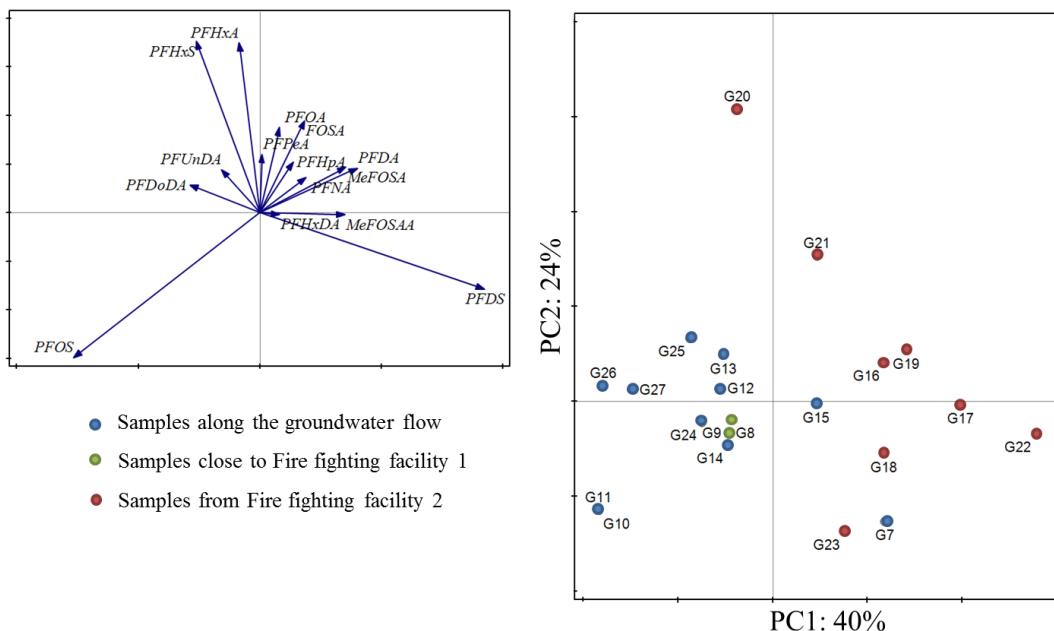
Figure 9: PCA of normalized groundwater data. Left: loading plot and right: score plot. Green dots represent groundwater samples near Fire fighting facility 1 (G8-G9), red dots represent Fire fighting facility 2 (G16-G23) and blue dots represent the groundwater samples along the groundwater flow (G7, G10-G15, G24-G27). PC1 and PC2 explained together 64% of the variance.

4. Discussion

This study was based on grab samples and thus the PFASs concentrations in the different compartments should be interpreted with care.

4.1 Occurrence of PFASs in soil and groundwater

The leaching behavior and the mobility of PFASs in soil are dependent on their different chemical properties such as the chain length and functional group and the amount of PFASs that will leach into groundwater is affected by the contamination level, soil characteristics and chemical properties (Higgins and Luthy, 2006; Gellrich et al, 2011).

The partitioning coefficients, K_{ow} and K_{oc} are often used to predict the mobility of PFASs between the solid and water phase during leaching (Wang et al, 2011; Ahrens et al, 2009[b]). The K_{ow} and K_{oc} for PFASs are in most cases increasing with increasing chain length (Wang et al, 2011; Ahrens et al, 2010; Higgins and Luthy, 2006). Because of the hydrophobic chain, a longer chained PFASs (> 7 perflourocarbon chain length) adsorb more strongly to particles and have a lower water solubility compared to shorter chained PFASs (< 7). This was in agreement with the results where the longer chained PFASs were dominating in soil and sediment and shorter chained PFASs were more dominant in the water samples. This is because of larger hydrophobicity and adsorption capacity of the longer chained PFASs. PFOS (C_8) has a higher Log K_{oc} (4.8 L kg_{OC}^{-1}) and Log K_{ow} (8.07) than PFHxS (C_6) (Log K_{oc} = 3.7 L kg_{OC}^{-1} and Log K_{ow} = 7.55) which show that PFOS adsorb stronger to particles than PFHxS, which instead is more mobile. PFHxS has also a higher water solubility ($10^{-2.24}$ mg L^{-1}) than PFOS ($10^{-3.92}$ mg L^{-1}) and will therefore dissolve easier in water. This is in agreement with previous studies where longer chained PFASs has been more frequently detected in soil and shorter chained PFASs in groundwater (Gellrich et al, 2011; Ahrens et al, 2010; Houtz et al, 2013). This was also in agreement with this study showing that PFOS was the main PFAS in soil (81% of the ∑PFASs, So1-So12, Se1-Se2) (Figure 2, Table A2), followed by FOSA (C_8, 5%) and PFDS (C_{10}, 4%). They all have a long perflourocarbon chain, low water solubility, high K_{oc} and K_{ow} which explain their higher abundance in soil compared to groundwater. In groundwater were PFHxS was the main PFAS along Uppsalaåsen (54% of the ∑PFASs, G1-G15, G24-G28), followed by PFOS (14%), PFBS (C_4, 10%), PFHxA (C_5, 8%). All except PFOS have ≤ 6 perfluorocarbon atoms and these PFASs are more frequently detected in water because of the higher water solubility (Figure 3, Table A3). The abundance of PFOS in the water samples is because of the lagre concentrations of PFOS in the used AFFFs (Herzke et al, 2012). The functional group can also affect the mobility and leaching behavior of PFASs. PFSAs bind stronger to particles than PFCAs (Ahrens et al, 2010; Higgins and Luthy, 2006). This could also be seen in the results where PFSAs were the dominant compounds in soil and sediment (Figure 6, Figure 7). This was in agreement with Houtz et al. 2013, who also showed higher concentrations of PFSAs than PFCAs close to fire fighting facilities. This may also be due to the dominant PFSAs in the AFFFs used at the fire fighting facilities (Herzke et al, 2012).

High concentrations of 6:2 FTSA (51% of the ∑PFASs, G16-G23) and PFOS (21%, G16-G23) were detected in the groundwater at Fire fighting facility 2 (G17, G19, G21 and G16-G19, G21-G23 respectively). 6:2 FTSA and PFOS were the major composition of the new and old AFFFs products which indicated that both the new generation of AFFF and old generation of AFFFs has been used at this site. 6:2 FTSA was only detected at this site since Fire fighting facility 2 was the only location where the the new generation of AFFFs has been used. 6:2 FTSAs has 8 carbon atoms but only 6 perfluorocarbons and a low Log K_{ow} of 4.44 (Wang et al, 2011). The low K_{ow} makes the adsorption capacity low and the abundance in groundwater more frequent than in soil and sediment (0.6%, So6-

So9, Se1-Se2). The high concentrations of PFOS in groundwater at Fire fighting facility 2 (average 272 ng L^{-1}, median 13 ng L^{-1}, G16-G23) may be explained by the frequent use of the PFOS-containing AFFF for six years (1990-1996). PFOS-containing AFFFs were also used at Fire fighting facility 1 since the beginning of 1980s until 2005, but the concentrations of PFOS in groundwater near Fire fighting facility 1 were lower (average 99 ng L^{-1}, G8-G9) than at fire fighting facility 2 (average 272 ng L^{-1}, median 13 ng L^{-1}, G16-G23). This might be because of the higher amount AFFFs used at Fire fighting facility 2. Furthermore had Fire fighting facility 2 higher concentrations of $\sum$PFASs in groundwater (average $\sum$PFASs 1316 ng L^{-1}, median 24 ng L^{-1}, G16-G23) and soil (278 ng g^{-1} dw, 120 ng g^{-1} dw, So6-So9) than at Fire fighting facility 1 (groundwater: average 660 ng L^{-1}, G8-G9, soil: average 75 ng g^{-1} dw, median 86 ng g^{-1} dw, So1-So5) and Fire fighting facility 3 (groundwater: 64 ng L^{-1}, G15, soil: average 2 ng g^{-1} dw, median 1.4 ng g^{-1} dw, So10-So12).

High concentrations at Fire fighting facility 2 were only found at some groundwater samples ($\sum$PFASs, G17 = 2110 ng L^{-1}, G19 = 342 ng L^{-1}, G21 = 8015 ng L^{-1}) (Figure 3). The different spatial distribution of PFASs at Fire fighting facility 2 can be explained by its soil type and its groundwater flow, which probably flows towards north and then south-west. A thick clay layer is dominating the area which makes the groundwater flow slow and the adsorption of PFASs greater. Johnson et al, 2007 also recorded a higher adsorption of PFOS to clay particles compared to sand particles. This is likely why the PFASs contamination is high at these wells. In contrast, G19 close to the fire fighting training grounds (F3-F4) showed lower concentrations ($\sum$PFASs = 342 ng L^{-1}) compared to the other two wells further away (G17, G21). Bjerking (2014) also sampled at Fire fighting facility 2 and found high values at this area with the highest at G17 ($\sum$PFASs = 992 ng L^{-1}) and lower values at G16 ($\sum$PFASs = 84 ng L^{-1}), located north of the fire fighting grounds. Bjerking, 2014 detected $\sum$PFASs concentrations of 22000 ng L^{-1} at the area.

The PFAS pattern and concentrations can thus be affected by the soil characteristics. PFASs sorbs stronger to clay compared to sandy soils, and PFASs also adsorb stronger to soil with high TOC (Higgins and Luthy, 2006, Johnson et al, 2007). At Fire fighting facility 2, F4 (So6-So7) mostly sandy soils were dominant (64%) but had a higher TOC (2.55%) compared to F3 (So8-So9) which was a clayish soil (~58%) with a lower TOC (~1.9%). Higher $\sum$PFAS concentrations in soil were found at F3 (average 401 ng g^{-1} dw, So8-So9) than F4 (average 10 ng g^{-1} dw, So6-So7). More AFFFs has been used at F4 but the higher concentrations at F3 may be affected by the clayish soil at F3 and the closer location of the samples relative to the fire training ground. The sediment samples from the pond (Se1-Se2) had the highest $\sum$PFAS concentrations (average 408 ng g^{-1} dw) and also the highest clay content (58%), but a lower value of TOC (1.12%). The high PFAS concentrations in the pond can be explained by the fact that the water and AFFF used during the fire trainings at site F3 and F4 is directly introduced into the pond. At Fire fighting facility 1, F1 (So1-So2), the particle sizes were bigger (34% clay, 54% silt) than at F2 (So3-So4) (46% clay, 42% silt) but the $\sum$PFAS concentrations were higher at F1 (average 107 ng g^{-1} dw) compared to F2 (average 10 ng g^{-1} dw). This indicated that F1 has been used more intense for fire fighting practice. At F5 (So10-So12), silt was dominant (45%) and the TOC content was low (1.79%). The low $\sum$PFAS concentrations detected at this location is probably because this fire fighting facility was less used as a fire training area.

It is important to note that the PFAS pattern in soil and groundwater can change over time due to leaching of PFASs into groundwater, adsorption of PFAS to particles and degradation of PFAS precursors (Houtz et al, 2013). EtFOSAA and EtFOSE were found in soil at F5 (4% and 3% of the $\sum$PFASs, respectively, So10), F3 (0.4% and 0%, So8-So9) and F4 (0.3% and 0%, So6-So7) but not at F1-F2 (So1-So5). This can be because of two reasons, these two PFASs are precursors and degradation to PFCAs and FOSAs may occur or the AFFFs used at F1-F2 did not contain these PFASs

(Yeung and Mabury, 2013; McNeill et al, 2009). FOSA had a higher contribution in F3-F4 (5% of the $\sum$PFASs, So6-So9) and in F1-F2 (12%, So1-So5) while FOSA was not detected at F5 (So10-So12). At F1-F4, EtFOSAA and EtFOSE may have degraded to FOSA whereas at F5, EtFOSAA and EtFOSE have not degraded. FOSA, EtFOSAA and EtFOSE binds strongly to particles (FOSA: Log K_{ow} 5.62 and Log K_{oc} of 4.5 L kg_{OC}^{-1}, EtFOSE: Log K_{ow} 6.52, EtFOSAA: Log K_{ow} n.a) and only low concentration were detected in groundwater samples (average 0.2 ng L^{-1}, median <0.1 ng L^{-1}, G1-G28) (Ahrens et al, 2010). The 6:2 FTSA, which were detected in high concentrations in groundwater at Fire fighting facility 2 (673 ng L^{-1}, <0.1 ng L^{-1}, G16-G23), is known to degrade to PFPeA, PFBA and PFHxA (Yeung and Mabury, 2013). This can explain the high concentrations of PFHxA and PFPeA in groundwater at Fire fighting facility 2 (PFHxA: average 102 ng L^{-1}, median 3 ng L^{-1}, PFPeA: average 71 ng L^{-1}, median 2 ng L^{-1}, G16-G23). High concentrations of PFOS, 6:2 FTSA and PFPeA has also been found in soil at fire fighting training grounds in Norway (Kärrman et al, 2011) and USA (Houtz et al. 2013).

Even though leaching of PFASs from AFFF contaminaded soil has been going on since 1980s, the upper layered soil is still contaminated which indicates a very slow movement of PFASs from soil to groundwater.

4.2 Transport of PFASs in different compartments including soil, sediment, groundwater, surface water and drinking water

PFASs have been detected in soil after the usage of AFFF at fire training facilities even after decades after application (Ahrens et al, 2014; Houtz et al, 2013; Awad et al, 2011). PFASs can also potentially leach into the groundwater or surface water and can also potentially contaminate drinking water (Skutlarek et al, 2006; Murakami et al, 2009).

In this study, the highest concentrations were found in soil and groundwater near the fire fighting facilities (Figure 2, Figure 3). The contamination plume at fire fighting facility 1 is transported south by the water flow of Uppsalaåsen, which potentially can transport large amounts of PFAS with a water flow of ~260 L/s (VBB, 1955). The watershed at Fire fighting facility 1 transports the groundwater towards south-west into Jumkilsåsen which explains the low $\sum$PFAS concentrations in the samples located on the north part of Uppsalaåsen, G10 and G11 (1 ng L^{-1}, 2 ng L^{-1} respectively). Jumkilsåsen is then flowing towards south-east into Uppsalaåsen. Highest ΣPFAS concentrations in groundwater has been found at G8 and G9 along the pathway of Jumkilsåsen to Uppsalaåsen (275 ng L^{-1} and 1000 ng L^{-1}, respectively), near Fire fighting facility 1 (Figure 3). The ΣPFAS concentrations decrease towards the south (G12-G14 with 210 ng L^{-1}, 137 ng L^{-1}, 83 ng L^{-1}, respectively) and continuous decreasing south (G15-G28). This was also seen by Moody and Field, 1999 who found the highest concentrations closes to a fire fighting facility in USA ($\sum$PFASs = 298 µg L^{-1}) and decreasing concentrations further away ($\sum$PFASs = 124 µg L^{-1}). The concentrations of the longer chained PFOS (C_8 perflourocarbon atoms) were higher at G8-G9 near Fire fighting facility 1 (15% of $\sum$PFASs) than in southern G12-G14 (12%), while the shorter chained PFBS (C_4) increased from 8% of $\sum$PFASs at G8-G9 to 22% at G12-G13. A similar trend was observed for PFCAs with PFHxA (C_5) decreasing from north (9%, G8-G9) to south (7%, G12-14), while PFBA (C_3) increased (from 2% G8-G9 to 6% G12-G14). At the southern sites (G24-G28), PFOS was either not detected or detected in low concentrations (<1 ng L^{-1}, G24-G28). In the southern samples, G27-G28, only PFHxS (C_6) and PFPeA (C_4) were detected (61% and 39%, respectively, of the $\sum$PFASs, G27) or no PFASs detected at all (G28). The longer chained PFOS (C_8) will adsorb to particles along the groundwater flow which explaines the decrese of PFOS southern. PFBS (C_4) and PFBA (C_3) are shorter chained, more water soluble and will be transported a longer distance along the groundwater flow.

The groundwater flow Sävjaån, is located south of fire fighting facility 2 and ends up in the south part of Uppsalaåsen. The contamination plume at Fire fighting facility 2 can potentially be transported to Uppsalaåsen, which can affect the PFAS concentrations in groundwater in the southern part of Uppsala. The high concentrations in groundwater at Fire fighting facility 2 (average ∑PFASs 1316 ng L^{-1}, median 24 ng L^{-1} G16-G23) and the low concentrations in the southern part of Uppsala (average ∑PFASs 26 ng L^{-1}, median 22 ng L^{-1}, G24-G28) show that the contaminants have not reached Uppsalaåsen yet. Potentially, PFASs can also be transported to the west directly into Uppsalaåsen from Fire fighting facility 2. However, the PFAS contamination is limited locally (average ∑PFASs 3490 ng L^{-1}, median ∑PFASs = 2110 ng L^{-1}, G17, G19, G21) and the groundwater concentrations around this hot spot were low (average ∑PFASs 12 ng L^{-1}, median ∑PFASs = 7 ng L^{-1}, G16, G18, G20, G22-G23), which indicates a very slow water transport. A layer of clay is dominating the area of Fire fighting facility 2 and contamination of the surrounding area might take a very long time. The contaminants can also be transported though the bedrock though cracks which makes the determining of the water flow direction impossible.

The transports of these contaminatated soil could either be to by surface runoff to nearsest river or by leaching down to groundwater (Skutlarek et al, 2006; Murakami et al, 2009). When comparing the ∑PFASs concentrations in groundwater (average ∑PFASs 442 ng L^{-1}, median 13 ng L^{-1}, G1-G28) and river water (average ∑PFASs 10 ng L^{-1}, median 11 ng L^{-1}, W1-W5) conclusions can be made that PFASs had mainly leached down to groundwater instead of flowing into the Fyrisån or Sävjaån. The river water samples near Fire fighting facility 1, upstream Fyrisån have lower concentrations (8 ng L^{-1}, W2) than river water samples downstream Fyrisån south of Uppsala city (average 12 ng L^{-1}, W3,W5). This can be explained by the effluents water from the WWTP and Fire fighting facility 3 that is located close to Fyrisån upstream W3 (Figure 4). Other studies have shown higher concentrations of PFASs in river water samples downstream of WWTPs (Zhao et al, 2014; Ahrens, 2011). But the PFASs concentrations in the river water can also be affected by the water flow and particle amount (Zhao et al, 2014). A lower water flow in rivers makes it easier for PFASs to accumulate in the sediments (Qiu et al, 2010). The water flow in Fyrisån is varying both along Fyrisån but also between different seasons. But the water flow variations along Fyrisån are not big and the concentrations do not seem to be influenced by the water flow. W2 had a concentration of 8 ng L^{-1} and a modelled water flow of 2.78 m^3 s^{-1} and W3 had instead a higher concentration, 11 ng L^{-1} but a lower water flow, 1.57 ng L^{-1}. The higher concentrations in W3, even if the water flow is low can instead depend on the WWTP located upstream the sampling location. PFHxS and PFOS were the dominating PFASs in the river water samples, and this is in agreement with Ahrens et al, 2014. The higher concentrations of PFOS in river water (47%) compare to groundwater (14%) and drinking water (8%) may be because of the higher amount of particles in this phase where a partitioning between particles and soil will occur. The higher concentration of PFOS in river water disagrees with Murakami et al, 2009 who showed higher concentration of PFOS in groundwater compare to rivers, wastewater and street runoff. No PFASs were detected at the reference point north of Uppsala (W1) which shows that the source of PFASs to river water in Uppsala is located south of the reference point, W1.

At Fire fighting facility 2, high ∑PFAS concentrations were found in the pond (3026 ng L^{-1}, W6) which were much higher than in the river samples (<15 ng L^{-1}, W1-W5). The surface water at Fire fighting facility 2 is drained into the pond and it might be connected to Sävjaån. The ∑PFAS concentrations in Sävjaån (W4), 15 ng L^{-1} is low compared to the pond, 3026 ng L^{-1}, thus, is it unlikely that any water from the pond was flowing into Sävjaån during the sampling period in May/June 2014. However, the sampling occurred during a dry period and one part of the pond was dried out, thus,

during the sampling time there was no water connection between the pond and Sävjaån. High PFAS concentrations during wet periods can not be excluded.

The drinking water is collected from different groundwater wells in Uppsala and from infiltrated river water from Fyrisån. Depending on where the drinking water is collected and distributed, it will have different PFAS concentrations. Groundwater is collected from Storvad (G6), Galgbacken (G10) and Sunnersta (G28) and distributed to the drinking water treatment plants and further to the consumers (Uppsala Vatten, 2014-08-11). The river water that is pumped up into the infiltration plants is collected from north of the fire fighting facilities. The PFASs analysis of the infiltrated water at the infiltration plants were low ($\sum$PFASs concentration 16 ng L^{-1}). Futhermore is the water at the infiltration plants naturally cleaned from PFASs that adsorbs to particles, thus an impact from the river water is excluded. The concentrations of PFASs in drinking water were low (<8 ng L^{-1}, D1-D4) since only low contaminated drinking water wells is used (<2 ng L^{-1}). Furthermore is the drinking water treated by sand filter and carbon filter at Uppsala's drinking water treatment plant in Bäcklösa and Gränby (Uppsala Vatten 2014-08-11). The source of the higher concentrations in the drinking water compare of the drinking water wells is unknown. Furthermore, most of the drinking water samples contained PFHxS (73%, D1-D4), just as the groundwater samples (100%, G6, G10, G28). At D1, PFPeA (0.4 ng L^{-1}) and PFOS (1.3 ng L^{-1}) were detected while at D2-D4 only PFHxS and PFBS were detected. Since only PFHxS was detected in the drinking water wells (G6, G10 and G28) is the source of PFPeA, PFOS and PFBS in the drinking water unknown.

The transport of PFASs from the soil at fire fighting trainings sites to groundwater, and drinking water exposes humans for these contaminants. No limits of PFASs in drinking water exist in Sweden but Sweden has guidance levels of 350-1000 ng PFOS L^{-1} (Swedish Enviromental Protection Agency, 2008). However lower guidance levels exist in other countries. For example, the government of New Jersey in United States have a guidance levels of 200 ng L^{-1} for PFOS a short time exposure and life time exposure of 20 ng L^{-1} for PFOA while Germany has a guidance level of 300 ng L^{-1} for the sum of PFOS and PFOA (State of New Yersey Department of Health 2014-08-11; TWK, 2006). The PFASs concentrations measured in the drinking water samples in Uppsala were below these limits. Based on an average drinking water consumption of 2 L per day and average $\sum$PFAS concentration of 4.2 ng L^{-1}, the average intake of $\sum$PFASs for an inhabitant in Uppsala is estimated to be 0.2 ng day^{-1}. If assumed an average body weight (bw) is 70 kg and the amount drinking water consumed per day is 2 L then the average inhabitant in Uppsala is exposed to 0.009 ng kg^{-1} bw day^{-1} of PFOS and 0.12 ng kg^{-1} bw day^{-1} of $\sum$PFASs. The estimated intake of PFOS by drinking water in Uppsala is below the TDI for PFOS which is 150 ng kg^{-1} bw day^{-1} according to the European Food Safety Authority (European Food Safety Authority, 2008). However, the TDI is the maximum concentration of the total PFOS intake from food, drinking water and air where no adverse effect has been detected on humans (European Food Safety Authority, 2008). Furthermore, there is a lack of knowledge about the effects of the exposure of PFASs to humans in particular for long term exposure effects.

4.3 Source tracing of PFASs using finger printing

To be able to trace the sources of pollutants, fingerprint analysis can be used. Fingerprinting analysis is a useful tool as a complement to concentration measurements as environmental levels of pollutants can be highly variable on a temporal scale, while fingerprints are relatively stable over time. The PFAS pattern in soil and groundwater is different primarily depending on the physicochemical properties of the substance (Ahrens et al, 2009[b]).

The Pearson correlation of groundwater samples showed stronger correlations than soil/sediment samples. PFHxA, PFHpA, PFPeA correlated strongly (p<0.0001) and correlation could be seen between PFBS, PFHxS, PFPeA, PFHpA, PFHxA with a stronger correlation between PFHxS and PFHxA (p<0.001). This means that these PFASs likely origin from the same source. PFOS was only correlated with PFBS (p<0.01) which can depend on the concentration similarities of PFOS and PFBS in the groundwater samples. A PCA was also done for groundwater samples including samples taken near Fire fighting facility 1 (G8-G9) and at Fire fighting facility 2 (G16-G23) and samples taken along the groundwater flow (G7, G10-G15, G24-G27) (Figure 9). The samples from the Fire fighting facility 2 (G16-G23) were scattered along the right side of the score plot (Figure 9) and G7 was located close the the samples at Fire fighting facility 2. At G7 were PFOS (67% of the ΣPFASs) and PFHxS (33%) dominating, which also was the case for the the samples close to G7 in the score plot (G23: PFOS 55%, PFHxS 45%; G18: PFOS 57%, PFHxS 25%). At G15, which was located closer to the samples at Fire fighting facility 2 in the score plot, higher concentrations of shorter chained PFCAs were detected (PFBA 14%, PFHxA 8%, PFPeA 5%) similar to the groundwater samples at Fire fighting facility 2 (PFBA 2%, PFHxA 8%, PFPeA 6%). In the score plot, the groundwater sites along the groundwater flow (G10-G15, G24-G27) are located near G8-G9 indicating impact from a similar or the same source. The sites G10-G11 are located on the north-east side of Fire fighting facility 1 and only low concentrations of PFHxS were detected (1 ng L^{-1}, 2 ng L^{-1} respectively), which corresponds to the position further away from the other samples (G8-G9, G12-G15, G24-G27) in the score plot. Along the groundwater flow in Uppsalaåsen was the pattern in the groundwater alike and dominating compounds were PFHxS (54% of the ∑PFAS, G1-G15, G24-G28) and PFOS (14%) (Figure 3, Figure 6). The groundwater patterns at Fire fighting facility 2 were different. The 6:2 FTSA (51%), PFOS (20%) and PFPeA (5%) showed higher fractions at G16-G23 (Figure 3, Figure 6) than in the groundwater samples in Uppsalaåsen (0%, 14% and 2% respectively, G1-G15, G24-G28). The score plot showed that the groundwater samples along the groundwater flow from north to south in Uppsalaåsen (G8-G15,G24-G27) are closely related to each other, indicating an impact from similar PFAS sources, whereas the groundwater samples from the fire fighting facility 2 (G16-G23) seemingly are impacted from pollution with different composition and is not related to the contamination of Uppsalaåsen. This concludes that the groundwater at Fire fighting facility 2 has not the same pattern as the groundwater along the groundwater flow in Uppsalaåsen which in turn indicates that the PFAS contamination at Uppsalaåsen groundwater was not influenced by Fire fighting facility 2.

The Pearson correlations for soil and sediment showed that most PFCAs correlated significantly with eachother which indicates that they originate from the same source (p<0.001). There was strong correlation between PFOS och PFHxS (p<0.0001), and also FOSA, PFOS and PFHxS (p<0.01). A correlation between PFCAs and PFSAs could be detected in soil. PFOS (81% of the ∑PFAS), PFHxS (3%) and FOSA (5%) correlated well with PFHxA (1%) (p<0.01, p<0.01, p<0.001 respectively) which therefore seem to origin from the same source. PFOA is also correlated with PFHxS (p<0.01) and FOSA (p<0.001) while PFHxS correlated with the longer chained PFDoDA which was detected at Fire fighing facility 2 (1%, So6-So9, Se-Se2) and 3 (4%, So10-So12). PCA was also used to investigate the relations between the soil and sediment samples from Fire fighting facilities 1 and 2 (So1-So9, Se1-Se2). The soil and sediment samples So5, So1, and So6, So8-So9 Se1-Se2 were projected close together on the left side of the score plot indicating a similar PFAS pattern, whereas So2-So4 and So7 were sqattered over the right side of the score plot (Figure 8). This shows that the PFAS patterns of soil samples differ within the same fire fighting facility, which in turn indicates that different types of AFFFs were used at the different areas of that site. Due to the usage of different

amount and brands of AFFF, the composition profile of PFASs was different in soil from the different fire fighting facilities.

4.4 Future perspectives

PFASs are persistent chemicals, and the use and production of them can lead to environmental problems during a very long time period. A deeper understanding of the extent and severity of PFAS pollution in the Uppsala area is needed. In this study, PFASs were detected in soil and sediment at Fire fighting facility 1 and 2 at elevated concentrations ($\sum$PFASs = 139 ng L^{-1} and 608 ng L^{-1}, respectively). Even though AFFFs have been used since 1990 at Fire fighting facility 2, the PFAS contamination in groundwater appears to be restricted to a relativelly small area (G17, G19, G21) which indicates a strong bond of PFASs to the dominating clayish soil and slow mobility in this area. In contrast, the PFAS contamination in Uppsalaåsen was found from G8 in the north of Uppsala to G27 in the south of Uppsala showing a spreading over a larger area and a higher mobility. It seems as the current contamination plume at Uppsalaåsen is now located between G8 and G15 and might move further south of Uppsala over time while the contamination at Fire fighting facility 2 may be transported to Uppsalaåsen and further. The possible distribution of PFASs from Fire fighting facility 2 to Uppsalaåsen could be further evaluated if more samples around this location were analysed, and analysis of more samples west and east of Uppsalaåsen could also improve the current pollution scenario. The soil samples in this thesis were collected at the surface (depth of 10-30 cm), and thus no depth profiles were determined. A vertical sampling in soil could give further insight into the leaching process from soil to groundwater. It would also be useful for an inventory of the amounts of PFASs left in soil that potentially can contaminate the groundwater. Sampling during seasonal changes can show how different hydrological conditions will affect the transport of PFASs from soils, river water and groundwater. During wet periods, the groundwater direction may change, which could affect the distribution of PFASs. The long term changes of PFAS contamination in the environment is also important to investigate to be able to see the concentration changes in Uppsalaåsen over a long time period. Modelling is one way to investigate these changes.

Gellrich et al (2011) assumed that the PFASs concentrations will increase in groundwater over time due to the desorption of PFASs from soil and sediment to groundwater and the current use of both shorter chained PFASs and PFAS precursors, which can degrade to other PFASs. Studies have shown that shorter chained PFASs, which are widely used in the new generation of AFFFs, have a low bioaccumulation potential (BFR, 2014). But knowledge of the health risks of different PFASs is largely lacking, and more research must be done. Today, most studies focus on PFOS and PFOA; however chemical properties, bioaccumulation potential, half-life and toxicity is different for individual PFASs (Haukåsa et al, 2007; BFR, 2014). Due to the lack of knowledge, there is a high uncertainty about the risks of PFASs originating from drinking water. Thus, a better understanding of the risks of PFASs caused by intake of PFASs contaminated drinking water is needed.

It might be that higher PFASs concentrations in the groundwater are reached in the future, as a result of a moving contamination plume which also can contaminate the drinking water wells. Already today, the treatment of PFASs contaminated raw water is a big challenge for the drinking water treatment plants, and improved and optimized strategies are needed. Furthermore, environmental concentrations will not decrease if PFASs are still being used in AFFFs. Stricter regulation and control of the production and usage of PFAS-containing AFFFs is needed to decrease the emissions of PFASs into the environment.

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Appendix

Materials and other chemicals

The solvents used in this experiment were methanol (LiChorosolv ® from Merck KGaA, Darmstadt, Germany), acetone (Suprasolv® Merck KGaA, Darmstadt, Germany), ethanol (95% Solveco, Rosenberg, Sweden) and Millipore water (filtered with MilliPak® 0.22 µm filters). Other chemicals used in experiments were acetic acid (99.7%), ammonium acetate (Fluka Analytical, Sigma Aldrich, Netherlands), ammonium hydroxide (28-30%) purchased from Sigma-Aldrich, Steinheim, Germany, and sodium hydroxide (NaOH, 99.9%, Merck, Darmstadt, Germany), and glacial acetic acid (Surapur®, Merck KGaA, Darmstadt, Germany), GFF-filters for filtration, ENVICARB for cleaning (Supraclean ENVIcarb SupELCO, 120/400).

The equipment used in this experiment was; centrifuge (5810, Eppendorf), nitrogen evaporator (N-Evap™112, Organomation Associates Inc, Berlin, USA, wrist shaker (Gerhardt), sonication bath (Branson 5510), Vortexmixer (Analog VortexMixer, VWR), Glass Fibre Filters (Whatman™ glass microfibre filters, GE Healthcare UK Limited, Buckinghamshire, United Kingdom with 47 mm in diameter), pH-meter (VWR pHenomenal™), PP-tubes (Corning Incorprated) PP-bottles (VWR International, Radnor, India) , centrifuge tubes (Eppendorf micro centrifuge tubes), 2 mL glass vials (Agilent Techologies), SPE cartrigde (Oasis weak anion exchange (WAX) 6 cc cartridge, 500 mg, Waters).

Table A1: Sampling date, coordinates, moisture content (%), OM content (%), TIC (%), TOC (%), TC (%), clay (%), silt (%) and sand content (%), pH, temperature (°C), water level (m), pumping level (m) and concentrations (ng L^{-1}, ng g^{-1} dw) of each sample.

Soil	Sampling date	Latiude (North)	Longitude (East)	Moisture Content %	OM content (%)	TIC (%)	TOC (%)	TC (%)	Clay <0,002 mm (%)	Silt 0,002-0,05 mm (%)	Sand >0,05 mm (%)
So1	2014-05-22	59°50'39"	17°43'08"	23	29	0.04	2.37	2.41	34	54	12
So2	2014-05-22	59°50'41"	17°43'07"	23	27						
So3	2014-05-22	59°50'41"	17°43'08"	18	23	0.06	2.46	2.52	46	42	12
So4	2014-05-22	59°53'05"	17°37'4"	19	24						
So5	2014-05-22	59°53'33"	17°36'30"	19	24	n.a.[a]	n.a.	n.a.	n.a.	n.a.	n.a.
So6	2014-05-29	59°50'39"	17°43'08"	24	31	3.19	2.55	5.75	12	24	64
So7	2014-05-30	59°50'40"	17°42'59"	7	9						
So8	2014-05-29	59°50'40"	17°42'59"	18	24	0.28	1.98	2.26	59	27	15
So9	2014-05-29	59°50'38"	17°39'09"	16	21	0.06	1.91	1.97	58	29	13
So10	2014-05-29	59°50'37"	17°39'11"	10	17	n.a.	n.a.	n.a.	n.a.	n.a.	n.a
So11	2014-05-29	59°50'36"	17°39'09"	15	19	0.39	1.79	2.19	29	45	10
So12	2014-06-11	59°53'32"	17°37'15"	13	20						

Sediment	Samplingdate	Latiude (North)	Longitude (East)	Moisture content (%)	OM content (%)	TIC (%)	TOC (%)	TC (%)	Clay <0,002 mm (%)	Silt 0,002-0,05 mm (%)	Sand >0,05 mm (%)
Se1	2014-05-29	59°50'39"	17°43'08"	23	26	1.62	1.12	2.75	58.1	33.7	8.2
Se2	2014-05-29	59°50'39"	17°43'08"	23	26						

Groundwater	Date	Latiude (North)	Longitude (East)	Height (m)	Temp (°C)	pH	Water level (m)	Pumping level (m)
G1	2014-05-30	60°01'47.0"	17°33'08.1"	n.a.	n.a.	n.a.	n.a.	n.a.
G2	2014-05-30	60°01'47.0"	17°33'08.1"	n.a.	n.a.	n.a.	n.a.	n.a.
G3	2014-05-30	59°57'34.7"	17°42'13.6"	n.a.	n.a.	n.a.	n.a.	n.a.
G4	2014-05-30	59°57'34.7"	17°42'13.6"	n.a.	n.a.	n.a.	n.a.	n.a.
G5	2014-06-27	59°54'05"	17°38'22"	17	8.5	7.2	10.4	15.2
G6	2014-05-30	59°53'40"	17°37'10"	110	5.6	7.14	21.8	23.8
G7	2014-05-30	59°53'25"	17°37'14"	75	8.7	7.14	12.8	14
G8	2014-06-27	59°52'35"	17°36'21"	23	8.4	7.2	n.a	n.a
G9	2014-06-27	59°52'38.0"	17°37'00.0"	17	8.4	7	8.3	9.5
G10	2014-06-04	59°52'35.4"	17°37'29.6"	n.a.	n.a.	n.a.	n.a.	n.a.
G11	2014-06-04	59°52'59.6"	17°39'58.6"	n.a.	n.a.	n.a.	n.a.	n.a.

G12	2014-06-04	59°51'11.8"	17°38'33.4"	n.a.	n.a.	n.a.	n.a.	n.a.
G13	2014-06-04	59°51'11.8"	17°38'33.4"	n.a.	n.a.	n.a.	n.a.	n.a.
G14	2014-06-04	59°51'08.2"	17°38'38.2"	n.a.	n.a.	n.a.	n.a.	n.a.
G15	2014-05-29	59°50'38.8"	17°39'07.5"	n.a.	n.a.	n.a.	n.a.	n.a.
G16	2014-05-29	59°50'44"	17°42'55"	n.a.	n.a.	n.a.	n.a.	n.a.
G17	2014-05-29	59°50'04"	17°42'52"	n.a.	n.a.	n.a.	2.4	n.a.
G18	2014-05-29	59°50'43.4"	17°42'46.2"	n.a.	n.a.	n.a.	2.3	n.a.
G19	2014-06-27	59°50'51"	17°42'07"	n.a.	14.8	7.4	7.1	7.25
G20	2014-06-27	59°50'47"	17°43'07"	n.a.	8.0	7.0	7.0	9.5
G21	2014-06-29	59°50'38.1"	17°42'48.6"	n.a.	n.a.	n.a.	7.2	7.2
G22	2014-06-27	59°50'45"	17°42'37"	n.a.	10.7	n.a.	6.9	n.a.
G23	2014-06-27	59°50'20"	17°41'48"	n.a.	9.1	7.1	4.8	4.8
G24	2014-06-01	59°49'36"	17°39'46	7.5	8.4	7.14	1.4	1.78
G25	2014-05-31	59°48'11"	17°39'46"	21	7	6.56	1.5	1.75
G26	2014-05-31	59°47'56"	17°39'38"	29.5	7.9	7.15	11	11.3
G27	2014-05-31	59°47'50"	17°39'13"	31	7.1	7.3	7.3	n.a.
G28	2014-06-08	59°47'23.8"	17°39'38.6"	n.a.	n.a.	n.a.	n.a.	n.a.

River water	Date	Latiude (North)	Longitude (East)	Height (m)	Temp (°C)	pH
W1	2014-05-30	60°00'40"	17°42'60"	63	11.5	7.77
W2	2014-05-30	59°52'10.9"	17°37'20.9"	50	13.1	7.6
W3	2014-05-30	59°49'53.6"	17°41'27.2"	39	12.7	7.5
W4	2014-05-30	59°49'54.0"	17°39'40.6"	37	12.8	7.4
W5	2014-05-30	59°48'55.1"	17°40'12.2"	14	13	n.a.
W6	2014-05-29	59°50'42"	17°42'60"	n.a.	n.a.	n.a.

Drinking water	Date	Latiude (North)	Longitude (East)	Temp (°C)	pH
D1	2014-06-15	59°53'00.3"	17°39'57.8"	n.a.	n.a.
D2	2014-06-15	59°50'59"	17°34'52.6"	14.1	8.1
D3	2014-06-15	59°51'37"	17°42'23"	13.6	8.2
D4	2014-06-15	59°49'00.3"	17°39'43.1"	12.9	8

Soil (ng g^{-1} dw)	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxDA	PFOcDA	PFBS	PFHxS	PFOS	PFDS	6:2 FTSA
So1	<1.15[b]	2.74	1.36	0.43	0.37	<0.01	0.10	0.04	<0.05	<0.01	<0.04	<0.01	<0.01	<0.01	2.02	79.0	0.21	<0.01
So2	2.96	11.0	2.26	0.60	2.20	1.50	1.18	0.52	0.23	0.10	0.04	0.02	<0.01	<0.01	0.74	71.5	0.09	<0.01
So3	<1.15	1.13	1.35	0.51	0.76	<0.01	0.04	<0.03	<0.05	<0.01	<0.04	<0.01	<0.01	0.15	1.54	11.9	<0.01	<0.01
So4	<1.15	<0.40	0.20	<0.01	0.02	<0.01	<0.04	<0.03	<0.05	<0.01	<0.04	<0.01	<0.01	<0.01	0.74	2.10	<0.01	<0.01
So5	2.80	1.41	1.03	0.11	0.59	<0.01	<0.04	<0.03	<0.05	<0.01	<0.04	<0.01	<0.01	0.65	4.88	127	<0.01	<0.01
So6	<1.15	<0.40	0.45	0.35	0.50	0.26	0.92	0.37	0.57	0.12	0.29	0.04	0.02	0.03	2.71	38.9	1.44	<0.01
So7	<1.15	<0.40	<0.08	<0.01	<0.01	<0.01	0.12	0.13	0.04	0.03	<0.04	<0.01	<0.01	<0.01	<0.31	1.63	0.32	<0.01
So8	<1.15	1.38	0.88	0.65	0.92	1.23	0.58	0.30	0.23	<0.01	<0.04	<0.01	<0.01	0.13	4.83	164	10.7	0.73
So9	<1.15	1.63	2.46	0.40	1.01	0.17	0.31	0.30	0.45	<0.01	0.08	0.01	<0.01	1.22	16.44	486	54.9	<0.01
So10	<1.15	<0.40	0.05	<0.01	0.24	0.41	0.87	0.32	0.30	0.07	0.12	0.03	<0.01	<0.01	<0.31	2.54	0.23	<0.01
So11	<1.15	<0.40	0.17	<0.01	<0.01	<0.01	<0.04	<0.03	<0.05	<0.01	<0.04	<0.01	<0.01	<0.01	<0.31	0.05	<0.01	<0.01
So12	<1.15	<0.40	<0.08	<0.01	<0.01	<0.01	<0.04	<0.03	<0.05	<0.01	<0.04	<0.01	<0.01	<0.01	<0.31	1.43	<0.01	<0.01

Sediment (ng g^{-1} dw)	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxDA	PFOcDA	PFBS	PFHxS	PFOS	PFDS	6:2 FTSA
Se1	2.11	2.71	0.49	1.45	0.45	5.91	1.27	4.52	0.41	1.08	0.23	0.05	0.66	13.7	276	11.9	2.97	19.3
Se2	2.60	2.02	0.31	0.99	0.59	5.98	1.16	3.14	0.26	0.78	0.16	0.03	0.38	11.2	410	8.96	4.69	13.5

Ground water (ng L^{-1})	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxDA	PFOcDA	PFBS	PFHxS	PFOS	PFDS	6:2 FTSA
G1	<6.04	2.10	0.87	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	<0.50	<1.13	<0.10	<0.10
G2	<6.04	1.22	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	<0.50	<1.13	<0.10	<0.10
G3	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	<0.50	<1.13	<0.10	<0.10
G4	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	1.06	<0.10	<0.10	<1.08	<0.50	<1.13	<0.10	<0.10
G5	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	<0.50	<1.13	<0.10	<0.10
G6	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	<0.50	<1.13	<0.10	<0.10
G7	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	0.64	1.31	<0.10	<0.10
G8	7.8	6.53	33.9	4.3	22.3	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	25.7	162	42.7	<0.10	<0.10
G9	18.3	19.2	80.2	15.1	33.8	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	76.1	617	155	<0.10	<0.10
G10	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	2.12	<1.13	<0.10	<0.10
G11	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	0.78	<1.13	<0.10	<0.10
G12	11.9	1.44	10.2	1.5	5.88	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	26.6	71.5	16.1	<0.10	<0.10
G13	14.3	3.35	14.3	2.5	7.49	0	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	63.5	91.4	23.6	<0.10	<0.10

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxDA	PFOcDA	PFBS	PFHxS	PFOS	PFDS	6:2 FTSA
G14	<6.04	1.06	5.78	0.9	3.87	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	7.83	54.0	14.5	<0.10	<0.10
G15	8.5	2.88	5.00	1.2	1.88	<4.96	<1.27	<1.20	<14.4	<0.10	0.93	<0.10	<0.10	3.14	20.0	20.5	<0.10	<0.10
G16	<6.04	3.54	3.99	0.8	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	2.55	3.91	14.8	<0.10	<0.10
G17	38.7	32.2	57.1	23.7	48.7	10.8	22.0	6.51	<14.4	<0.10	<0.84	<0.10	<0.10	61.7	123	1679	<0.10	3.63
G18	<6.04	1.40	2.07	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	4.75	10.8	<0.10	<0.10
G19	20.7	39.2	27.2	17.6	17.4	6.42	1.96	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	2.57	31.3	146	<0.10	30.4
G20	<6.04	0.79	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	1.93	<0.50	<1.13	<0.10	<0.10
G21	109	490	728	314	191	9.35	10.4	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	70.4	412	323	<0.10	5351
G22	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	<0.50	1.72	<0.10	<0.10
G23	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	3.0	3.63	<0.10	<0.10
G24	<6.04	1.95	5.59	0.78	2.60	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	5.27	35.8	5.49	<0.10	<0.10
G25	10.5	3.34	8.56	2.32	3.75	<4.96	1.27	1.25	<14.4	<0.10	<0.84	<0.10	<0.10	5.39	21.3	1.23	<0.10	<0.10
G26	<6.04	0.50	<0.55	<1.59	1.70	<4.96	1.57	1.34	<14.4	<0.10	<0.84	<0.10	<0.10	3.58	15.4	<1.13	<0.10	<0.10
G27	<6.04	0.51	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	0.8	<1.13	<0.10	<0.10
G28	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	<0.50	<1.13	<0.10	<0.10
River water (ng L⁻¹)	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxDA	PFOcDA	PFBS	PFHxS	PFOS	PFDS	6:2 FTSA
W1	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	<0.50	<1.13	<0.10	<0.10
W2	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	4.28	3.65	<0.10	<0.10
W3	<6.04	1.08	1.43	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	3.34	9.62	<0.10	<0.10
W4	<6.04	0.54	1.03	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	7.23	4.72	<0.10	<0.10
W5	<6.04	<0.34	0.95	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	5.39	5.12	<0.10	<0.10
W6	49.0	178.0	187.0	74.1	69.1	13.4	19.8	1.94	<14.4	0.16	<0.84	<0.10	<0.10	59.1	303	1292	1.93	763
Drinking water (ng L⁻¹)	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxDA	PFOcDA	PFBS	PFHxS	PFOS	PFDS	6:2 FTSA
D1	<6.04	0.43	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	1.38	2.08	1.32	<0.10	<0.10
D2	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	0.84	<1.13	<0.10	<0.10
D3	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	<1.08	3.34	<1.13	<0.10	<0.10
D4	<6.04	<0.34	<0.55	<1.59	<0.53	<4.96	<1.27	<1.20	<14.4	<0.10	<0.84	<0.10	<0.10	1.49	6.18	<1.13	<0.10	<0.10

Soil (ng g^{-1} dw)	FOSA	MeFOSA	EtFOSA	MeFOSE	EtFOSE	FOSAA	MeFOSAA	EtFOSAA
So1	0.40	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02
So2	29.0	1.02	<0.01	<0.01	<0.01	1.87	0.08	<0.01
So3	0.44	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
So4	0.04	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
So5	1.28	0.06	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
So6	0.58	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.10
So7	0.07	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04
So8	5.97	0.18	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
So9	36.8	2.26	0.16	<0.01	<0.01	0.41	<0.01	3.26
So10	<0.01	<0.01	<0.01	<0.01	0.14	<0.01	<0.01	0.22
So11	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
So12	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Sediment (ng g^{-1} dw)	FOSA	MeFOSA	EtFOSA	MeFOSE	EtFOSE	FOSAA	MeFOSAA	EtFOSAA
Se1	0.44	<0.01	<0.01	<0.01	0.25	0.71	2.29	2.23
Se2	0.15	<0.01	<0.01	<0.01	0.10	0.19	1.28	1.28

Ground water (ng L^{-1})	FOSA	MeFOSA	EtFOSA	MeFOSE	EtFOSE	FOSAA	MeFOSAA	EtFOSAA
G1	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G2	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G3	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G4	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G5	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G6	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G7	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G8	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G9	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G10	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G11	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10

River water (ng L^{-1})	FOSA	MeFOSA	EtFOSA	MeFOSE	EtFOSE	FOSAA	MeFOSAA	EtFOSAA
G12	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G13	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G14	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G15	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G16	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G17	3.15	<0.10	<0.10	<0.10	<0.10	0.11	<0.10	<0.10
G18	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G19	5.76	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G20	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G21	6.47	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G22	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G23	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G24	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G25	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G26	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G27	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
G28	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
River water (ng L^{-1})	**FOSA**	**MeFOSA**	**EtFOSA**	**MeFOSE**	**EtFOSE**	**FOSAA**	**MeFOSAA**	**EtFOSAA**
W1	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
W2	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
W3	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
W4	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
W5	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
W6	12.9	<0.10	<0.10	<0.10	<0.10	0.53	0.82	0.31
Drinking water (ng L^{-1})	**FOSA**	**MeFOSA**	**EtFOSA**	**MeFOSE**	**EtFOSE**	**FOSAA**	**MeFOSAA**	**EtFOSAA**
D1	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
D2	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
D3	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
D4	<2.61	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10

[a], not available. [b], <MDL

Table A2: Concentrations (ng g^{-1} dw) of PFASs in each compartment, soil and sediment.

	Soil (*n*=12)				Sediment (*n*=2)			
	Average	Median	Min	Max	Average	Median	Min	Max
PFBA	2.88	<1.15[a]	<1.15	2.96	<1.15	<1.15	<1.15	<1.15
PFPeA	19.9	1.13	<0.04	11.0	2.35	2.35	2.11	2.60
PFHxA	2.55	0.88	<0.08	2.46	2.37	2.37	2.02	2.71
PFHpA	1.60	0.35	<0.01	0.65	0.40	0.40	0.31	0.49
PFOA	2.05	0.50	<0.01	2.20	1.22	1.22	0.99	1.45
PFNA	2.48	<0.01	<0.01	1.50	0.52	0.52	0.45	0.59
PFDA	1.40	0.12	<0.04	1.18	5.94	5.94	5.91	5.98
PFUnDA	0.95	0.13	<0.03	0.52	1.21	1.21	1.16	1.27
PFDoDA	0.75	0.04	<0.05	0.57	3.83	3.83	3.14	4.52
PFTriDA	0.02	<0.01	<0.01	0.12	0.33	0.33	0.26	0.41
PFTeDA	0.51	<0.04	<0.04	0.29	0.93	0.93	0.78	1.08
PFHxDA	0.01	<0.01	<0.01	0.04	0.20	0.20	0.16	0.23
PFOcDA	0.00	<0.01	<0.01	0.02	0.04	0.04	0.03	0.05
PFBS	1.90	<0.01	<0.01	1.22	0.52	0.52	0.38	0.66
PFHxS	2.96	1.54	<0.31	16.4	12.5	12.4	11.2	13.7
PFOS	66.2	6.11	276	486	343	343	276	409
PFDS	4.52	<0.01	<0.01	54.9	10.4	10.4	8.96	11.9
6:2 FTSA	0.06	<0.01	<0.01	0.73	3.83	3.83	2.97	4.69
FOSA	4.97	0.07	<0.01	36.8	16.40	16.4	13.5	19.3
MeFOSA	0.23	<0.01	<0.01	2.26	0.30	0.30	0.15	0.44
EtFOSA	0.01	<0.01	<0.01	0.16	<0.01	<0.01	<0.01	<0.01
MeFOSE	<0.01	<0.01	<0.01	0.00	<0.01	<0.01	<0.01	<0.01
EtFOSE	0.01	<0.01	<0.01	0.14	<0.01	<0.01	<0.01	<0.01
FOSAA	0.15	<0.01	<0.01	1.87	0.17	0.17	0.10	0.25
MeFOSAA	0.01	<0.01	<0.01	0.08	0.45	0.45	0.19	0.71
EtFOSAA	0.24	<0.01	<0.01	3.26	1.78	1.78	1.28	2.29

[a], <MDL.

Table A3: Concentrations (ng L^{-1}) of PFASs in each compartment, groundwater, river water, pond and drinking water.

| | Groundwater (*n*=28) | | | | River water (*n*=5) | | | | Pond (*n*=1) | Drinking water (*n*=4) | | | |
	Average	Median	Min	Max	Average	Median	Min	Max	Average	Average	Median	Min	Max
PFBA	8.57	<6.04[a]	<6.04	109	<6.04	<6.04	<6.04	<6.04	49.0	<6.04	<6.04	<6.04	<6.04
PFPeA	21.8	1.14	<0.34	490	0.32	<0.34	<0.34	1.08	178	0.11	<0.34	<0.34	0.4
PFHxA	35.1	0.43	<0.55	728	0.68	0.95	<0.55	1.43	187	<0.55	<0.55	<0.55	<0.55
PFHpA	11.2	<1.59	<1.59	314	<1.59	<1.59	<1.59	<1.59	74.1	<1.59	<1.59	<1.59	<1.59
PFOA	9.77	<0.53	<0.53	191	<0.53	<0.53	<0.53	<0.53	69.1	<0.53	<0.53	<0.53	<0.53
PFNA	0.95	<4.96	<4.96	10.8	<4.96	<4.96	<4.96	<4.96	13.4	<4.96	<4.96	<4.96	<4.96
PFDA	1.33	<1.27	<1.27	22.0	<1.27	<1.27	<1.27	<1.27	19.8	<1.27	<1.27	<1.27	<1.27
PFUnDA	0.33	<1.20	<1.20	6.5	<1.20	<1.20	<1.20	<1.20	1.94	<1.20	<1.20	<1.20	<1.20
PFDoDA	<14.4	<14.4	<14.4	<14.4	<14.4	<14.4	<14.4	<14.4	<14.4	<14.4	<14.4	<14.4	<14.4
PFTriDA	<0.10	<0.10	<0.10	<0.10	0.04	<0.10	<0.10	<0.10	0.16	<0.10	<0.10	<0.10	<0.10
PFTeDA	0.07	<0.84	<0.84	1.06	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84	<0.84
PFHxDA	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
PFOcDA	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
PFBS	12.7	0.96	<1.08	76.1	<1.08	<1.08	<1.08	<1.08	59.1	0.72	0.69	<1.08	1.5
PFHxS	59.7	3.47	<0.5	617	4.05	4.28	<0.5	7.23	303	3.11	2.71	<0.5	6.2
PFOS	87.9	1.51	<1.13	1679	4.62	4.72	<1.13	9.62	1292	0.33	0.33	<1.13	1.3
PFDS	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	1.93	<0.10	<0.10	<0.10	<0.10
6:2 FTSA	192	<0.10	<0.10	5351	<0.10	<0.10	<0.10	<0.10	763	<0.10	<0.10	<0.10	<0.10
FOSA	0.55	<2.61	<2.61	6.47	<2.61	<2.61	<2.61	<2.61	13	<2.61	<2.61	<2.61	<2.61
MeFOSA	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
EtFOSA	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
MeFOSE	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
EtFOSE	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
FOSAA	<0.10	<0.10	<0.10	0.11	<0.10	<0.10	<0.10	<0.10	0.53	<0.10	<0.10	<0.10	<0.10
MeFOSAA	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.82	<0.10	<0.10	<0.10	<0.10
EtFOSAA	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0,31	<0.10	<0.10	<0.10	<0.10

[a], <MDL.