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**Faculty of Natural Resources and Agricultural Sciences (NJ)**

# Uptake of per- and polyfluoroalkyl substances by plants

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Department of Aquatic Sciences and Assessment
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# Statutory Declaration

Herewith I declare the present work to be written single handed without using any references or implements other than declared. Literal and analogous citations are indicated as such. All graphs, figures and tables are own drafts if not stated otherwise. Furthermore, I am aware that the electronic version can be checked for plagiarism by software analysis. Dr. Lutz Ahrens (SLU), supervisor of this thesis, holds an unencrypted electronic version (in the format *.doc and *.pdf) of this document that corresponds exactly in content and wording to the printed copy. This thesis has been submitted at the University of Hohenheim, Hohenheim, Germany and the Swedish University for Agricultural Sciences, Uppsala, Sweden as part of the study programme *EnvEuro Environmental Management in Europe – Soil, Water and Biodiversity*.

Uppsala, 11th October, 2016

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Laura Gobelius

# Abstract

The extensive use of per- and polyfluoroalkyl substances (PFASs) as surfactants in, for example textiles, cookware and aqueous firefighting foams (AFFFs) during the last decades has resulted in widespread environmental contamination. Due to the persistent and bioaccumulative characteristics of PFASs, they are ubiquitously found in the environment, wildlife and humans. Currently, the knowledge of remediation techniques for environments contaminated with PFASs is limited. Therefore, this study aims at evaluating the potential of plant uptake of 26 different PFASs from contaminated soils and groundwater. Arlanda airport, Sweden's biggest airport, has a fire training facility that is suffering from severe PFAS contamination due to former regular practices with PFAS-containing AFFFs for safety purposes. Samples from different plant species, namely silver birch (*Betula pendula*), Norway spruce (*Picea abies*), bird cherry (*Prunus padus*), mountain ash (*Sorbus aucuparia*), ground elder (*Aegopodium podagraria*), long beechfern (*Phegopteris connectilis*) and wild strawberry (*Fragaria vesca*), surface soil and groundwater were taken near the fire training site to assess the accumulation potential and eligibility of selected plants for phytoremediation. In comparison to typical background levels, elevated ∑PFAS levels were detected in soil and groundwater ranging from 16-156 ng $g^{-1}$ dry weight (dw) and 1,200 and 34,000 ng $L^{-1}$, respectively. The plants showed a high variability of concentrations with highest ∑PFAS concentrations in vegetative compartments, particularly the foliage. Birch leaves exceeded all other sampled tissues and species with a maximum of ∑PFAS 327 ng $g^{-1}$ dw, followed by spruce needles with 222 ng $g^{-1}$ dw. The leaves and twigs of mountain ash were generally the least contaminated (<10 ng $g^{-1}$ dw), while the other twigs had concentrations of up to 76 ng $g^{-1}$ dw (birch). Interestingly, the annual ground cover plants were highly contaminated and accumulated high amounts of PFASs. The bioconcentration factors (BCFs; plant/soil ratios) were found to be as high as 143,700 for 6:2 FTSA (birch leaves), which turned out to have the highest accumulation potential in plants. Moreover, the BCFs were highest for short-chained $C_3$-$C_5$ perfluoroalkyl carboxylic acids (PFCAs; median ~0.9) and decreased for the longer chained $C_7$-$C_9$ PFCAs (~0.4), while being lowest for the long-chained $C_6$-$C_8$ perfluoroalkane sulfonic acids (PFSAs; ~0.2). In conclusion, silver birch, Norway spruce, bird cherry and long beechfern seem promising candidates for phytoremediation of PFASs.

*Keywords:* phytoremediation, PFAS, silver birch, Norway spruce, groundwater, Arlanda airport

# Popular science summary

Plants are like vacuum cleaners. They will soak up everything in their surroundings that is water soluble to be able to grow and produce biomass. This characteristic comes so handy when you want to remove something that is not supposed to be in the soil or groundwater, i.e. pollutants.

Per- and polyfluoroalkyl substances (PFASs) might not sound familiar to you, however, they are present in your blood and are potentially harmful. You wonder how they got there? Well, despite the carcinogenic and persistent character of these substances, they can be quite helpful in waterproofing your jacket and creating the non-sticky surface of your Teflon® pan. Other than that, they have been used in firefighting foams for many decades and finally ended up in our environment. In some places, like airports, where fire safety trainings are happening regularly, the release of the foams and included PFASs has resulted in severe contamination of soil and groundwater. So why not use the vacuuming properties of plants and get rid of them afterwards?

For that purpose, tree (i.e. birches and spruce), bush (i.e. bird cherry) and annual plant (i.e. strawberries) samples were taken around the fire training site at Arlanda airport, Sweden, to assess the accumulation of the pollutants in plant tissues. All plants took up the contaminants from the highly polluted soil and groundwater and mainly allocated them in the leaves and needles. While some species, i.e. bird cherry, showed moderate accumulation, the birches and the fern accumulated high amounts of the contaminants and thereby removed them from the soil and the groundwater.

Now it is time to introduce you to the concept of phytoremediation, which basically means that you take the full dust bag and throw it away. So after the plants have accumulated the pollutants, one can remove them either by mowing (i.e. strawberry), collecting the leaves or the birch sap (i.e. birch) or completely felling the whole tree (i.e. spruce) and dispose them properly, hence protecting the soil and groundwater and making it safer for future generations.

Despite all the good news, there is also bad news for you. The investigated plants are suitable to remediate soil and groundwater contaminated with PFASs, however, this is a process that takes a few decades if not hundreds of years. So while you and your kids might not profit directly from the results, your grandchildren will be able to enjoy safe drinking water!

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# Abbreviations

| | |
|---|---|
| 6:2 FTSA | Fluorotelomer sulfonate |
| AFFF | Aqueous firefighting (or film forming) foam |
| BCF | Bioconcentration factor |
| bw | Body weight |
| CMR | Carcinogenic, mutagenic and toxic |
| DBH | Diameter at breast height |
| dw | Dry weight |
| EFSA | European Food Safety Authority |
| EPA | Environmental Protection Agency |
| F | Fluorine |
| FOSA | Perfluorootanesulfonamide |
| GFF | Glass fiber filter |
| H | Hydrogen |
| IS | Internal standard |
| $K_{ow}$ | Octanol-water partition coefficient |
| LC-MS/MS | Liquid chromatography - mass spectrometry/mass spectrometry |
| LPE | Liquid phase extraction |
| LRAT | Long range atmospheric transport |
| MDL | Method detection limit |
| MW | Molecular weight |
| OECD | Organisation for Economic Co-operation and Development |
| OM | Organic matter |
| PAH | Polycyclic aromatic hydrocarbon |
| PBT | Persistency, bioaccumulation and toxicity |
| PFASs | Per- and polyfluoroalkyl substances |
| PFBA | Perlfuorobutanoate |
| PFBS | Perfluorobutane sulfonate |
| PFCAs | Perfluoroalkyl carboxylic acids |
| PFDA | Perfluorodecanoate |
| PFDoDA | Perfluorododecanoate |
| PFHpA | Perfluoroheptanoate |
| PFHxA | Perfluorohexanoate |
| PFHxS | Perfluorohexane sulfonate |
| PFNA | Perfluorononanoate |

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|---|---|
| PFOA | Perfluorooctanoate |
| PFOS | Perfluorooctane sulfonate |
| PFOSF | Perfluorooctanesulfonyl fluoride |
| PFPeA | Perfluorobutanoate |
| PFSAs | Perfluoroalkane sulfonates |
| PFTeDA | Perfluorotetradecanoate |
| PFUnDA | Perfluoroundecanoate |
| $pK_a$ | Acid dissociation constant |
| POPs | Persistent organic pollutants |
| PP | Polypropylene |
| ppb | Parts per billion |
| REACH | Registration, Evaluation, Authorisation and Restriction of Chemicals, European Regulation |
| rpm | Rotations per minute |
| SD | Standard Deviation |
| SPE | Solid phase extraction |
| SVHC | Substance of very high concern, REACH classification |
| $S_W$ | Water solubility |
| TCE | Trichloroethylene |
| TDI | Tolerable daily intake |
| TSCA | Toxic Substances Control Act, US EPA |
| VOC | Volatile organic compound |
| ww | Wet weight |
| WWTP | Waste water treatment plant |

# 1 Introduction

The extensive use of per- and polyfluoroalkyl substances (PFASs) as surfactants in, for example, textiles (e.g. GORE-TEX®), cookware (e.g. Teflon®), paper packages and aqueous firefighting foams (AFFFs) during the last decades has resulted in widespread environmental contamination (Buck et al., 2011). Due to the persistent and particularly chemically stable characteristics of PFASs, the impact of direct discharges into the environment, like manufacturing industries or runoff from firefighting facilities, is remarkably long-lasting (Awad et al., 2011). In Sweden, there are no facilities manufacturing PFASs, consequently, textiles, paper packaging, cookware and firefighting applications are the main input source for PFASs in Sweden, with AFFFs most probably constituting the biggest proportion (National Food Agency Sweden, 2014). Despite ongoing public health discussions in Sweden and severe safety concerns with AFFFs, the use of the foam for municipal application in Sweden has doubled from 26,000 L in 1998 to >48,000 L in 2014 (SR, 2015). The contamination of drinking water wells has been observed near Gammelby and Surahammar (municipalities of Sala and Surahammar, Västmanland), where AFFFs had been applied to fight a wildfire (SR, 2014). Another prominent case is the contamination of drinking water supplies for 5,000 residents of Kallinge (Ronneby municipality, Blekinge County) in 2013 through the firefighting training site emissions at the local air force (SR, 2016). In Uppsala County, Glynn et al. (2012) conducted a study from 1996 to 2010 looking at PFASs serum concentrations of primiparous women. While perfluorooctanesulfonate (PFOS)-related chemicals were decreasing in the serum by up to 22%/year, short-chained PFASs like perfluorobutanesulfonate (PFBS) increased by up to 11%/year. They concluded a shift in exposure to perfluoroalkyl carboxylic acids (PFCAs) with longer chains than PFOA ($C_7$) and PFSAs (perfluoroalkane sulfonic acids) with shorter chains than PFOS ($C_8$), most probably linked to the phase-out of PFOS production by the main manufacturer 3M in 2002.

The high persistence and potential for bioaccumulation and biomagnification of PFASs, have led to a ubiquitous distribution of PFASs even in remote environments (Martin et al., 2004). PFASs have been detected in fish and wildlife samples around the world (Giesy and Kannan, 2001), with particularly high levels found close to production sites and industries/application hot spots (Davis et al., 2007). Human exposure pathways include dust, drinking water, food, and indoor and outdoor air (Moriwaki et al., 2003; Washburn et al., 2005; OECD, 2013). Various studies have detected PFASs, mainly PFOS and PFOA in human serum, blood and breast milk. Concentrations are positively correlated with age, showing slight differences in concentrations and compounds between female and male (Kärrman et al., 2006). The half-lives of PFOA and PFOS in human serum were studied by Olsen et al. (2005) and determined to be 4 to 9 years, respectively. The environmental fate of PFASs is depending on the perfluoroalkyl chain length and functional group. Short-chained PFASs (<7 $CF_2$) are considered more mobile, particularly due to a higher water solubility ($S_W$) and lower sorption onto soil particles (Wang et al., 2011). However, PFOA and PFOS, the two most studied PFASs, are omnipresent in spite of moderate $S_W$ and

non-volatility (Jahnke, 2007). Despite increased attention on this topic, the knowledge about the toxicology of PFASs is still limited and mainly derived from animal studies (Ahrens et al., 2014). Reported adverse health effects in humans include various types of cancer, reduced birth weight, reduced humoral immune response in children, thyroid diseases and high cholesterol (Itoh et al., 2016; Papadopoulou et al., 2016; Rosenmai et al., 2016; Webster et al., 2016; OECD, 2013).

Since PFOA and PFOS do not degrade, they accumulate in the natural environment and the research on efficient remediation technologies is of high importance. Phytoextraction, the uptake of contaminants into above-ground biomass (Schnoor, 1997), has shown promising results when applied in artificial wetlands. Through the incorporation of the contaminants into the plants, these can easily be removed by harvesting. Chen et al. (2012) have determined soil sorption and phytoextraction to be the most significant mechanisms for PFOA and PFOS demobilization in constructed wetlands, with root density and -size being important performance factors for increased uptake. However, there is still a rather sparse amount of studies on plant uptake of PFASs (Yoo et al., 2011; Schachtschneider et al., 2010). Mudumbi et al. (2014) provided one of the first field studies of PFASs accumulation by plants, thus being more realistic for remediation scenarios than laboratory studies that have proven PFAS accumulation, e.g. in lettuce (Felizeter et al., 2012) or aquatic plants (Chen et al., 2012). Yet, the lack of attempts to determine the accumulation potential of established plant communities emphasizes the relevance of this topic. Accordingly, it should be highlighted that this study is unique in its nature and that no field trial with local vegetation had been conducted before. The few studies available are limited to greenhouse experiments with fertilization and controlled spiking of the alimental substrate (soil or water) (e.g. Felizeter et al., 2012; Stahl et al., 2009 and 2013; Lechner and Knapp, 2011) or have been conducted on agricultural fields where water and nutrient availability were artificial (Yoo et al., 2011). Hence, the comparability of the findings is moderate. The extent of the study and the high heterogeneity of data increase the difficulty of final evaluation.

## 1.1 Objectives

The aim of this study is to determine the accumulation potential of 26 target PFASs in local vegetation at Arlanda airport, Stockholm, in a multiple media approach including plants, surface soil and groundwater to evaluate the feasibility of remediation using phytoextraction. More in detail, the objectives are to

- assess the distribution of PFASs in plants including roots, stem, branches, leaves, needles, birch sap and berries (if applicable) for silver birch (*Betula pendula*), Norway spruce (*Picea abies*), bird cherry (*Prunus padus*), mountain ash (*Sorbus aucuparia*), ground elder (*Aegopodium podagraria*), long beechfern (*Phegopteris connectilis*) and wild strawberry (*Fragaria vesca*).

- investigate the total tree burden for PFASs and the bioconcentration factor (BCF) of individual PFASs based on the perfluoroalkyl chain length and functional group.

- evaluate the groundwater and soil remediation potential of silver birch, Norway spruce, bird cherry, mountain ash, ground elder, long beechfern and wild strawberry at contaminated airport sites.

## 1.2 Limitations

This master thesis focused on the distribution and accumulation of PFASs among different environmental media, namely soil, groundwater and plants. The study was limited to 26 PFASs for which an analytical method is established at SLU where this thesis was conducted. This is only a fraction of the existing range of PFASs and derivatives; however, the selected PFASs are assumed to be the most important ones due to their frequent application and ubiquitous detection in the environment (Ahrens, 2011).

Additionally, this thesis is based on a field study where all samples were taken directly from the environment. Consequently, factors like water availability, rooting depth and nutrient availability are not known and have not necessarily been equal at all three sites. However, they influence growth rate and biomass production and therefore contaminant uptake and translocation within the plant. The limited time frame of five months and plant species available at the sampling site are further restricting the extent of this study.

Furthermore, the age of the trees and bushes investigated was not known. Therefore, the period of exposure to and potential uptake and accumulation of PFASs remains unknown. All trees were approximately 15 meters tall and had a diameter at breast height (DBHs) of 20-35 cm. Consequently, they were considered mature trees of at least 15 years of age.

Lastly, there is a lack of knowledge of the containing PFASs of the AFFFs used at the fire training site at Arlanda airport.

# 2 Background

PFASs belong to the group of persistent organic pollutants (POPs) and are common environmental pollutants. PFASs contain a hydrophobic alkyl chain and a hydrophilic end group, leading to their highly demanded properties as surfactants (Buck et al., 2011). PFASs can be divided into several sub-groups depending on their number and type of C-F-bonds and functional groups. A rough overview of the sub-groups studied in this thesis and their relations is summarized in Figure 1 below:

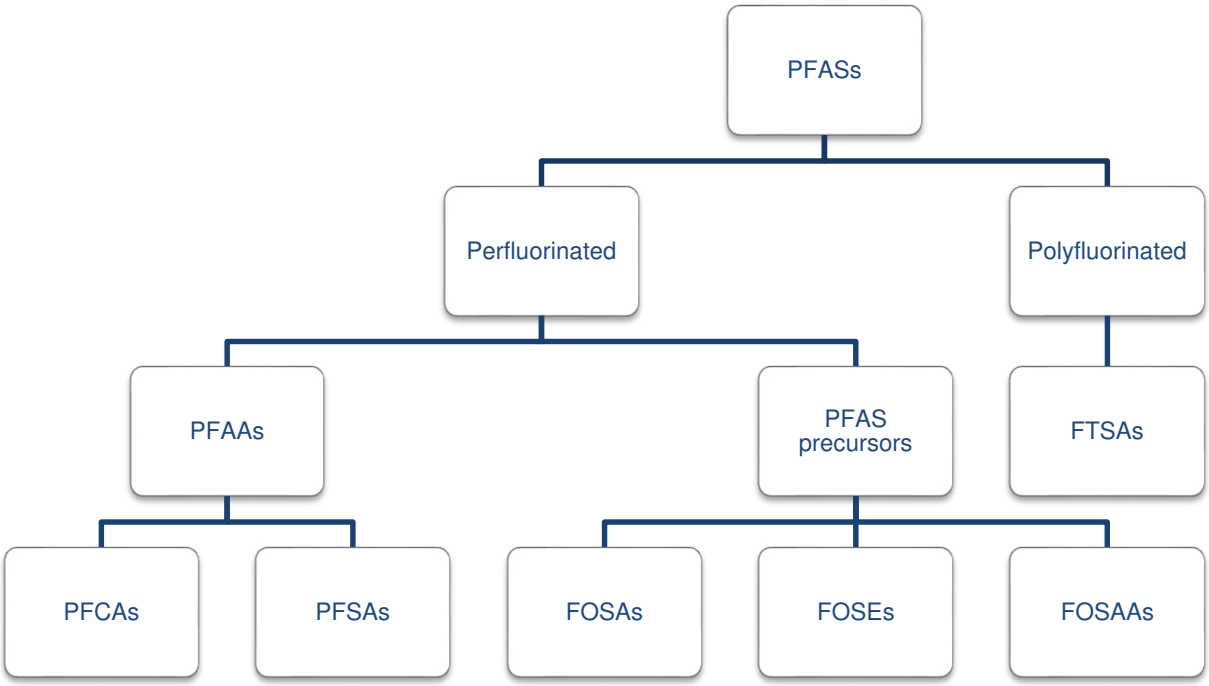


**Figure 1 Studied PFASs classified into sub-groups: the perfluorinated substances, including perfluoroalkyl acids (PFAAs) which comprise perfluoroalkyl carboxylates (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) and the PFAS precursors like perfluorosulfonamides (FOSAs), perfluorosulfonamidoethanols (FOSEs) and perfluorosulfonamidoacetic acids) and the group of polyfluorinated substances with fluorotelomer sulfonic acids (FTSAs).**

## 2.1 PFASs

Perfluoroalkyl substances are aliphatic substances in which all hydrogen (H) atoms have been replaced by fluorine (F) atoms ($C_nF_{2n+1}$), except for those H atoms which are part of functional groups (Buck et al., 2011). Polyfluoroalkyl substances are aliphatic substances in which all H atoms attached to at least

one (but not all) C atoms have been replaced by F atoms (Buck et al., 2011). Polyfluoroalkyl substances can be degraded, biotically or abiotically, to perfluoroalkyl substances in the environment.

Another distinctive feature for PFAS characterization is the chain length. PFCAs with ≥ eight carbon atoms (out of which are ≥ seven perfluorinated carbons) and PFSAs with ≥ six carbons (≥ 6 perfluorinated carbons) are regarded as long-chained PFASs (Buck et al., 2011). There is a difference in between these two groups due to different tendencies for bioaccumulation/-concentration (Buck et al., 2011).

Precursors are chemicals that can transform into particular compounds, preceding that compound in the degradation reaction. PFASs precursors are inter alia FOSAs, FOSEs, FOSAAs and FTSAs. These groups are distinguished by their functional groups, which are octanesulphonamides, octanesulfonamidoethanols, octanesulfonamidoacetic acids and telomersulfonates, respectively. They degrade to either PFCAs or PFSAs. In this study, 26 individual PFASs were included from six different PFAS classes including PFCAs, PFSAs, FOSAs, FOSEs, FOSAAs and FTSAs.

## 2.2 Physicochemical properties

The physicochemical properties of PFASs are particularly influenced by the perfluoroalkyl chain length and the functional group. The combination of the hydrophobic alkyl chain and a hydrophilic functional group is regarded as amphiphilic (Jahnke, 2007). The partly- or fully-fluorinated tail of PFASs has hydrophobic properties and can either have a branched or linear structure (Buck et al. 2011). Long range atmospheric transport (LRAT) of PFAS's precursors implies volatility (Kärrman et al., 2006). Short chain PFASs show a higher $S_W$ and therefore increased mobility (Collins and Finnegan, 2010), due to a shorter hydrophobic tail than that of long-chained PFASs. Short-chain PFASs also show a greater tendency for bioaccumulation and biomagnification (Martin et al., 2004). The highly stable carbon-fluorine bond provides chemical and thermal resistance (OECD, 2013).

## 2.3 Manufacture and applications

All PFASs with a carbon chain length ≥2 are considered anthropogenic (Jahnke, 2007). There are two major manufacturing processes for PFASs. On the one hand, telomerisation is creating solely linear per- and polyfluorinated compounds and has been in use since the 1950s (Jahnke, 2007). On the other hand, electrochemical fluorination, deployed since the 1970s, produces a mixture of branched and linear isomers (Giesy and Kannan, 2002).

3M, the formerly main producer of PFOS, stopped manufacturing PFOS-containing products in 2002. PFOS is currently only produced in China (CFFF, 2014). Sweden has no production facilities for PFASs.

Consequently, traces in the environment originate from industrial use, leakage from landfills, LRAT and subsequent degradation of PFASs precursors and PFASs-containing consumer products.

The application spectrum of PFASs is broad. Due to the unique surface properties, they have been used for water-, dirt- and oil-proofing clothing, domestic textiles (carpets, upholstery) or as paper protectors in food packaging (Jahnke, 2007). The stain and grease repellency are valuable characteristics for non-stick surfaces on cookware and commonly used in aerospace, automotive, electronics and other industry segments (e.g. paints and coatings; US EPA, 2016).

AFFFs commonly rely on fluorosurfactants as their key ingredient and are used to extinguish flammable liquid fires (class B fires which refer to flammable liquids) in military, industrial, aviation and municipal applications (FFFC.org, 2014).

AFFFs were known to be exceptionally safe for application by firefighters while providing less damage to property and the environment through rapid extinguishment of the fire (FFFC.org, n.d.). These characteristics arise from the low surface tension and the positive spreading coefficient of fluorosurfactants that enable film formation on top of lighter fuels (FFFC.org, 2014). This film-forming ability is unique to fluorosurfactants and stops the flames while further providing protection against vapour release and resulting flashbacks (Cortina, 2010).

After the discovery of the harmful properties of PFOS in the 1990's, most manufacturers have phased out production and replaced PFOS by short-chain PFASs ($<C_6$), which are known to be persistent but less bioaccumulative or toxic (Cortina, 2010). Additionally, the environmental impact has been reduced by minimization of foam discharges (Cortina, 2010).

Currently, the fluorine-free alternatives are not sufficiently efficient as they are lacking the essential properties (low surface tension, spreading coefficient), particularly film formation, which improves fire suppression performance by 20% (Williams et al., 2011). Consequently, they need essentially longer to extinguish a fire and do not fulfil the conditions for military application (MilSpec; extinguishing time <30 seconds; Williams et al., 2011) while producing up to three times the runoff (Cortina, 2010).

## 2.4 Sources and fate

PFASs in the environment can originate from direct and indirect sources. Direct sources are either local point sources (such as unintentional spills from fire training facilities, production industries, waste dumps, waste water treatment plant's (WWTP) effluents) or consumer use of products containing PFASs (Naturvårdsverket/Swedish EPA, 2012). Indirect sources refer to the formation of PFASs from degradation of atmospherically imported volatile precursors (OECD, 2013). A spatial survey from Awad

et al. (2011) shows that the major impact of PFASs occurs rather locally in the point-source affected area. Due to the high persistence of PFASs, the impact of these direct discharges (like AFFF runoff) on the ambient environment are particularly long-lasting (Awad et al., 2011). Consequently, the PFASs concentration in global river surface water varies from 10 ng $L^{-1}$ to 100 ng $L^{-1}$ (Ahrens, 2011).

## 2.5 Legislation

Due to their harmful characteristics the most common PFASs are subject to regulation. PFOS and perfluorooctanesulfonyl fluoride (PFOSF) are restricted under the Stockholm Convention on POPs since 2010. PFOA is categorized as a substance of very high concern (SVHC) due to persistence, bioaccumulation and toxicity (PBT) in the European regulation "Registration, Evaluation, Authorisation and Restriction of Chemicals" (REACH) (since 2013 and PFOA and PFOS are regulated in the Toxic Substances Control Act (TSCA) by US EPA).

Since 2009, PFOS is listed in Annex B (restrictions) of the Stockholm Convention on POPs and the production and use are restricted to a limited number of "acceptable purposes" (Stockholm Convention, SC-4/17, 2009) that are listed in the convention text. Registered companies that work with PFOS are requested to stop using PFOS or otherwise have to provide information every four years about their progress in replacing or eliminating PFOS (SC-4/17, 2009).

The US EPA started a voluntary PFOS Stewardship Program in 2010 with eight companies working towards the elimination of PFOS in their manufacturing chain until 2015. Furthermore, the long-chain perfluorinated substances (LCPFS) like PFOA and PFOS are part of the TSCA by US EPA since 2012 allowing US EPA to ban, restrict, and prohibit import, processing or use of them (US EPA, 2009). Moreover, the "New Chemical's Program" is actively seeking alternatives for the harmful PFASs for better management options in the future.

In Europe, PFOA has been classified as an SVHC under the REACH regulation (SVHC, article 57d) in 2013 due to persistency, bioaccumulation and toxicity (PBT). Furthermore, PFOA inhibits the characteristics carcinogenic, mutagenic and toxic (CMR).

As a result of the regulations for PFOS and PFOA, the environmental and human exposure pattern has shifted from PFOS and PFOA to shorter chain PFASs (Möller et al., 2010). D'Agostino and Mabury (2014) discovered that the proportion of unknown PFASs, newly invented as surrogates for PFOS and PFOA, in the environment is increasing. However, there is hardly any information available about these new substances and due to their lower efficiency, higher quantities are supposedly required. So far, no studies on the health effects of these substances or risk assessments have been conducted.

## 2.6 Human exposure and toxicity

Due to the lack of PFAS' production in Sweden, the occupationally exposed groups are connected to textile, paper production, metal plating and ski waxing industry (Freberg et al., 2010; Olsen et al., 2003). Major exposure routes for humans are diet, particularly seafood and fish, as well as drinking water but also inhalation of contaminated dust (indoor and outdoor) (Swedish EPA, 2012; Moriwaki et al., 2003). For infants, main exposure pathways are placental transfer and breast milk (Kärrman et al., 2007).

There is no legal threshold on PFASs in the EU or Sweden, but the European Food Safety Authority (EFSA) has made an attempt in 2008 by proposing tolerable daily intake (TDI) values for PFOS and PFOA of 0.15 and 1.5 $\mu$g $kg^{-1}$ bw/day (EFSA, 2008). For the environment, the Swedish EPA has suggested limits for PFOS in limnic (30 $\mu$g $L^{-1}$) and marine (3 $\mu$g $L^{-1}$) waters as well as for biota (6 $\mu$g $g^{-1}$ wet weight) (Swedish EPA, 2008). For the general population, which is exposed to PFASs directly via dietary uptake and indirectly via the environment, serum levels were found at low ppb (ng $mL^{-1}$) concentrations (Swedish EPA, 2012). In the absence of PFAS limits for drinking water, the Swedish National Food Agency has set action levels after which a total sum of PFASs of 90 ng $L^{-1}$ must not be exceeded (Livsmedelsverket, 2016).

Common adverse effects of PFASs have shown to be carcinogenicity, hepatotoxicity, structural malformations, obesity, delayed sexual maturation, decreased body weight and immunotoxicity (Lau et al., 2007). Yet, the available risk assessments contain data gaps and uncertainties and the mechanisms of action of the PFASs remain unknown.

## 2.7 Remediation and phytoextraction

Remediation is defined as the reversal or stopping of damage to the environment seeking to diminish physical, chemical or biological hazardous changes of the local environment through the elimination or containment of pollutants. Bioremediation is commonly referred to projects involving microorganisms for degrading contaminants (US EPA, 2016), with phytoremediation being a related technology using vegetation for remedy purposes.

Phytoremediation is the *in situ* treatment of contaminated environments (soil, sediment, water) by vegetation. It is particularly effective at low contamination levels and can be applied on large areas at comparably low cost (Schnoor, 1997). Phytoextraction is one particular kind of phytoremediation. As the name suggests, it relies on the extracting properties of plants. According to Schnoor (1997), phytoextraction is the "uptake […] (of contaminants) into above-ground biomass" and has successfully been applied in pilot studies and field experiments to extract metals and radionuclides in the past.

There are several uptake pathways, like foliar uptake of particulate (also fugitive substances) contaminants deposited from the air or root uptake of soluble contaminants with water. The soil-air-plant pathway implies the volatilization of contaminants from the soil and subsequent precipitation on the plant's surface for uptake. There is also direct uptake via the leaves after aerial deposition from ambient air (Collins and Finnegan, 2010). Peverly et al. (2015) have shown accumulation of POPs in tree bark from high ambient air concentrations, indicating that even the bark has to be considered as a potential organ for uptake pathways. Furthermore, Collins and Finnegan (2010) determined the gas phase to be the primary uptake route for different POPs (mainly polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds) with the deposition via the soil-air-plant pathway being the dominating process (in comparison to direct deposition from background air) if soil concentrations exceed 10-100 mg $kg^{-1}$.

When taking up nutrients and water via the roots, plants also withdraw other substances like soluble contaminants from soil and sediment. The octanol-water partitioning coefficient ($K_{ow}$) represents the ratio of the solubility of a compound in octanol (a non-polar solvent) to its solubility in water (a polar solvent). Log $K_{ow}$ values were used as relative indicators of the tendency of an organic compound to adsorb to soil and are inversely related to aqueous solubility (US EPA, 1995). Therefore, high log $K_{ow}$ (>5) values indicate low aqueous mobility and prevent transportation within the plant from root to shoot (Collins and Finnegan, 2010). Log $K_{ow}$ values increase with increasing fluorinated chain length of PFASs (Table 3). Consequently, short-chain PFASs can be expected to bioaccumulate in the leaves of plants while long-chain PFASs are more likely to accumulate in roots and/or soils (Felizeter et al., 2012).

Phytoextraction is performed *in situ*, avoiding transfer or relocation of the contaminated commodities (soil, water, sediment) and, hence, offers significant cost advantages over alternative schemes of soil excavation and treatment or disposal. It further minimizes environmental disturbance and post-clean-up costs can be reduced (USGS, 1995). A high accumulation factor, expressed via the ratio of contaminant in the plant tissue to that in the soil, and high plant productivity (kg of dry matter that is harvestable each season) are important characteristics of successful phytoremediators (Schnoor, 1997).

Other than a fast growth rate and high biomass production, a deep root system and the ability to grow in nutrient-poor soils are beneficial for phytoremediators (Punshon and Dickinson, 1999). As noted in previous research projects, many birch species, particularly *B. pendula* (silver birch), meet these requirements (Dmuchowski et al., 2014). While Dmuchowski et al. (2014) have identified *B. pendula* as a hyperaccumulator of zinc (*Zn*) during a field study with exceptionally high accumulation in the leaves and trunks, Marguí et al. (2007) have even reported lead (*Pb*) and *Zn* concentrations in *B. pendula* leaves ten times higher than the background values. In 2013, Lewis et al. conducted a study in central Sweden with a mature *B. pendula* at a trichloroethylene (TCE) contaminated site, reporting high TCE values, most likely derived from the groundwater plume, in the birch sap and sapwood.

Another field study of Placek et al. (2016) determined Norway spruce (*P. abies*) to be highly suitable for remediation due to its excellent adaptability and bioaccumulation factors (BAF; mg $kg^{-1}$) ranging from 1-3 for *Zn*. Furthermore, they observed a high translocation factor within the plant from the roots to the shoots, leading to remarkably high *Cd* values in the needles. However, most remediation studies with *Betula* and *Picea* have been limited to metal contamination and no studies with PFASs are available for these species.

## 2.8 Bioconcentration factors

BCFs describe the accumulative potential of an organism or plant and were originally developed in the aquatic sciences. They are used to relate the pollutant residues in plants or organisms to the pollutant concentrations in the ambient environment like water, soil or air (Caesar-project.eu, n.d.). The simplest way to express this ratio is $BCF_{plant} = C_{plant}/C_{reference\ media}$ with $C$ being the concentration of the contaminant, i.e. in ng $kg^{-1}$ ww for solids and ng $L^{-1}$ for liquids.

BCFs have been proven helpful to determine a plant's ability to accumulate contaminants from surrounding media and therefore allow comparisons of different species' effectivity. Zhao et al. (2014) describe the linear decrease of $BCF_{wheat/soil}$ with increasing perfluorocarbon chain length of PFASs, suggesting decreased mobility/$S_W$ of long-chained PFASs. Therefore, a higher bioaccumulative potential is expected for long chained PFASs in comparison to short-chain substances (D'Agostino et al., 2014). Furthermore, Mudumbi et al. (2014) found the rooting system to be a relevant factor for the uptake rate and persistence of contaminants in several riparian plant species.

# 3 Materials and Methods

## 3.1 Sampling location Stockholm Arlanda airport

Arlanda airport is the largest airport in Sweden and located in the municipality of Sigtuna at 40 m a.s.l. It officially opened for civil traffic in 1962 and primarily serves the cities of Stockholm and Uppsala with >22 million passengers and 179,000 tonnes of cargo freight in 2014 (Swedavia, 2016). The airport has a fire training site north of the northern runways, established before 1987 with a functioning runoff collection system since 1997 (Figure 2).

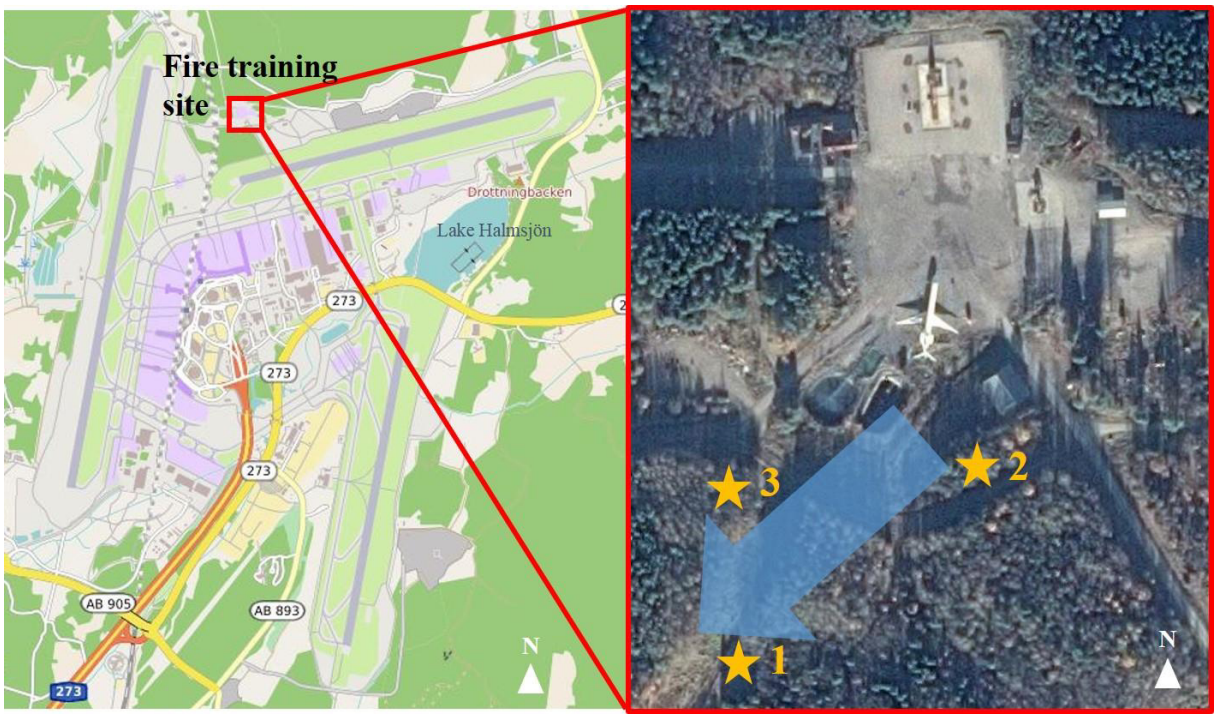


**Figure 2 Overview of Arlanda airport (left) and the fire training site (right). The three sampling sites (stars) and the groundwater flow direction (blue arrow) are indicated on the fire training site (map taken from openstreetmap.de/karte (left) and google.de/maps (right)).**

For training purposes, PFOS-containing AFFFs (STHMEX-AFFF 3%, Dr. Richard Sthamer GmbH & Co. KG, Hamburg, Germany) were applied frequently from the 1980's until 2003. Since 2003, the remaining stocks of PFOS-containing AFFFs have been depleted and replaced by PFOS-free AFFFs

(Presto AFFF and Moussol APS-P, Dr. Richard Sthamer GmbH & Co. KG, Hamburg, Germany) that still contain >10% PFASs. From 2011, only fluorine-free AFFF (Moussol FF 3/6, Dr. Richard Sthamer GmbH & Co. KG, Hamburg, Germany) has been bought (Ahrens et al., 2015). PFASs have been detected in water, sediment and fish in the nearby environment of Stockholm Arlanda airport (Ahrens et al., 2015). PFASs levels up to 4,000 ng $L^{-1}$ were detected in surface waters at and south of the fire training facility in 2009-2013 (Ahrens et al., 2015), indicating severe contamination.

## 3.2 Sample collection

The samples were collected from three sampling locations south of the fire training site on the 22nd of March and the 30th of June 2016 (Figure 2). The sampling sites were chosen according to following criteria i) existence of a groundwater well, ii) proximity (<500 m) to the fire training site and within estimated groundwater flow direction, iii) availability of mature birch and spruce trees, and iv) accessibility for sampling. All sites were equal and representative for the area. There was no reference site. In March, the temperatures were around 0°C with slight snowfall, whereas in June it was a sunny day with temperatures around 25°C. The local vegetation mainly consists of birches, spruce, various bushes and common European ground cover vegetation. The local aquifer is located at approximately 1-4 m depth with a south-western flow direction at the sampling sites.

The samples taken in March included 3 groundwater, 1 surface water, 3 mixed soil and 17 tree samples, comprising of root, leaf, twig and core tissues from birch and spruce. However, birch twigs were not sampled in March. In June, 3 mixed soil samples and 17 plant samples, particularly from bushes and annual plants were taken, as well as birch twigs and another set of fresh birch leaves. In total, 4 water samples, 6 soil samples and 44 plant samples (i.e. silver birch (*Betula pendula*), Norway spruce (*Picea abies*), bird cherry (*Prunus padus*), mountain ash (*Sorbus aucuparia*), ground elder (*Aegopodium podagraria*), long beechfern (*Phegopteris connectilis*) and wild strawberry (*Fragaria vesca*)) were collected (Table 1).

**Table 1 Summary of the three sampling locations showing ID, coordinates, and number of samples for groundwater, surface water, soil and total number of plant samples (number of plant species in brackets, see Table 2 for details)**

| | Coordinates | | Number of samples | |
|---|---|---|---|---|
| ID | Latitude/Longitude | Sample type | March 2016 | June 2016 |
| 1 | 59°39‘41.93308“ N/ 17°56‘6.28575“ E | Groundwater | 1 | - |
| | | Surface water | - | - |
| | | Soil | 1 | 1 |
| | | Plant species(no of species) | 4(2) | 7 (4) |
| 2 | 59°39‘43.00477“N/ 17°56‘11.08658“ E | Groundwater | 1 | - |
| | | Surface water | - | - |
| | | Soil | 1 | 1 |
| | | Plant species | 8 (2) | 11 (5) |
| 3 | 17°56‘4.54373“ E/ 17°56‘4.54373“ E | Groundwater | 2 | - |
| | | Surface water | 1 | - |
| | | Soil | 1 | 1 |
| | | Plant species | 5 (2) | 9 (4) |
| | | ∑plant samples | 17 | 27 |

### 3.2.1 Groundwater and surface water sampling

The three groundwater grab samples (each 1 L) and one surface water grab sample (1 L) were taken on the 22nd of March in2016 from the wells GV15-0010 (Site 1), GV50 (Site 2) and GV15-0012 (Site 3) and an open ditch close by Site 3. The groundwater level was measured with an electrical contact gauge (Eijkelkamp, The Netherlands) and the water was collected using a field peristaltic pump (12V DC, Eijkelkamp, The Netherlands). The samples were collected in 1 L polypropylene (PP) bottles (Nalgene, USA), that had been rinsed three times with methanol, transported and stored at 6°C until further processing.

### 3.2.2 Soil sampling

Composite soil samples (consisting of ~15 individual samples) were taken at approximately 0-10 cm depth at all three sites close to the existing groundwater wells using a steel shovel in March and June 2016, respectively. The samples were collected in 500 mL zip-lock bags and transported and stored at 6°C.

### 3.2.3 Plant sampling

The plants were sampled in 1-3 L zip-lock bags in March and June 2016 and transported and stored at 6°C. All sampled trees have DBHs of 20-35 cm and were identifiable as mature trees.

In March, roots, cores, twigs, leaves, needles and sap samples were collected for silver birch and Norway spruce (Table 2). Birch leaves were collected from the ground (due to a lack of fresh foliage) and spruce needles were picked directly from the tree. Twigs were sampled with a stainless steel knife and roots were dug out with a steel spade. The cores were sampled according to the method described by Larsen et al. (2008) using an increment borer (Ø 1cm, Suunto, Finland) that was drilled into the trunk at chest height. The resulting holes in the birch trees were used for the collection of birch sap. A small, food-grade plastic tap (Atkinson maple syrup supplies, Canada) was inserted and a 1 L PP-bottle (Nalgene, USA), taped with duck-tape and pre-rinsed three times with methanol, was placed directly underneath for collection of the sap. The bottles were covered with duck-tape to protect the sample from UV radiation, as the effect of UV on PFASs degradation remains unknown. The bottles were left for ten days in March (22nd-1st of April) and then replaced with empty ones to collect sap for approximately three months until the end of June. In June, all plant samples were directly taken from the trees, bushes and ground cover species (Table 2). Berries, leaves, twigs, roots and birch sap were sampled. The bushes and ground cover species were chosen due to their high frequency and occurrence at a minimum of two out of three sampling sites.

**Table 2 Sampled species, sampled plant tissues and number of samples in brackets from the three sampling locations in March and June 2016**

| Species | Species name English | Site 1 | Site 2 | Site 3 |
|---|---|---|---|---|
| March 2016 | | | | |
| *Betula pendula* | silver birch | root (1), cores (2), twigs (1), leaves (1) | root (1), cores (2), twigs (1), leaves (1) | root (1), core (1), leaves (1) |
| *Picea abies* | Norway spruce | - | root (1), core (1), twig (1), needles (1) | core (1), twig (1), needles (1) |
| June 2016 | | | | |
| *Betula pendula* | silver birch | leaves (1) | leaves (1) | leaves (1) |
| *Prunus padus* | bird cherry | - | twigs (1), leaves(1),berries (1) | twigs (1), leaves(1),berries (1) |
| *Sorbus aucuparia* | mountain ash | twigs (1), leaves (1) | twigs (1), leaves (1) | twigs (1), leaves (1) |
| *Aegopodium podagraria* | ground elder | leaves (1) | stems (1), leaves (1) | stems (1), leaves (1) |
| *Phegopteris connectilis* | long beechfern | root (1), leaves (1) | - | - |
| *Fragaria vesca* | wild strawberry | - | leaves (1), berries (1) | - |

## 3.3 Target analytes

The samples were analysed for 26 different PFASs (Table 3): thirteen PFCAs (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA and PFOcDA), four PFSAs (PFBS, PFHxS, PFOS, PFDS), three FOSAs (FOSA, MeFOSA, EtFOSA), two FOSEs (MeFOSE, EtFOSE), three FOSAAs (FOSAA, MeFOSAA, EtFOSAA) and 6:2 FTSA. Additionally, the branched isomers of PFHxS, PFOS and FOSA were studied as they have shown to behave differently in the environment and showed higher accumulation in fish than the linear isomers (Ahrens et al., 2015). All samples were spiked with 100 $\mu$L of an internal standard (IS) mix containing $^{13}C_4$ 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, $^{13}C_8$ FOSA, $d_3$-*N*-MeFOSA, $d_5$-*N*-EtFOSA, $d_7$-*N*-MeFOSE, $d_9$-*N*-EtFOSE, $d_3$-*N*-MeFOSAA, $d_5$-*N*-Et-FOSAA. The IS mix was used to correct for variations and losses during sample preparation and instrumental analysis.

**Table 3 The 26 PFASs studied in this thesis, including their acronyms, molecular formulas, structural formulas, molecular weights (MW), water solubility (*Sw*), acid dissociation constant (*pKa*) values and the octanol-water partition coefficient (log *Kow*). Compilation of characteristics see Englund (2015).**

| | Substance | Acronym | Molecular Formular | MW [g mol$^{-1}$] | $S_w$ [mg L$^{-1}$] | $pK_a$ | Log $K_{ow}$ [L kg$^{-1}$] |
|---|---|---|---|---|---|---|---|
| PFCAs | perfluorobutanoate | PFBA | $C_3F_7CO_2^-$ | 214 | 563[a] | 0.05[b]<br>0.4[c] | 2.91[d]<br>2.82[a] |
| | perfluoro-pentanoate | PFPeA | $C_4F_9CO_2^-$ | 264 | 113000[a] | -0.10[b] | 3.69[d]<br>3.43[a] |
| | perfluorohexanoate | PFHxA | $C_5F_{11}CO_2^-$ | 314 | 15700[c]<br>21700[a] | -0.17[b]<br>-0.16[c] | 4.50[d]<br>4.06[a] |
| | perfluoro-heptanoate | PFHpA | $C_6F_{13}CO_2^-$ | 364 | 118.0[e]<br>4180[a] | -0.20[b] | 5.36[d]<br>4.67[a] |
| | perfluorooctanoate | PFOA | $C_7F_{15}CO_2^-$ | 414 | 4340[e]<br>3400[c] | -0.21[b,c] | 6.26[d]<br>5.30[a] |
| | perfluorononanoate | PFNA | $C_8F_{17}CO_2^-$ | 464 | 131[a] | -0.21[b] | 7.23[d]<br>5.92[a] |
| | perfluorodecanoate | PFDA | $C_9F_{19}CO_2^-$ | 514 | 260[e]<br>25[a] | -0.22[b] | 8.26[d]<br>6.50[a] |
| | perfluoro-undecanoate | PFUnDA | $C_{10}F_{21}CO_2^-$ | 564 | 92.3[e]<br>4.13[a] | -0.22[b] | 2.32[e]<br>7.15[a] |
| | perfluorodo-decanoate | PFDoDA | $C_{11}F_{23}CO_2^-$ | 614 | 7.05 * 10$^{-1}$[a] | -0.22[b] | 7.77[a] |
| | perfluorotri-decanoate | PFTriDA | $C_{12}F_{25}CO_2^-$ | 664 | 1.71 * 10$^{-1}$[a] | -0.22[b] | 8.25[a] |
| | perfluorotetra-decanoate | PFTeDA | $C_{13}F_{27}CO_2^-$ | 714 | 2.71 * 10$^{-2}$[a] | -0.22[b] | 8.90[a] |
| | perfluorooctа-decanoate | PFHxDA | $C_{15}F_{31}CO_2^-$ | 814 | n.a. | -0.22[b] | n.a. |
| | perfluorooctа-decanoate | PFOcDA | $C_{17}F_{35}CO_2^-$ | 914 | n.a. | -0.22[a] | n.a. |
| PFSAs | perfluorobutane-sulfonate | PFBS | $C_4F_9SO_3^-$ | 300 | 510[e]<br>46200[c] | 0.14[b,c] | 3.90[a] |
| | perfluorohexane-sulfonate | PFHxS | $C_6F_{13}SO_3^-$ | 400 | 1400[c] | 0.14[b,c] | 0.97[e]<br>5.17[a] |
| | perfluorooctane-sulfonate | PFOS | $C_8F_{17}SO_3^-$ | 500 | 570[c,e] | 0.14[b]<br>-3.27[c] | 4.67[d]<br>7.66[a] |
| | perfluorodecane-sulfonate | PFDS | $C_{10}F_{21}SO_3^-$ | 600 | n.a. | 0.14[b] | 7.66[a] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **FOSAs** | perfluorooctane-sulfonamide | FOSA | $C_8F_{17}SO_2NH_2$ | 499 | 1850000[a] | 6.56[b] | 2.56[e] |
| | methylperfluoro-octansulfonamide | MeFOSA | $C_8F_{17}SO_2NHCH_3$ | 513 | 0.81[e] 263000[a] | 7.69[b] | 6.07[a] |
| | ethylperfluoro-octanesulfonamide | EtFOSA | $C_8F_{17}SO_2NHCH_2CH_3$ | 527 | 306[a] | 7.91[b] | 6.71[a] |
| **FOSEs** | methylperfluoro-octanesulfo-amidoethanol | MeFOSE | $C_8F_{17}SO_2N(CH_2)_2CH_3OH$ | 557 | 0.81[e] | 14.4[b] | n.a. |
| | ethylperfluoro-octanesulfonamido-ethanol | EtFOSE | $C_8F_{17}SO_2N(CH_2)_3OH$ | 556 | n.a. | 14.4[b] | n.a. |
| **FOSAAs** | perfluorooctane-sulfonamidoacetic acid | FOSAA | $C_8F_{17}SO_2NHCH_3CO_2$ | 557 | n.a. | n.a. | n.a. |
| | methylperfluoro-octanesulfonamido-acetic acid | MeFOSAA | $C_8F_{17}SO_2NCH_3CH_2CO_2$ | 558 | n.a. | -3.27[f] | n.a. |
| | ethylperfluoro-octanesulfonamido-acetic acid | EtFOSAA | $C_8F_{17}SO_2N(CH_2)_2CH_3CO_2$ | 584 | n.a. | n.a. | n.a. |
| **FTSAs** | 6:2 Fluorotelomer-sulfonate | 6:2 FTSA | $C_8H_4F_{13}SO_3^-$ | | n.a. | n.a. | n.a. |

[a]Wang et al., 2011
[b]Ahrens et al., 2012
[c]Du et al., 2014
[d]Rayne and Forest, 2009
[e]Rahman et al., 2013
[f]Brooke et al., 2004
Not available (n.a.)

## 3.4 Sample preparation, extraction and analysis for PFASs

All glassware was washed with tap water, rinsed with ethanol, cleaned in the dishwasher, baked out in the oven at 450°C and rinsed three times with methanol before usage. The PP tubes were also rinsed three times with methanol before being used. All tools and devices were rinsed three times with methanol before sample preparation. The glass fiber filters (GFFs) were burned in the oven at 400°C before usage.

### 3.4.1 Extraction of soil and plant material

The soil and plant material was extracted based on a method described previously (Ahrens et al., 2009). Each soil and plant sample was freeze-dried for approx. seven days until the samples were dry. The soil and dried berry samples were homogenized using a mortar and a pestle. The needles were homogenized in 7 mL tubes using a homogenizer (*Precellys Evolution*, Bertin, France) set to four repetitions of 40 s each and 20 s breaks in between with 7500 rpm. This procedure was repeated until at least 4 grams of plant material per sample had been homogenized. The dried leaves were crushed by rubbing them through a stainless-steel sieve (pore size: 0.5 mm) and root, core and twig samples were grinded in a coffee mill (*GVX 2*, Krups, Germany) set to finest grade. The tree core samples were divided into two parts, the central piece that was withdrawn from the middle of the trunk and represents the older part of the tree, and the outer part of the core which also includes the bark of the tree which represents the younger part (hence, more recent contamination).

After homogenization, 1-4 grams of dry and homogenized sample were weighed into a 50 mL PP-tube (1) with one replicate each. A solution (a) of 2 mL of 100 mM sodium hydroxide (NaOH) in 80%/20% methanol/Millipore water was added and left to soak for 30 minutes. 20 mL of methanol and 100 $\mu$L of PFAS-IS-standard mix were added before the tube was closed and placed on a wrist-action shaker in horizontal position at 200 rpm for 60 minutes. Afterwards, the tube was centrifuged at 3000 rpm for 15 minutes and the supernatant was decanted into another 50 mL PP-tube (2). The extraction was repeated in tube (1) using 1 mL of 100 mM NaOH solution and 10 mL of methanol. The sample was then shaken at 200 rpm for 30 minutes on the wrist-action shaker and then centrifuged for 15 minutes at 3000 rpm and the supernatant from tube (1) was decanted into tube (2). Then, 0.1 mL 4 M hydrochloric acid (HCl) was added to tube (2) followed by shaking by hand. The tube (2) was centrifuged again at 3000 rpm for 5 minutes. Afterwards, 8.3 mL (one fourth) of the sample was transferred into a 15 mL PP-tube and concentrated to 0.5 mL using a nitrogen stream. The inner PP-tube wall was rinsed twice with methanol during the concentration process. A 1.7 mL Eppendorf centrifuge tube was prepared with 25 mg ENVI-Carb 120/400 (Supelco, USA) and 50 $\mu$L glacial acetic acid (Merck, Germany). 0.5 mL of supernatant extract was transferred to the Eppendorf centrifuge tube. Then, the cap was put on tight and the tube was vortexed thoroughly, followed by 15 minutes centrifugation at max. 4000 rpm. The supernatant solution was transferred to an autoinjector vial (Eppendorf, Germany) and the sample was analysed using LC-MS/MS analysis. If it was not analysed immediately, the sample was stored in the freezer at -18°C until analysis.

### 3.4.2 Extraction of water and birch sap samples

All liquid samples (i.e. groundwater, surface water and birch sap) were filtered with GFFs (Grade GF/C, diameter: 4.7 cm, pore Size: 1.2 $\mu$m; GE Healtcare Life Sciences, Whatman, UK) prior to extraction (for details see Ahrens et al., 2010). Particularly the birch sap samples collected in June had impurities from dead insects and mould. All filtration equipment was rinsed three times with methanol. The filtration equipment and the GFFs (showing the wavy side on top) were connected. The 1 L samples were shaken and sonicated for 5 minutes in a sonication bath, after which they were filtered with a vacuum pump. The GFF's were replaced if filtration went slow due to blocked filters. Methanol rinsed PP-bottles were weighed before and after being filled with the filtered water. The walls of the filtration funnel and the filtration bottle was rinsed three times with methanol (two times ~2 mL) and the solvent was added to the filtered water. All filtration equipment was rinsed six times with methanol before starting with a new sample.

The cartridge adapters and stop cocks were placed in beakers filled with methanol and sonicated twice for 15 minutes each. The syringes (reservoirs during filtration) and the 15 mL PP tubes were rinsed three times with methanol. The SPE equipment (inlet, adapter, stop cocks) was rinsed three times with methanol and dried by air. Each water sample was spiked with 100 $\mu$L IS mixture (20 pg $\mu L^{-1}$) and shaken subsequently. The SPE cartridges (Oasis® WAX, 6cc, 500 mg, 60 $\mu$m, Waters Corporation, USA) were preconditioned using 4 mL 0.1% ammonium hydroxide in methanol, then with 4 mL of methanol and subsequently with 4 mL of Millipore water. Afterwards, the equipment was loaded with the filtered samples (~300 mL). The vacuum and stop cock were used to regulate the flow to approximately one drop per second. Subsequently, the washing of the cartridge was performed using 4 mL 25 mM ammonium acetate buffer in Millipore water directly into the cartridges. The cartridges were dried by centrifugation at 3000 rpm for 2 minutes. For elution, 15 mL PP tubes were placed below the cartridges to collect the samples. The cartridges were eluted with 4 mL methanol and 8 mL 0.1% ammonium hydroxide in methanol and dried subsequently with a vacuum for 1 min. The extracts were concentrated to about 1 mL under a nitrogen stream. The tube was then rinsed twice with methanol and the sample was concentrated again to 1 mL under the nitrogen stream. Afterwards, the sample was transferred into a 1 mL glass vial. The PP tube was rinsed three times with the solvent being added to the glass vial. The content of the glass vial was again concentrated to exact 1 mL. The vial was vortexed and stored in the freezer until analysis using HPLC-MS/MS.

### 3.4.3 Instrumental analysis

All samples were analyzed using high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS) (Agilent Technologies, USA). The analysis was done at the POPs laboratory, Department of Aquatic Sciences and Assessment, SLU (for details see Ahrens et al. (2015)). All data from the HPLC-MS/MS were evaluated using MassHunter Qualitative Analysis software (version 5, Agilent Technologies) and Microsoft Office 2013 Excel. The branched isomers (i.e. PFHxS, PFOS, FOSA) were quantified using the corresponding linear standard.

## 3.5 Determination of dry matter and organic matter (OM) content

For both, soil and plant samples, the dry matter content was determined. The fresh plant samples were weighed and then dried in the freeze-drier for seven days before the determination of the dry weight (dw). After weighing the fresh sample, the soil was dried in an oven (*ED115 E2*, Binder, Germany) at 105°C for 12 h before the next weighing. In addition, the soil samples were burned at 550°C in the muffle oven (Nabertherm, Germany) for 12 h to determine the OM content. The calculated ratios allowed for determination of contaminant concentration in the fresh samples after analysis.

## 3.6 Quality assurance and quality control

To avoid samples contamination during handling, all material and objects that could contain fluorinated compounds was avoided. Several blanks were used to determine background noise; a blank from the homogenizer vial, two blanks from the coffee mill, ten blanks for soil and plant samples and another four for the water samples. The blanks were used to determine the method detection limit (MDL)

**MDL** = mean blanks + (3* SD blanks)

with SD being the standard deviation (SD). For more information (blanks, duplicates and IS recovery) see appendix.

## 3.7 Data evaluation and statistical analysis

Initially, data analysis was performed using MassHunter Qualitative Analysis software (version 5, Agilent Technologies) to assess the interpretation of the peaks following an analysis with Microsoft Office 2013 Excel.

The BCFs were calculated as the contaminant concentration in the plant divided by the contaminant concentration in the soil or the groundwater at the specific site and month of the plant sampling.

$BCF = C_{plant}/C_{soil}$ and $BCF = C_{plant}/C_{groundwater}$

With $C_{plant}$ being the contaminant concentration in the plant [ng $kg^{-1}$ ww], $C_{soil}$ being the contaminant concentration in the soil [ng $kg^{-1}$ ww] and $C_{groundwater}$ being the contaminant concentration in the groundwater [ng $L^{-1}$].

# 4 Results

Overall, out of the 26 PFASs and 3 additional branched isomers (i.e. PFHxS, PFOS and FOSA), the long-chained PFCAs (i.e. PFTriDA, PFTeDA, PFHxDA and PFOcDA) and three precursors (EtFOSE, MeFOSAA and EtFOSAA) could not be detected in any matrices.

## 4.1 Groundwater

In the groundwater and surface water samples, 13 out of 26 PFASs have been detected (Figure 3). The three groundwater samples showed elevated levels of PFASs, with ∑PFAS concentrations ranging between 1,200 and 34,000 ng $L^{-1}$. Site 1, which is furthest away from the fire training site, had the lowest ∑PFAS concentration with 1,200 ng $L^{-1}$. Site 2 and Site 3 showed ∑PFAS levels of 31,000 and 34,000 ng $L^{-1}$, respectively. The dominant PFASs in the four samples were PFOS, linear (3-35%) and branched (3-36%), and PFHxS, linear (5-36%) and branched (2-7%). However, 6:2 FTSA had a high content at Sites 2 and 3 (0.8-12%) as well, which was reflected in the surface water sample (8%). Site 1 varied slightly in composition with PFCAs (48%) being equally represented like PFSAs (51%), whereas Site 2 and 3 had 10-20% PFCAs content. Site 1 is also the only site where PFDA and FOSA (linear and branched) could not be detected, while the concentrations were up to 1.3ng $L^{-1}$ (PFDA), 4.2 ng $L^{-1}$ (FOSA linear) and 3.8 ng $L^{-1}$ (FOSA branched) in the other three water samples (groundwater from Site 2 and 3 and surface water from Site 3). Site 1 had an equal proportion of linear and branched PFOS isomers (2.7 and 2.5%, respectively), as well as Site 2 (35 and 36%, respectively). On the other hand, Site 3 showed a different composition. The groundwater sample contained mainly branched PFOS (on average 29%) compared to linear PFOS (17%), whereas the surface water sample contained more linear PFOS (48%) compared to branched PFOS (16%). Site 3 contained the highest fraction of PFBS (10%), which is not reflected in the surface water sample. Sites 1 and 2 contained approx. 4% of PFBS. The highest concentration of all PFASs measured was 9,617 ng $L^{-1}$ for branched PFOS in the groundwater from Site 3.

The surface water sample, which was taken from a ditch near Site 3, showed a comparable PFASs composition like the groundwater in Sites 2 and 3; however, the ∑PFAS concentration was lower than the groundwater concentrations with 652 ng $L^{-1}$. Comparing the three main groups of PFASs (i.e. PFCAs, PFSAs, other PFASs) in groundwater and surface water, the surface water sample had a similar PFAS profile compared to Site 2 in groundwater for PFCAs (~10%), PFSAs (~80%) and other PFASs (FOSAs, FOSEs, FOSAAs, 6:2 FTSA) (~10%). The highest concentration measured in the surface water sample was 316 ng $L^{-1}$ for linear PFOS.

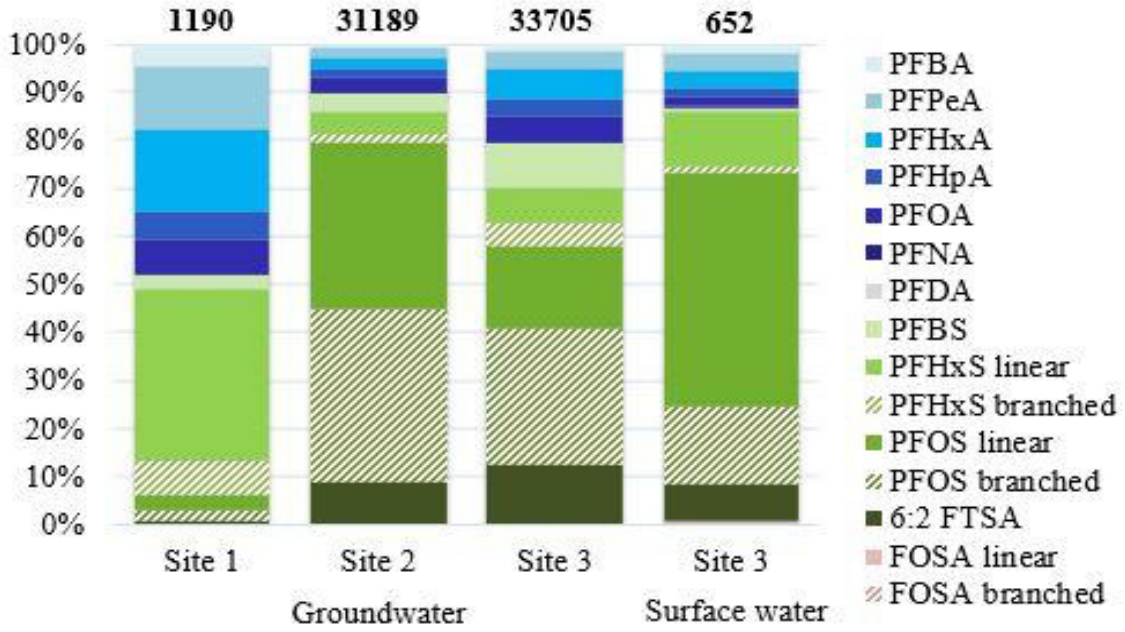


**Figure 3 Composition profiles of PFASs in water samples. ∑PFAS concentration [ng $L^{-1}$] indicated in bold numbers at the top of the bars.**

## 4.2 Soil

In the six soil samples, 17 out of 26 PFASs were detected (Figure 4). The six soil samples showed ∑PFAS concentrations between 16 ng $g^{-1}$ dw and 156 ng $g^{-1}$ dw. The highest concentrations were found at Site 3 (156 ng $g^{-1}$ dw and 97 ng $g^{-1}$ dw for March and June, respectively), followed by Site 2 (20 ng $g^{-1}$ dw and 35 ng $g^{-1}$ dw) and Site 1 (22 ng $g^{-1}$ dw and 16 ng $g^{-1}$ dw), which is furthest away from the training site. Except for Site 2, March concentrations exceeded June concentrations. MeFOSE (0.37 ng $g^{-1}$ dw) and FOSAA (0.11 ng $g^{-1}$ dw) were exclusively detected in the June sample from Site 3 and have not been detected in any other samples investigated in this study. However, the fraction was low (<0.4% for MeFOSA, <0.24% for MeFOSE and <0.08% for FOSAA based on the ∑PFAS concentration, respectively).

All samples were dominated by PFSAs (66-83% of the ∑PFASs), with the linear PFOS as the predominant compound (53-72% of the ∑PFASs), followed by branched PFOS (7-17%) and linear PFHxS (2-7%). The PFCAs varied between 6 and 32%, always being slightly higher in June in comparison to March. The short-chain PFCAs ($C_3$-$C_5$, ~5% of the ∑PFASs) prevailed over the long-chained PFCAs (>$C_5$, ~0.6%) in all samples. Although the fraction of PFBA and PFPeA declined from Site 1 (5.6 and

12% of the ∑PFASs, respectively) to Site 3 (2 and 5%, respectively), the PFBA and PFPeA concentrations increased from Site 1 (1.0 and 2.2 ng $g^{-1}$ dw) to Site 3 (2.0 and 5.8 ng $g^{-1}$ dw). The branched isomers of PFHxS, PFOS and FOSA were present in all samples; however, the proportion of linear isomers was exceeding the proportion of branched isomers up to tenfold. The linear PFHxS concentrations varied between 0.8-3.4 ng $g^{-1}$ dw, the linear PFOS and FOSA concentrations ranged from 8-96 and 0.3-1.4 ng $g^{-1}$ dw, respectively, whereas the branched PFHxS, PFOS and FOSA concentrations fluctuated between 0-0.2, 1.2-26 and 0.08-1.1 ng $g^{-1}$ dw. The concentrations of 6:2 FTSA ranged from 0.01 ng $g^{-1}$ dw in June (Site 1) to 16 ng $g^{-1}$ dw in March (Site 3). This pattern was also reflected in the other samples, where 6:2 FTSA concentrations in March were exceeding those of June. PFDA and PFUnDA were measured in concentrations below 0.1 ng $g^{-1}$ dw, having a fraction of ~0.5% in the total composition. The highest measured concentration in any soil sample was linear PFOS with a concentration of 97 ng $g^{-1}$ dw in the March sample from Site 3.

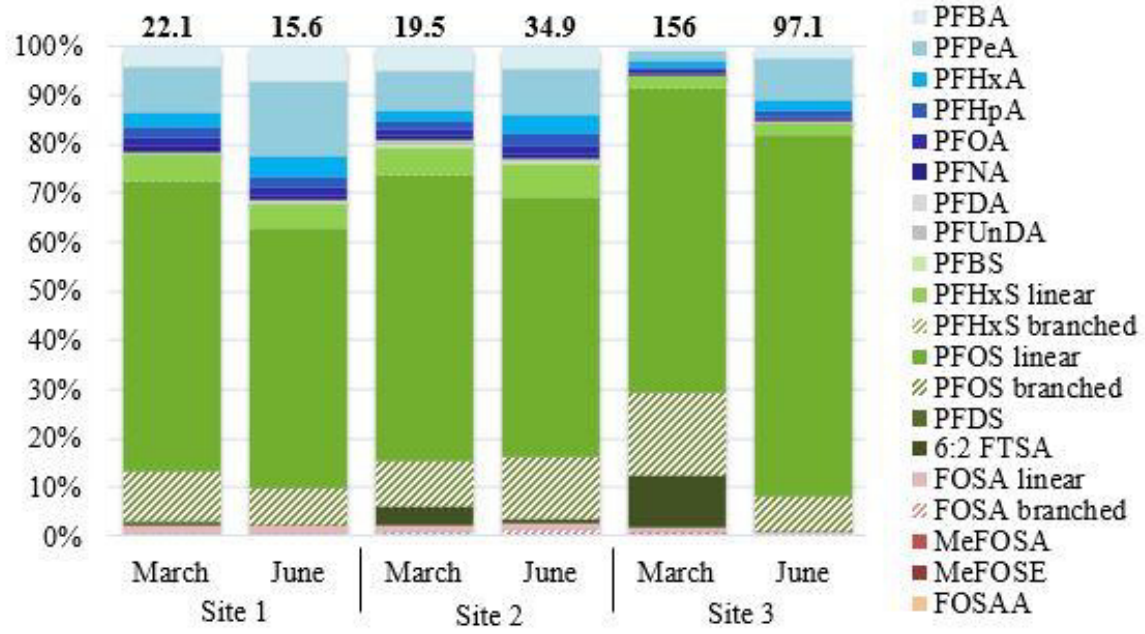


**Figure 4 Soil PFAS composition profiles. Bold numbers show measured ∑PFAS concentrations [ng $g^{-1}$ dw].**

## 4.3 Plants

### 4.3.1 Birch

In all silver birch samples, eleven out of the 26 PFASs were detected (Figure 5). The birch trees have been sampled for roots, cores (with and without bark), twigs (except for Site 3) and leaves. The leaves were the only tissue that was sampled twice, in March and June, with June concentrations being on average 27 times higher than March concentrations. The leaves collected in March had been half decomposed already and were excluded in the graph to provide better comparability with the concentrations found in the needles. The ∑PFAS concentrations ranged from 0.4 ng $g^{-1}$ dw (Site 1) in the core (with bark) to 327 ng $g^{-1}$ dw in the leaves (Site 2).

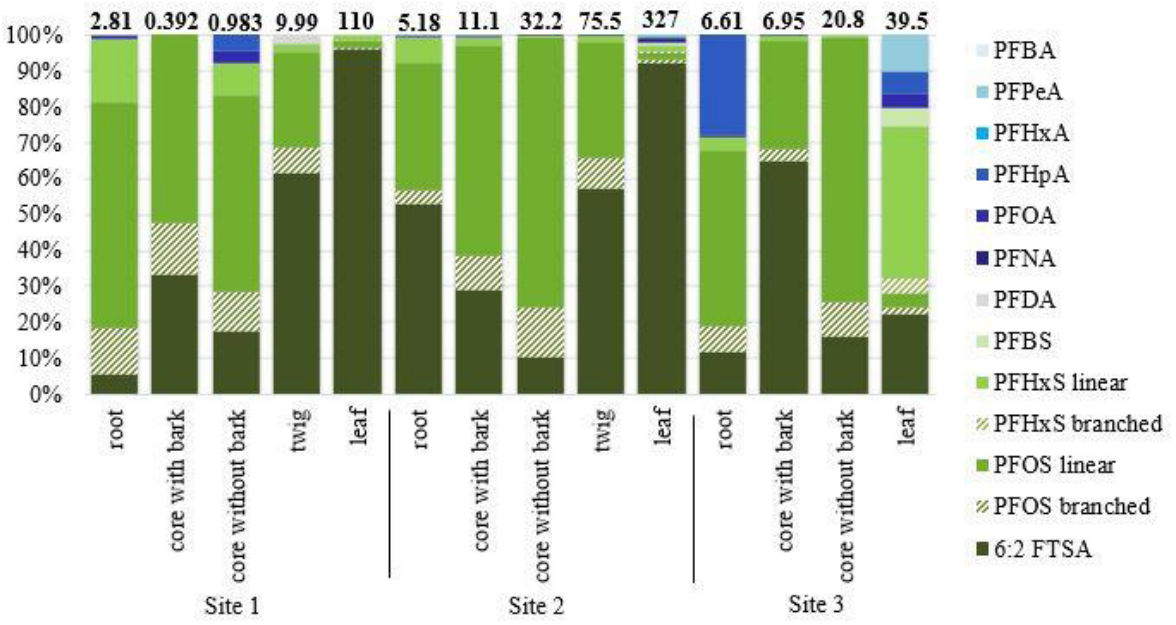


**Figure 5 Birch PFAS composition profiles. ∑PFAS concentrations [ng $g^{-1}$ dw] in bold at the top of bars.**

All samples were dominated by PFSAs (2-93%, on average 55%), mainly 6:2 FTSA (5-96%, on average 41%), PFOS (linear isomer (2-75%, on average 40%) and branched isomer (0.6-15%, on average 7.5%). From the three branched isomers, only branched PFOS was detected (in concentrations <6.3 ng $g^{-1}$ dw for twigs from Site 2 and a maximum fraction of 15% for the ∑PFASs in the core with bark from Site 1). Furthermore, PFOS was dominating (49-63%) in all roots and the root at Site 3 showed a high fraction of PFHpA (28%), which was not represented in the roots from the other two locations.

Only six PFASs were measured in the core samples with PFHpA and PFOA being the only PFCAs. However, PFHpA was solely detected in the core without bark from Site 1 (0.05 ng $g^{-1}$ dw). Linear PFOS showed the highest individual PFASs' concentration with 24 ng $g^{-1}$ dw in the core (without bark) at Site 2. All six core samples had the same pattern of about a three times higher ∑PFASs concentration in the central core piece (0.9-32 ng $g^{-1}$ dw) in comparison to the core with bark (0.4-11 ng $g^{-1}$ dw). The latter contained a higher 6:2 FTSA fraction (10-18% in the tree core without bark vs 29-65% in the tree core with bark), indicating a more recent uptake of 6:2 FTSA.

The $\sum PFAS_{twig}$ from Site 1 and 2 was 10 and 76 ng $g^{-1}$ dw, respectively. Despite the difference in concentrations, the compositions of these two samples were similar with approx. 60% 6:2 FTSA, 8% branched PFOS and at least 27% linear PFOS. Moreover, the two twig samples contained one PFCA each, either PFOA (0.26 ng $g^{-1}$ dw, Site 2) or PFDA (0.26 ng $g^{-1}$ dw, Site 1). Additionally, both samples had concentrations of linear PFHxS (0.2 and 1.5 ng $g^{-1}$ dw for Site 1 and Site 2) and branched PFOS (0.7 and 6.3 ng $g^{-1}$ dw), which are, together with linear PFOS, the only measured PFSAs. PFSAs made up 36 and 42%, respectively, of the ∑PFASs in Site 1 and 2 with linear PFOS as the dominant compound (27 and 32%, respectively).

Twelve different PFASs were detected in the leaves, which resulted in the most diverse composition profiles among all birch tissues. Moreover, the leaves showed the highest ∑PFAS concentrations of all birch tissues ranging from 40 ng $g^{-1}$ dw (Site 3) to 327 ng $g^{-1}$ dw (Site 2). Four different PFCAs were detected of which PFNA was only detected at Site 2 (1% of the ∑PFASs). While the composition profiles of Site 1 and 2 appeared similar, the leaves at Site 3 contained 10% PFPeA, a substance which had not been detected at Site 1 and comprised only 0.7% at Site 2. The leaves from Site 3 consisted of 20% PFCAs and 57% PFSAs. In contrast, 6:2 FTSA was dominant in the leaves at Site 1 and 2 with 92% of the ∑PFASs (with maximum concentration of 302 ng $g^{-1}$ dw at Site 2), while the composition of PFCAs (0% and 2%, respectively) and PFSAs (2 and 6%, respectively) was low. The three PFSAs detected, namely PFBS and both isomers of PFHxS and PFOS, were found in all leaves. Linear PFHxS constituted the highest fraction with 1-42% (on average 15%), followed by linear PFOS (2-4%, on average 2.5%). FOSA and its branched isomer were not detected in any of the samples. Primarily, the leaves from March contained lower levels of ∑PFAS than those sampled in June. Site 1 contained only 1.9 ng $g^{-1}$ dw, Site 2 had 16 ng $g^{-1}$ dw and 27 ng $g^{-1}$ dw were detected at Site 3. Accordingly, the values from March were deviating from those measured in June by a factor of 58 at Site 1, 20 at Site 2 and 1.5 at Site 3. Furthermore, Site 1 and 2 contained considerable amounts of PFBA (up to 0.33 ng $g^{-1}$ dw) in March, which was not detected in any of the June samples. The variety of PFAS detected was <6 and in comparison to the composition of the June leaves, the proportion of PFSAs was lower with 5% in March and 15% in June. According to the dw concentrations, the average accumulation potential of the different birch tissues (from low to high) was as follows: roots < core with bark < core without bark < twigs < leaves.

The birch sap was collected twice. However, as the flow is mainly occurring during spring time, the second collection originates from the same season. Two trees were sampled at Site 1. Ten different compounds were detected in the birch sap samples in total (Figure 6). They were comprised of five PFCAs, three PFSAs and isomers, 6:2 FTSA and FOSA. FOSA was solely detected in the June sample from Site 3 (0.42 ng $L^{-1}$ aka 0.1%). The total measured ∑PFAS concentrations were highest at Site 2 (974 and 2,717 ng $L^{-1}$ in March and June, respectively), followed by Site 3 (313 ng $L^{-1}$ and 337 ng $L^{-1}$) and Site 1 (24-71 ng $L^{-1}$).

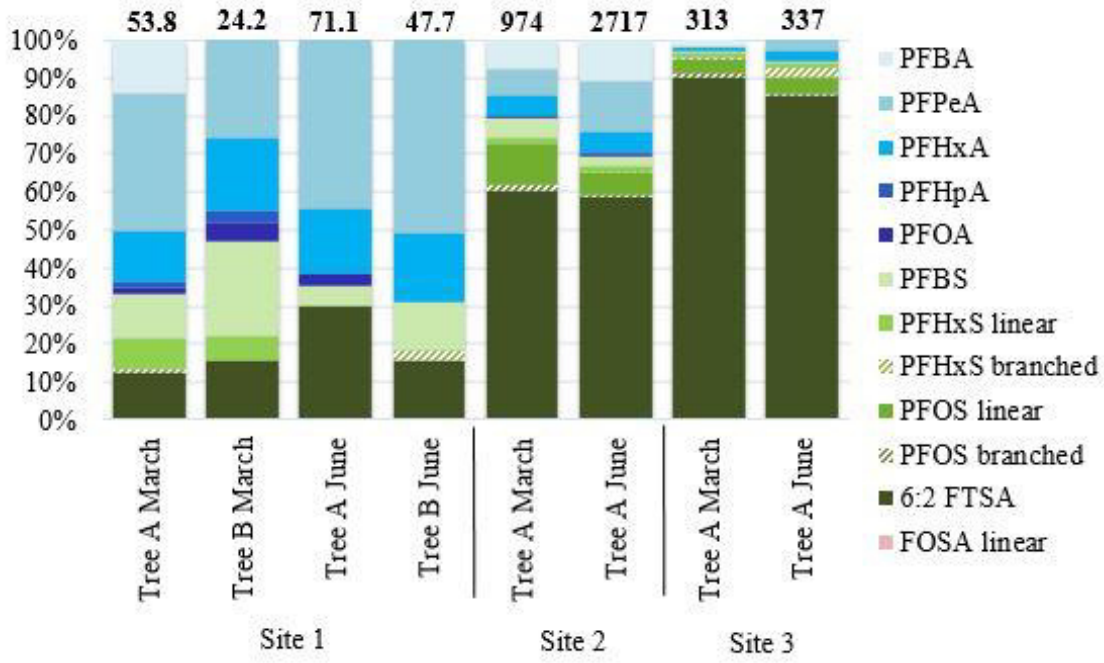


**Figure 6 Birch sap PFAS composition profiles with the ∑PFAS concentrations [ng $L^{-1}$] indicated at the top.**

The fraction of PFCAs was ranging from 53-69% at Site 1, whereas the fraction was less than 6% at Site 3 and below 31% at Site 2. PFHxA was the only PFCA measured in all samples, with concentrations ranging from 3.1-143 ng $L^{-1}$. While PFCA proportions were decreasing from Site 1 to 3, 6:2 FTSA showed the opposite pattern, with increasing fractions of 12% at Site 1 to a maximum of 90% at Site 3. Furthermore, the birch sap at Site 1 contained short-chain PFASs, while Site 2 and 3 contained long-chained PFASs. The group of PFSAs was fully represented, except for PFDS which was not detected. In contrast, PFBS was detected in all birch saps, ranging from 2.1 ng $L^{-1}$ (Site 3, March) to 75 ng $L^{-1}$ (Site 2, June). Both PFOS isomers were present in the sap from Site 2 and 3, with the linear isomer predominating over the branched isomers.

All samples at Site 1 were dominated by PFPeA (6.3-32 ng $L^{-1}$). There was a slight shift in the composition at Site 1 from March to June. In March, PFCAs were comprised of four to five different individual compounds, in contrast to only two to three individual compounds in June. However, PFPeA was the predominant PFCA, irrespective of the composition shift. Besides, PFBA (7.6 ng $L^{-1}$) and PFHpA (0.8 ng $L^{-1}$) occurred in the March, but not in the June samples from Site 1. Furthermore, Site 1 shows a high proportion of PFBS which was reduced from March to June in Tree A from 11.8 to 5% and 25 to 13% in Tree B. This reduction by ~50% was also visible for the PFBS fraction at Site 2 (5 to 3%, respectively), yet did not occur at Site 3, where the fraction of PFBS stayed constant at 0.7%. Linear PFHxS was exclusively detected in the March samples from Site 1 and did not occur in the June samples. Linear PFOS was not measured in any sample from Site 1 and branched PFOS was solely detected in the March sample from Tree A (0.6%).

Site 2 did not only have the highest ∑PFAS concentration in June, but also the highest concentration measured for an individual compound in all sap samples with 1594 ng $L^{-1}$ for 6:2 FTSA. The sap of Site 2 mainly comprised 6:2 FTSA (61 and 59% for March and June, respectively), followed by the linear PFOS isomer (10 and 5.6%), PFPeA (7 and 13%) and PFBA (8 and 11%). Both samples, from March and June, contained more than 70% long chained (≥ $C_8$) PFASs.

Site 3 showed a proportion of 90 and 85% of 6:2 FTSA for March and June, respectively. Linear PFOS was equally represented in March and June with 4%, followed by the linear PFHxS isomer with roughly 1% share. PFPeA and PFHxA were both comprising 3% of the June sample, however, PFPeA was not detected and PFHxA represented <1% in the March sample.

### 4.3.2 Spruce

The two spruces sampled were located at Site 2 and 3, all samples were taken in March (Figure 7). There were eleven out of 26 PFASs detected in the spruce tissues (i.e. 6:2 FTSA, seven PFCAs and three PFSAs). The FOSA isomers were not detected. From the PFCAs, PFBA (81 and 8 ng $g^{-1}$ dw), PFPeA (7.9 and 5.7 ng $g^{-1}$ dw) and PFHxA (19.2 and 0.7 ng $g^{-1}$ dw) were solely measured in the needles (values for Site 2 and Site 3, respectively), whereas PFNA (0.4 ng $g^{-1}$ dw) and PFDA (0.06 ng $g^{-1}$ dw) were exclusively measured in the roots from Site 2. PFOA is the most prevalent PFCA, occurring in the needles from Site 3 and all samples from Site 2 with concentrations ranging from 1-7.5 ng $g^{-1}$ dw.

There was just a single root sample, which belongs to Site 2 and mainly consisted of linear PFOS (61%), branched PFOS (17%) and 6:2 FTSA (12%). The root had the second highest concentration measured in all spruce tissues, 43 ng $g^{-1}$ dw of ∑PFASs, after the needles (222 ng $g^{-1}$ dw). Furthermore,

it was the only sample besides the needles were PFBS was detected. It constituted 0.2% in the roots and 0.6 and 0.4% in the needles from Site 2 and 3, respectively.

The spruce at Site 2 had higher concentrations in all sampled tissues than the spruce at Site 3. This trend was reflected in the birch sap, but not so much in the soil and groundwater values. Both sites, however, showed the highest ∑PFAS concentrations in the needles with 222 ng $g^{-1}$ dw for Site 2 and 33.3 ng $g^{-1}$ dw for Site 3.

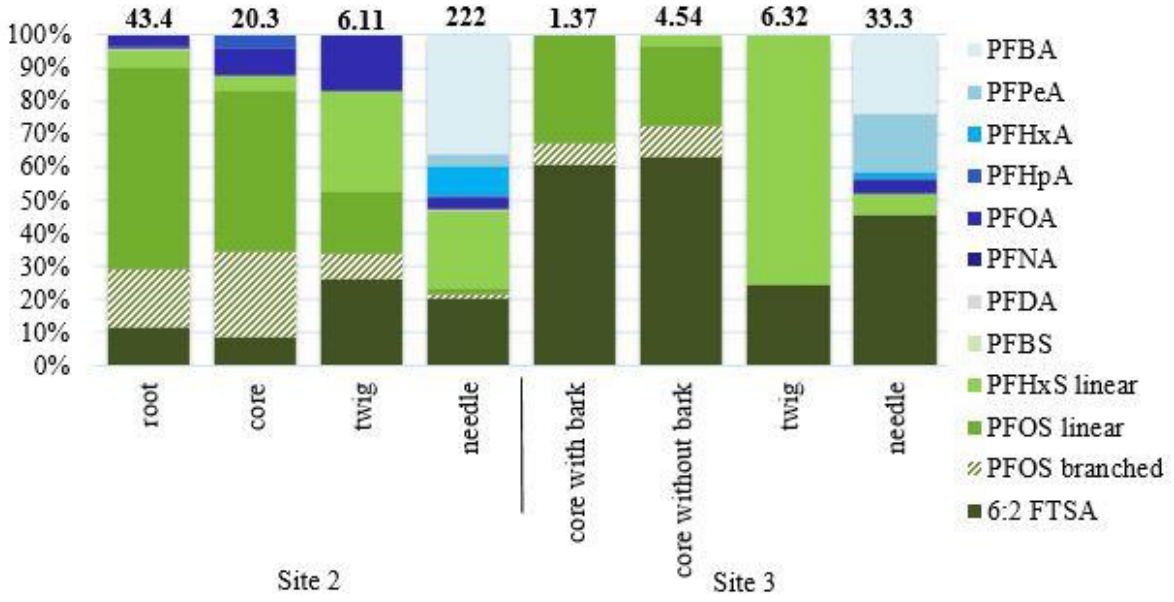


**Figure 7 Spruce PFAS composition profiles. The ∑PFAS concentrations [ng $g^{-1}$ dw] are indicated in bold at the top of each bar.**

The cores showed a similar trend as seen in the birch cores; the central core without bark had elevated PFASs concentrations in comparison to the core with bark. The core from Site 2 contained mainly linear (49%), then branched PFOS (26%), 6:2 FTSA (8%), PFOA (8%) and PFHpA (4%), while the cores from Site 3 were dominated by 6:2 FTSA (61 with and 63% without bark) and did not contain PFCAs. The core without bark from Site 3 contained linear PFHxS (4%), which was not detected in the sample with bark from the same tree.

Both twig samples contained around 6 ng $g^{-1}$ dw of ∑PFAS (6.1 and 6.3 ng $g^{-1}$ dw, for Site 2 and 3, respectively). In each of them high proportions of linear PFHxS (31 and 76% of the ∑PFAS) and 6:2 FTSA (26 and 24%) were detected, however, these are the only components detected in the twigs at Site

3, while Site 2 has three additional components: linear and branched PFOS (18 and 8%) and PFOA (17%). Despite the difference in composition, both twigs share a similarity; they had the highest PFHxS content detected at all sites.

The needles had the most diverse composition with 222 ng $g^{-1}$ dw at Site 2 and 33.3 ng $g^{-1}$ dw at Site 3 for the ∑PFASs as the highest concentrations measured in spruce tissues. The needles from Site 2 contained nine different substances, out of which PFBA (37%) was the predominant one, followed by linear PFHxS (23%) and 6:2 FTSA (20%). At Site 3, the dominant PFAS was 6:2 FTSA (46%), followed by PFBA (24%) and PFPeA (17%). Consequently, both needle samples contained a higher amount of short-chain PFASs than the other plant tissues.

### 4.3.3 Comparison of PFASs in twigs

Eight out of 26 substances have been detected in the twig tissues (i.e. four PFCAs, three PFSAs and 6:2 FTSA; Figure 8). Site 2 showed the highest concentrations (on average, 18 ng $g^{-1}$ dw), followed by Site 3 (on average, 8.7 ng $g^{-1}$ dw) and Site 1 (on average, 5.2 ng $g^{-1}$ dw).

Out of the PFCAs, PFHxA and PFHpA were exclusively measured at Site 3, with PFHxA being found in bird cherry (3%) and ground elder (15%) and PFHpA solely in the latter (3%). PFOA was detected at Site 2 in the twigs of birch (0.4%), spruce (17%) and bird cherry (2%). PFDA could solely be found in birch twigs (3%) at Site 1.

For the PFSAs, PFBS was detected at Site 2 and Site 3 only. Bird cherry leaves contained PFBS at both sites (1% and 0.3%, respectively), whereas it was solely measured in ground elder at Site 3 (12%). Furthermore, the bird cherry at Site 2 exclusively showed branched PFHxS (0.06 ng $g^{-1}$ dw) concentrations. 6:2 FTSA had the highest average share of any compound, ranging from 24% (spruce, Site 3) to 100% (mountain ash, Site 1), and was the only compound detected in all twig samples. The birch twigs, sampled at Site 1 and Site 2, had a similar composition, yet varied in concentration by a factor of 7.5 in favor of Site 2. The birch twigs from Site 2 had the highest ∑PFAS concentration of all twigs with 76 ng $g^{-1}$ dw. The birch at Site 1 contained PFDA (3%) that was not detected at Site 2, nor in any other sample. mountain ash had the lowest twig concentrations, with a high composition of 6:2 FTSA (100%, 88% and 90% at Site 1, Site 2, and Site 3, respectively), followed by ground elder (78 and 47%, Site 2 and Site 3 respectively) and bird cherry (36 and 79%, Site 2 and Site 3 respectively). The composition of ground elder twigs at Site 3 was the most diverse with six individual PFASs measured. Interestingly, it contained only branched but no linear PFOS (14% of ∑PFASs), and only linear PFHxS (8% of ∑PFASs) but no branched PFHxS. Both spruce twigs had a high proportion of 6:2 FTSA (26% and 24% at Site 2 and Site 3, respectively) and linear PFHxS (31% and 76%), being the only compounds detected

in spruce twigs at Site 3. To summarize, the predominant PFASs in twigs were 6:2 FTSA, linear PFHxS and PFOS.

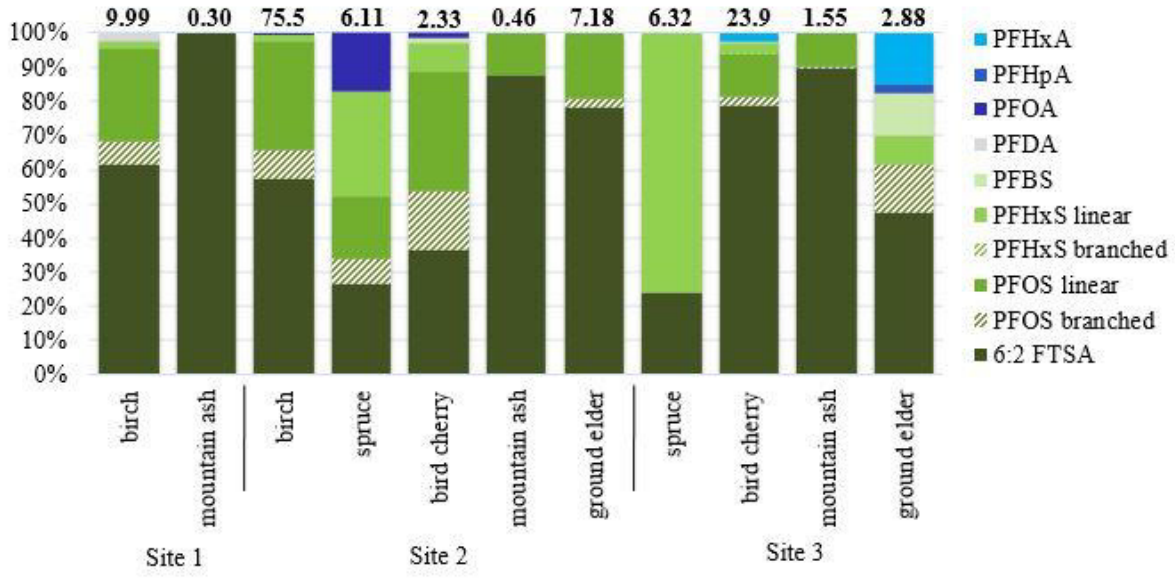


**Figure 8 Twigs' and stems' PFAS composition profiles. ∑PFAS concentrations [ng $g^{-1}$ dw] are given in bold at the top of each bar. The species are sorted in the following order: trees, bushes, ground cover species.**

### 4.3.4 Comparison of PFASs in leaves and needles

PFAS in leaves from mountain ash, ground elder, long beechfern, bird cherry, and wild strawberry were compared to needle concentration from spruces. A total of ten different PFASs were detected in the foliage with diverse composition profiles (Figure 9). The ∑PFAS concentrations were the highest measured in tissues and varied between 5.48 ng $g^{-1}$ dw (mountain ash, Site 2) and 327 ng $g^{-1}$ dw (birch, Site 2) with those from Site 2 (on average, 110 ng $g^{-1}$ dw) exceeding those at Site 1 (on average, 42 ng $g^{-1}$ dw) and 3 (on average, 28 ng $g^{-1}$ dw).

Six PFCAs were detected in the foliage samples with PFNA solely being measured in birch at Site 2 (1.1%). PFPeA and PFHpA were detected in eleven and ten out of fourteen foliage samples and constituted the most prevalent PFCAs. Their concentrations ranged from 1.1-28 ng $g^{-1}$ dw for PFPeA and 0.08-1.7 ng $g^{-1}$ dw for PFHpA, respectively. PFPeA is particularly dominant in mountain ash (88%, 63% and 34% from Site 1, Site 2 and Site 3), fern (79%; Site 1) and strawberry (52%, Site 2). PFBA had

highest shares at Site 2 in bird cherry (38%) and spruce (37%), followed by spruce at Site 3 (24%) and fern (14%) at Site 1. From all PFCAs represented, the shorter chained ones were more prevalent.

The PFSAs comprised three compounds, including PFBS, PFHxS with both isomers and PFOS with both isomers. PFDS was not represented in any twig sample. PFBS was measured in concentrations of 0.05 ng $g^{-1}$ dw (birch, Site 1) to 1.3 ng $g^{-1}$ dw (spruce, Site 2), however, its fraction was up to 15% in some leaves, like mountain ash (Site 2) and ground elder (Site 3). Linear PFHxS was detected in every sample except for ground elder at Site 1. It constituted (on average 6.3%), together with branched PFOS (on average 1.3%), the highest proportion of the PFSAs.

While birch and spruce foliage had by far the highest concentrations, they varied in composition across the three sites. The leaves of the birches at Site 1 and 2 mainly consisted of 6:2 FTSA (94% and 89%) and the profiles look alike. However, the two spruce profiles (20% and 46%) and the birch at Site 3 (22%) have rather low fractions of 6:2 FTSA and are dominated by short-chain PFCAs like PFBA (37 and 24% for spruce at Site 2 and 3, n. d. in birch at Site 3), PFPeA (4% and 17% for spruce at Site 2 and 3, 10% for birch at Site 3) and PFHxA (0.7% and 4% in spruce, n.d. in birch, respectively). ∑PFAS concentrations in birch leaves at Site 2 and 3 were 1.5 and 1.2 times higher than in spruce needles at Site 2 and 3.

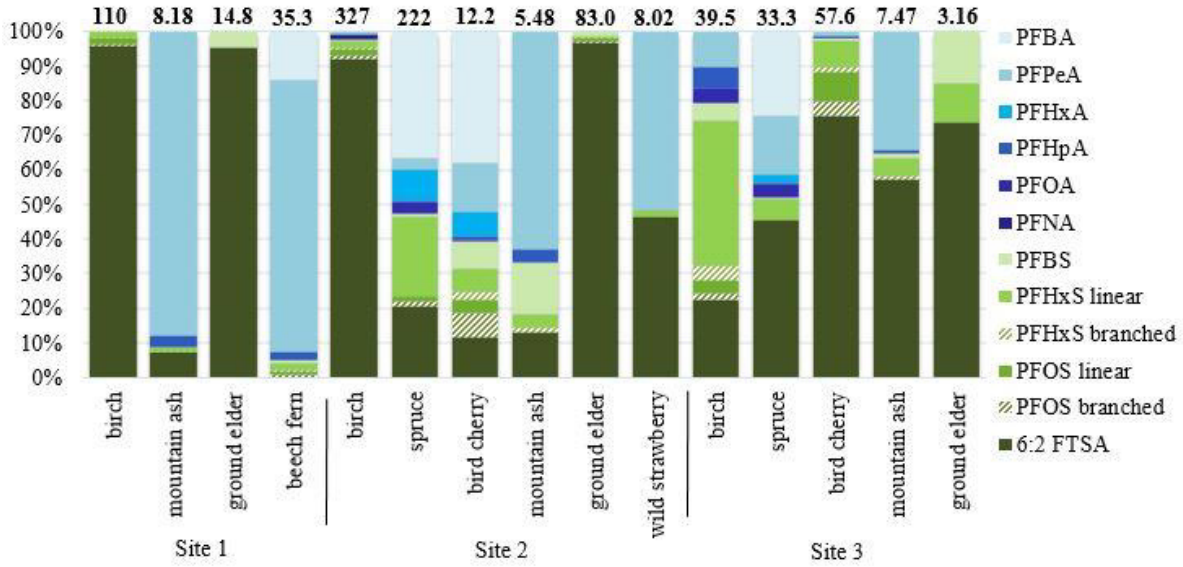


**Figure 9 Leave and needle PFAS composition profiles. ∑PFAS concentrations [ng $g^{-1}$ dw] are given in bold at the top of each bar. For the birches, only the values from June are included.**

When considering the different growth periods of the sampled species, it should be taken into account that birch, bird cherry and mountain ash are deciduous trees and shrubs that shed their leaves every autumn. Spruce is retaining its needles for 3-7 years and the ground cover species like ground elder, long beechfern and wild strawberry are annual plants that only grow over one season. However, the ∑PFAS in the bush species (on average 18 ng $g^{-1}$ dw) were generally 7-19 times lower than those in the birches. Furthermore, bird cherry had only been sampled at Site 2 and 3 but the concentrations exceeded those of mountain ash at both sites by a factor of approx. 2 and 8, indicating great differences within the group of bushes. High PFAS concentrations were found in long beechfern (Site 1; 35.3 ng $g^{-1}$ dw) and ground elder (Site 2; 83 ng $g^{-1}$ dw) leaves.

## 4.4 Total tree burden

The total tree burden is approximated with biomass proportions determined by Johansson, T. (2007) for the birches and Minerbi and Cescatti (2015) for the spruce, assuming a height of 15 meters and a total biomass of 900 kg per tree. The value for total biomass in kg is derived from the spruce (wood density of 470 kg/m³) but has been applied to both species for better comparability of accumulation potential (for details see appendix). The total tree burden was calculated as follows:

$\sum PFASs_{\text{tree tissue}}$ ($\mu$g) = $C_{\text{Average PFASs in tissue}}$ ($\mu$g $kg^{-1}$ ww)* Tissue fraction of total tree biomass (%) * tree biomass (kg)

Comparing all sampled trees, there is clear evidence that the birches are accumulating higher amounts of PFASs than the spruces (Figure 10). The birch at Site 2 had outstandingly high values of up to 23.6 mg per tree, followed by Site 3 (8.9 mg) and Site 1 (3.3 mg). The $\sum PFAS_{\text{spruce}}$ appeared to be highest at Site 2 with 17 mg, followed by Site 3 with 2.5 mg, reflecting the same pattern that was observed for the birches. Both tree species showed the same trend regarding the distribution within the tree. The highest amount of PFASs was allocated in the trunk (on average, 6.2 mg), followed by the foliage (on average, 2.6 mg) and twigs (on average, 1.7 mg). The roots contained an average of 1.1 mg. Birch leaves and spruce needles contained comparable amounts of ∑PFAS, however, the birch leaves at Site 2 contained 97 $\mu$g $kg^{-1}$ ww compared to spruce needles at Site 2 (94 $\mu$g $kg^{-1}$ ww), while the spruce needles contained 14 $\mu$g $kg^{-1}$ ww at Site 3.

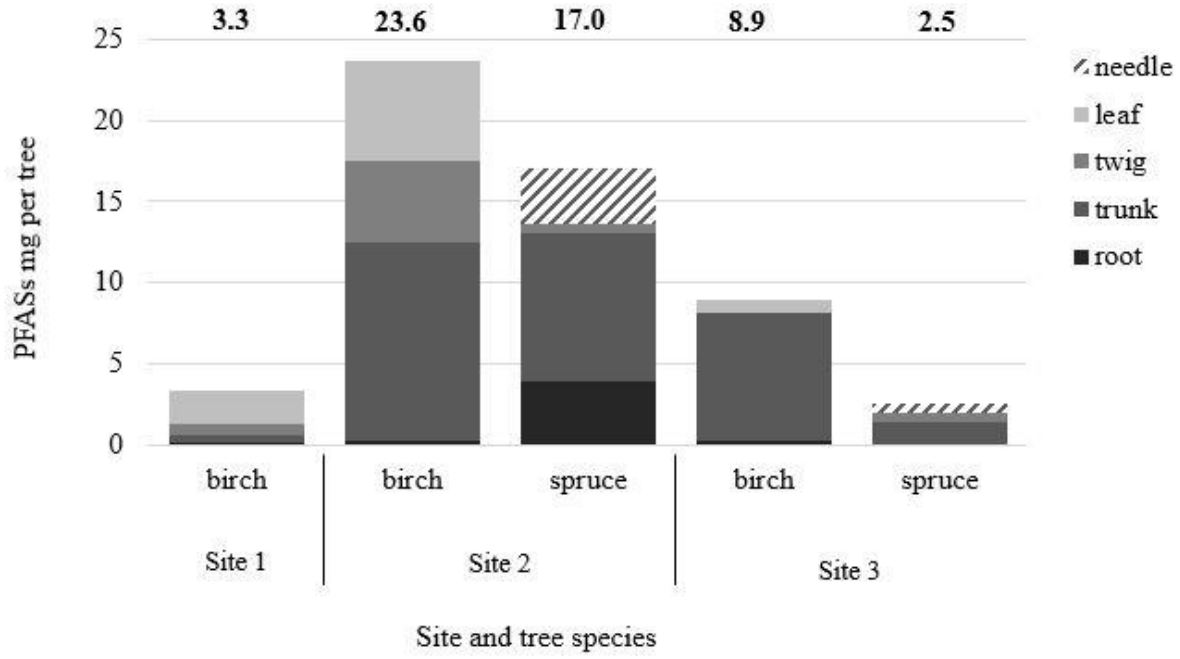


**Figure 10 Absolut PFASs concentration and distribution per tree, assuming a total biomass of 900 kg per tree. The ∑PFASs [mg] is given in bold at the top of the bars. Spruce was not sampled at Site 1.**

## 4.5 Bioconcentration Factors

The BCF is a ratio that can only be calculated when concentrations are available in the biota (plant) and in the reference material (groundwater or soil). The BCFs have been calculated to assess the plant's ability to accumulate contaminants and remediate the soil or groundwater. The higher the BCF, the more was accumulated by the plant. For all plant samples, a BCF of plant/soil has been calculated, as the roots are in direct contact with the soil and soil water and can take up (nutrients and) contaminants. For the trees, the BCFs have also been calculated for the groundwater, as the roots are deep enough to access the groundwater directly (rooting depth of birch up to 2.7 m reported by Laitakari, 1935). BCFs were calculated for seven PFCAs, three PFSAs and 6:2 FTSA. The three berry samples (strawberries and bird cherry berries from Site 2 and 3) were not part of the BCF calculations, as the DM content was not known and the BCF could therefore not be calculated. Due to low sample size and high SDs of the values for BCFs the results have to be interpreted with care.

The $BCFs_{plant/soil}$ were derived from all ratios that were calculated to be >0, comprising all birch sap samples and various tissue samples from the three sites. The BCFs for birch were ranging from 0.01 (i.e. for PFBA in leaves from Site 3 sampled in March) to 35 (for PFNA in birch leaves from Site 2, sampled in June) for the PFCAs. While six to 15 BCFs could be calculated per compound for the shorter chained PFCAs ($C_3$-$C_7$), there is a maximum of two BCFs per longer chained ($C_8$ and $C_9$) compound. PFPeA had the lowest BCFs in birch (median 0.09) whereas the highest BCFs were calculated for PFNA (median 18) and PFHpA (median 2.6). There was no clear correlation between chain length and BCF for the PFCAs; however, the BCFs were declining with increasing chain length for the PFSAs (from median 0.52 for PFBS to median 0.19 for PFHxS and median 0.11 for PFOS). Accordingly, the highest BCF for PFSAs was calculated for PFBS (13, in birch leaves from Site 3 picked in June). Also, there was a higher presence of PFSAs with 11 up to 24 BCFs found per compound. 6:2 FTSA yielded the most and highest BCFs with BCFs for 28 different tissue samples in total and a maximum of 13,700 in birch leaves (Site 1, June) whilst the median $BCF_{6:2\ FTSA}$ was 3.4. Birch sap and freshly picked leaves (June) from all sites showed usually BCFs for 7-10 different compounds and therefore, were the media with the highest concentration potential regarding quality and quantity.

The BCFs for PFCAs in spruce ranged from 0.2 for PFHpA (in needles from Site 2) to 98 for PFBA (needles, Site 2). PFOA accumulated in all tissues from Site 2 (BCF 9-41) and in the needles from Site 3 (BCF 1.5). Furthermore, the needles accumulated all PFCAs $C_3$-$C_7$ with an average BCF of 21. In contrast, the PFCAs $C_8$-$C_9$ were exclusively concentrated in the roots from Site 2 (BCF 2 and 5 for PFNA and PFDA, respectively). No correlation between BCF and perfluorocarbon chain length was observed. The PFSAs were ranging from 0.01 for linear PFOS (in core with bark from Site 3) to 56 for linear PFHxS (in needles from Site 2). They were present in all tissues, except for branched PFHxS for which BCFs could not be detected. Linear PFHxS and PFBS showed the most and highest BCFs for spruce tissues. Besides, the needles and the roots accumulated the greatest variety of compounds with 8-10 substances per tissue sample. The BCFs for 6:2 FTSA were calculated for all tissues at both sites and were ranging from 0.1 (core with bark, Site 3) to 68 (needles, Site 2). In contrast to Site 2, where all tissues showed accumulation of 6:2 FTSA, Site 3 did not accumulate 6:2 FTSA in any tissue.

Out of all PFCAs, mountain ash had only BCFs for PFPeA and PFHpA in the leaves at all three sites. The highest accumulation was found at Site 1 leaves for both substances, with a BCF of 2,000 for PFPeA and 98 for PFHpA, whereas the lowest concentrations were found at Site 3 with 0.6 and 0.2, respectively. The median $BCF_{PFPeA}$ was 3, while being 0.7 for PFHpA, indicating a decreasing accumulation with increasing chain length. The PFSAs enabled calculation of BCFs for all substances. The highest BCF was observed for PFHxS (39) in leaves from Site 1 while the lowest was detected for PFOS (0.01) in the stems of Site 2. Accordingly, the BCFs were decreasing with increasing chain length, with a median of 3.4 for PFBS to median 0.3 for PFHxS and median 0.01 for PFOS. Mountain ash accumulated (BCF

>1) 6:2 FTSA at both sites and in all tissues. Accordingly, the BCFs were ranging from 5 (stems, Site 2) to 223 (leaves, Site 1).

Five PFCAs were concentrated in bird cherry, with the leaves from Site 2 having BCFs for all of the PFCAs found. The highest BCF was found for PFHxA (1.9) in the leaves from Site 2 while the lowest BCF was detected in the leaves from Site 3 for PFBA (0.2). The median BCFs for PFCAs were decreasing from PFHxA (1.33) to PFOA (0.8). All PFSAs had BCFs in stems and leaves of bird cherry, except for the branched PFHxS which was not detected. The highest BCF was found for PFBS (6.7, leaves from Site 2) while the lowest was detected for PFOS (0.06) in the same sample. The BCFs were decreasing with chain length from 2.5 (median) for PFBS to 0.8 (median) for PFHxS and 0.11 (median) for PFOS. While the leaves accumulated 8-10 substances each, the stems accumulated only 6 substances. 6:2 FTSA accumulated in all samples with BCFs ranging from 12 (stem, Site 2) to 609 (leaves, Site 3).

The ground cover species (ground elder, wild strawberry, long beechfern), except for beechfern, hardly accumulated PFCAs. The long beechfern accumulated four PFCAs in total with BCFs ranging from 4.7 of PFBA (leaves) to 4050 for PFPeA (leaves), while the highest BCF in ground elder was calculated for PFHxA (0.3, stems, Site 3) and PFPeA (3) for strawberry leaves. PFSAs were more prevalent with BCFs ranging from 0.2 for PFHxS (strawberry leaves) to 906 for PFOS (fern roots). The BCFs were decreasing with increasing perfluorinated chain length in ground elder, however, this trend was not observed for the fern BCFs. 6:2 FTSA highly accumulated in strawberry leaves (BCF = 32) and even more in ground elder (3983, leaves at Site 1) in contrast to the fern samples, were it was not detected.

### 4.5.1 Birch groundwater BCFs

The birch/groundwater ratios were calculated using all individual tissue concentrations of birch in ng $kg^{-1}$ ww (except the March values for leaves) and the corresponding groundwater concentrations at the same site in ng $L^{-1}$. For better visualization, the BCFs were divided into the groups of PFCAs (Figure 11) and PFSAs (Figure 12).

The PFCAs varied in BCF from 0.01 for PFOA ($C_7$) in the birch core (with bark) at Site 3 to 19 for PFNA ($C_8$) leaves sampled in June at Site 2. No BCF was found for PFDA, whereas the BCF was 1 (PFHxA) to 9 (PFOA) for the other PFASs. The SD ranged from 0.18 (PFBA, n=2) to 13 (PFNA, n=2). According to the formation of box plots in the graph, PFPeA and PFNA were accumulated with a BCF >1. There was no clear trend noticeable that BCFs decrease with increasing perfluorocarbon chain length.

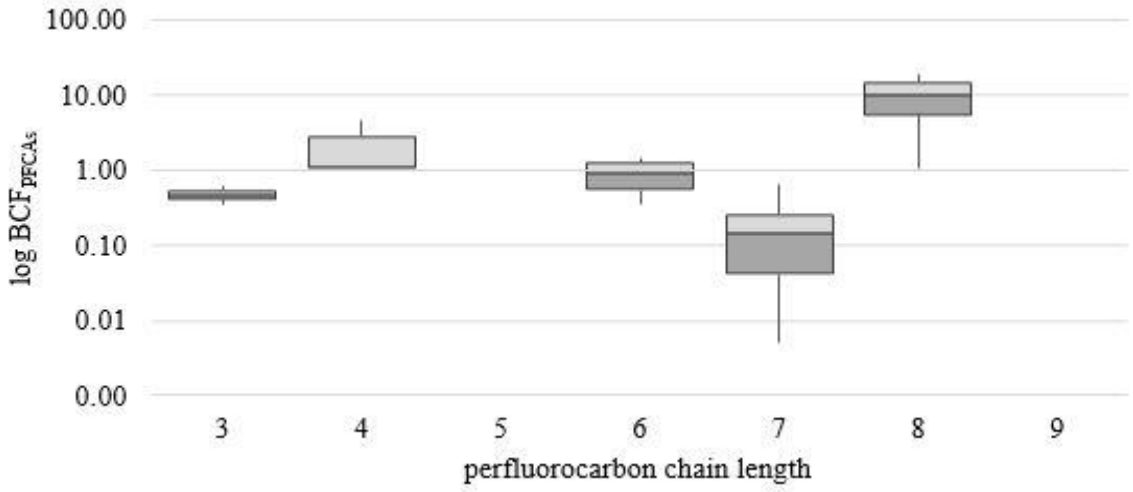


**Figure 11 Box plot of birch/groundwater BCFs (median) for PFCAs including all birch tissues and sap.**

For PFSAs, PFBS (n=3), PFHxS (n=18) and PFOS (n=20) were represented, however, PFBS never was accumulated with a BCF >1. The BCFs ranged from 0.01 for linear PFHxS in birch leaves (from March, Site 3) to 50 for linear PFOS in birch roots (Site 1). Accordingly, the SD varies from 0.3 to 750.

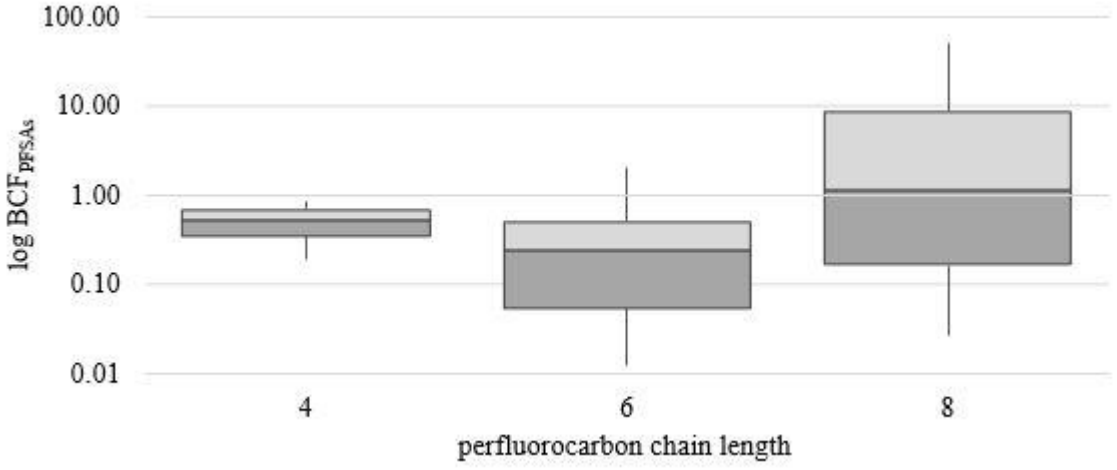


**Figure 12 Box plot of birch/groundwater BCFs (median) for PFSAs in roots, cores, sap, twigs and leaves.**

There were five different tissues included in the calculation of the BCF for birches, namely roots, core with and without bark, twigs and leaves, as well as the birch sap (Figure 13). The tissue concentrations are in ng $kg^{-1}$ ww, the sap concentration was in ng $L^{-1}$ and the ratio refers to the groundwater concentration (ng $L^{-1}$) as reference medium. For 6:2 FTSA, twenty BCFs were calculated for the birch/groundwater ratio. The ratios varied from 0.18 in birch roots (Site 3) to 3351 in birch leaves (June, Site 1). For the PFCAs, no clear trend is visible. PFHpA ($C_7$) is represented in most tissues, however, leaves exclusively accumulated PFHpA (BCF >1), while all other tissues have BCFs < 1 for this compound. From the five types of tissue and the sap, the leaves most often indicated accumulation potential with a BCF of 1.8 each for PFHpA and PFOA and a BCF close to 1 for PFPeA (0.7). Furthermore, the leaves contained the second highest quantity of PFCAs with three measured substances. While the sap even contained five different PFCAs, it never managed to accumulate them sufficiently (BCF always <1). The highest BCF was detected for PFDA in twigs (12.6).

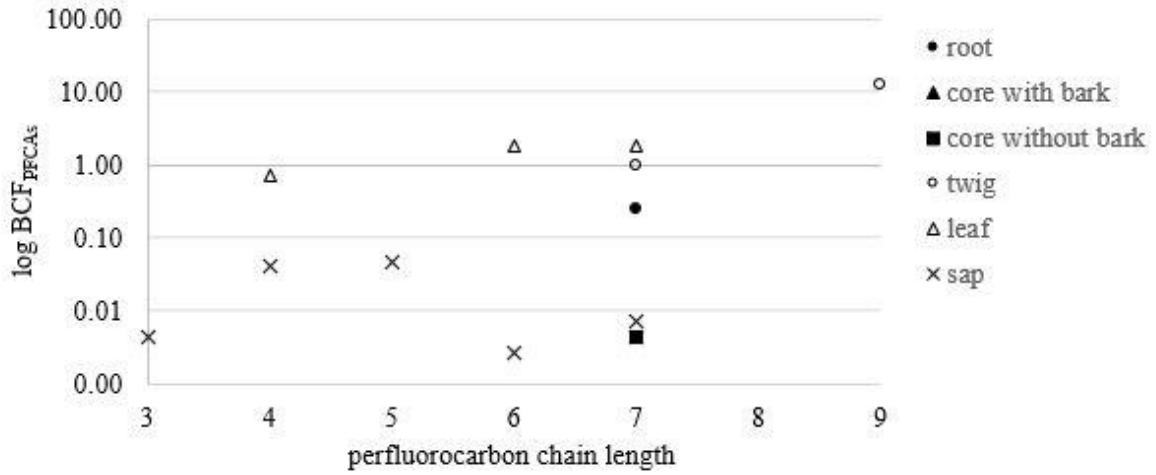


**Figure 13 BCFs for birch/groundwater (median) according to plant tissues and sap in silver birch shown for PFCAs.**

The PFSAs were better represented than the PFCAs, with six values for PFHxS, five values for PFOS and two for PFBS (Figure 14). The BCFs for PFBS were 0.5 in sap and 12 in the leaves, which is the highest BCF calculated for PFSAs in individual birch tissues. The leaves had BCFs for all three compounds and decreased with increasing perfluorocarbon chain length from 12 for PFBS, 6 for PFHxS and 0.64 for PFOS. The sap showed the same pattern with BCFs decreasing from 0.5 to 0.005 to 0.0003 for PFBS, PFHxS and PFOS, respectively. Accordingly, the sap had a low bioaccumulation potential for any PFSAs, in contrast to the twigs, which concentrated PFHxA (1.7) and PFOS (3.5). Roots, cores with bark and cores without bark had BCFs <0.9, showing a low bioaccumulation potential.

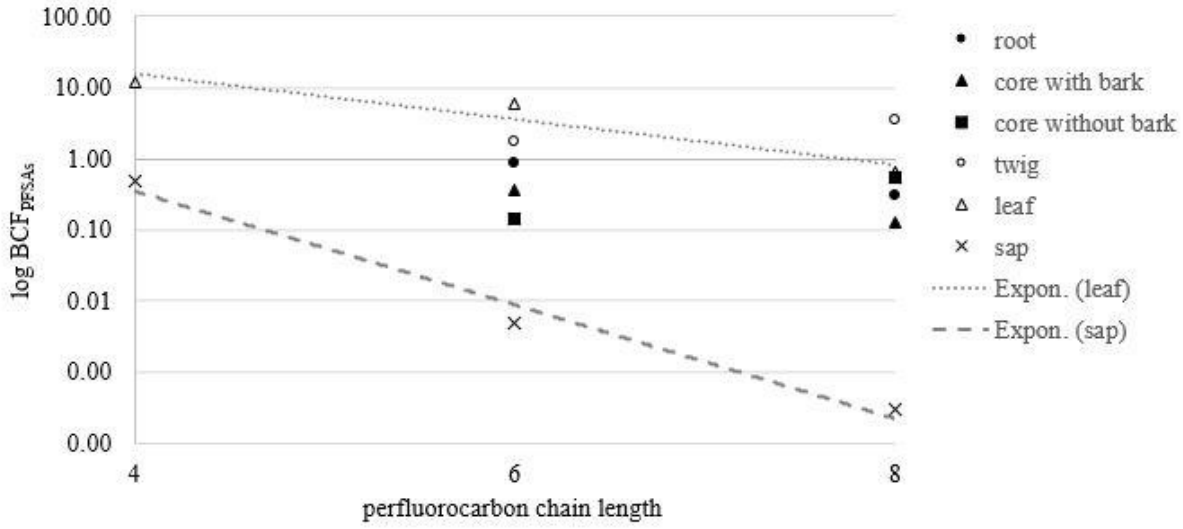


**Figure 14 BCFs for birch/groundwater (median) according to plant tissues and sap in silver birch for PFSAs. Trend lines have been added if applicable.**

6:2 FTSA achieved the highest accumulations. It was concentrated in all tissues, including sap, between 2.7 and 2300 times. The order of accumulation potential is accordingly: leaves (2300) > twigs (1000) > core without bark (3.8) > core with bark (3.3) > root (2.9) > sap (2.7).

# 5 Discussion

## 5.1 Contamination of soil and groundwater at Arlanda airport

Groundwater and soil concentrations confirmed high contamination at the fire training facility. Both media show an increase in contamination from Site 1 to Site 3 by a factor of 7.5 for soil and >28 for groundwater, which can be explained by the increasing proximity to the training site and the associated lack of dilution. The low concentration measured in the surface water (650 ng $L^{-1}$ for ∑PFASs) in comparison to the groundwater (1,200-34,000 ng $L^{-1}$ for ∑PFASs) indicates that recent contamination is rather low. This finding is confirmed by Ahrens et al. (2015) who measured a ∑PFAS concentration of ~4000 ng $L^{-1}$ in an artificial ditch downstream of the fire training site in 2011. This value is 6 times higher than the surface water concentration in this study (2016) but still lower than the groundwater concentrations (except for groundwater at Site 1). However, the runoff collection system for the fire training site was installed in 1997 and the usage of PFASs-free AFFFs since 2011 can explain the decreased recontamination. Despite varying concentrations in the surface water of the two studies, the composition profiles are similar. Ahrens et al. (2015) recorded a composition of 59% PFOS, 24% PFHxS, 7% PFHxA and 5% PFOA, in comparison to 48% PFOS, 11% PFHxS, 4% PFHxA and 2% PFOA in the present study. Furthermore, the PFOS/PFOA ratio was 6.5 ± 4 in surface water in Ahrens et al. (2015), 23.6 for the surface water from this study and 8.2 ± 7 for the groundwater in this study. Due to a higher water solubility of PFOA, the distribution is usually the other way around, leading to a ratio <1, and indicates, in this case, a local source of PFOS originating from the use of AFFFs (Awad et al., 2011). Site 1, which is furthest away from the fire training site, has a PFOS/PFOA ratio of 0.4 in groundwater as the PFOA concentration (86.4 ng $L^{-1}$) was exceeding that of PFOS (31.6 ng $L^{-1}$). This could imply that this site has no recent influence from the fire training site any longer. Another indicator of decreasing recent contamination are the tree cores, which had higher values in the central (older) part of the core (without bark) than in the outer, younger part of the core (with bark). It signals a decreased PFASs uptake in recent years which can most probably be attributed to dilution and/or dispersion of PFASs in soil and groundwater.

## 5.2 Distribution of PFASs in plant tissues

PFASs were detected in all plant species, however, the PFAS distribution was highly dependent on the tissue with decreasing concentrations (based on ng $g^{-1}$ ww) for "shoots to roots": leaves > twigs/stems > trunk > roots. This order has proven applicable to all samples and species. Hence, PFASs tend to accumulate in the vegetative parts rather than in the storage organs. This has been observed previously by Stahl et al. (2009) when investigating the uptake of PFOA and PFOS by spring wheat, oats, potatoes,

maize, and perennial ryegrass using spiked soil under controlled indoor conditions. Lechner and Knapp (2011) came to the same conclusion when planting carrots, cucumbers and potatoes in soil that previously had been spiked with PFOA and PFOS through the addition of contaminated sewage sludge. They recorded that >80% of the accumulated PFASs had been concentrated in the vegetative compartments of the plants. The higher accumulation of PFASs in the foliage was explained by Stahl et al. (2013) with the hypothesis that the root uptake and translocation of PFASs to the leaves occurs with the water transport within the plant. When the water reaches the leaves, it will eventually be transpired and thus, leads to concentration of the PFASs in the leaves.

## 5.3 Total tree burden and bioconcentration of individual PFASs

The total tree burden was calculated for birch and spruce and indicated highest amounts of PFASs in the trunk, followed by twigs and leaves, which is due to the trunk (67% for birch and 53% for spruce) and twigs (14% and 17%) constituting a greater proportion of the total biomass than the leaves/needles (7% and 4%, respectively). While birches accumulated 3.3-23.6 mg PFASs/tree, spruce yielded 2.5-17 mg PFAS/tree. The highest values were recorded at Site 2 and resemble the trend observed for all plant samples of highest concentrations at Site 2. Trees were not extensively studied for signs of intoxication, but appeared to be healthy and in good condition, indicating that the levels of PFASs they were exposed to had not reached harmful values yet (Stahl et al. 2009). Therefore, it was not possible to determine a threshold, at which point PFAS contaminated soil and groundwater become harmful for the local vegetation. Furthermore, the concentrations in the trees increased with increasing soil and groundwater values, suggesting that the full uptake potential is even higher with sufficient amounts of PFASs in the nourishing media and had not been reached. This observation is in accordance with Stahl et al. (2009), Zhao et al. (2014) and Lechner and Knapp (2011) who reported increasing accumulation with increasing amounts of PFASs. In this study, birch was accumulating PFASs mainly in the above-ground biomass (96-99%), whereas spruce concentrated a high amount of PFASs in the roots (23%). The amount of PFASs in the spruce root was 7 times higher than the highest birch root concentration, which confines its suitability for remediation (as the roots are the most complicated to harvest and will most likely not be removed). Both species accumulated >77% of the PFASs in the vegetative compartments, which is in accordance with Lechner and Knapp (2011) who reported values >80%.

All plant species sampled showed uptake of PFASs. However, the uptake was highly species and substance dependent, as there was a high deviation observed among species and substrates. This has been observed previously in corresponding literature by Stahl et al. (2009 and 2013) and Lechner and Knapp (2011). As a result, the uptake rates could not even be grouped by categories such as non-deciduous, deciduous and annual plants but have to be looked at separately for each species. The highest BCF was calculated for birch leaves (14,700, Site 1) for 6:2 FTSA. This example is extreme, however, it

reflects the two main trends that occurred in all samples: foliage was generally the tissue with the highest BCFs and 6:2 FTSA usually yielded the highest accumulation and was found to be accumulated in every single sample. High ∑PFAS concentrations were found in long beechfern (Site 1; 35.3 ng $g^{-1}$ dw) and ground elder (Site 2; 83 ng $g^{-1}$ dw) leaves, although these species have the shortest vegetation period, thus the shortest time for PFAS to accumulate; however the PFAS concentrations were comparable to those of birches and exceeded the bushes' concentrations.

In the following, the focus will be on PFOA and PFOS, as these substances allow for comparison with other studies. Yoo et al. (2011) investigated grasses from agricultural fields fertilized with sewage sludge and contaminated with PFASs. They calculated Grass-soil-accumulation factors (GSAF; based on ng $g^{-1}$ dw concentrations) based on their own data for grasses and those provided by Stahl et al. (2009) for oat, corn and wheat straw. For PFOA, the GSAFs were in the range of 0.25 ± 0.23 for grass, 0.25 ± 0.08 for corn straw, 1.95 ± 1.90 for oat straw and 3.99 ± 1.88 for wheat straw. In comparison, the BCFs in this study were on average of 0.25 ± 0.04 for bird cherry, 1.36 ± 1.69 for birch and 17.97 ± 17.21 for spruce, taking into account all vegetative compartments of the species, namely foliage, twigs and the trunk (if available; based on ng $g^{-1}$ ww). The BCF for bird cherry and birch fit well within the previous observations while this study was, to the best of my knowledge, the first study for spruce. According to Yoo et al. (2011) PFOS accumulation was 0.07 ± 0.04 for grass, 0.16 ± 0.04 for corn straw and 0.77 ± 0.55 for wheat straw (oat straw was recorded to be in between). They correspond well with 0.12 ± 0.05 for bird cherry, 1.35 ± 2.79 for birch and 0.57 ± 0.95 for spruce. Moreover, Zhao et al. (2014) found out that PFASs accumulation decreased with increasing perfluorocarbon chain length. This trend could not be observed for all PFCAs in the present study due to high variability of the data which can most probably be attributed to the influence of field conditions with contaminated soil. In contrast, most other studies were performed using spiked non-aged soil which results in a different availability of PFASs (Navarro et al, 2016; Sijm et al. 2000; Hatzinger and Alexander, 1995). In this study, the greatest BCFs were found for 6:2 FTSA, PFOS, PFHxS and PFOA which could attribute to the AFFF composition used at Arlanda airport, as it does not correspond with the findings from other studies where PFASs were usually spiked in equal amounts (Zhao et al., 2014, Stahl et al., 2009). Despite being subject to fluctuations, the PFSAs showed a slight correlation trend of decreasing BCF with increasing perfluorocarbon chain length (Figure 14).

According to Weiner et al. (2013), 6:2 FTSA, which was found in high concentrations in the plant samples of the present study, can potentially biotransform to PFCAs. However, PFCA concentrations were generally low indicating a slow degradation in the investigated plants.

## 5.4 Evaluation of remediation potential of investigated plant species

For efficient removal of a PFAS-mixture as it is present at Arlanda airport, for phytoremediation it is beneficial to have a high BCF for the PFASs dominating in soil and groundwater. Correspondingly, birch leaves, spruce needles, bird cherry leaves and fern leaves showed the highest potential. All of them accumulated 8-10 different PFASs with high BCFs (of up to 13698; birch leaves, Site 1, June). However, the representativeness of the fern values is questionable, as it grew only at Site 1 and hence, was only sampled once while there are at least duplicates for the other species.

BCFs could successfully be calculated for several birch tissues. The PFSAs were a lot better represented than the PFCAs, with six values for PFHxS, five values for PFOS and two for PFBS. The BCFs for PFBS were 0.5 in sap and 12 in the leaves, which is the highest BCF calculated for PFSAs in individual birch tissues. The leaves had BCFs for all three compounds and decreased with increasing perfluorocarbon chain length from 12 for PFBS, 6 for PFHxS and 0.64 for PFOS.

Furthermore, birch, especially *B. pendula*, has proven to successfully accumulate heavy metals, particularly *Zn* and *Pb* (Dmuchowski et al., 2014; Marguí et al., 2007), and TCE (Lewis et al., 2013) while having low requirements and being very common in the Nordic countries. Furthermore, it showed high potential to accumulate seven different PFCAs, three PFSAs (including isomers) and 6:2 FTSA. In contrast to the other plants sampled, it offers several applications for PFASs removal as it naturally sheds its leaves in autumn that could be collected without felling the whole tree and produces the highly contaminated birch sap, which can be collected with maple syrup taps. Both methods are suitable for annual application, as the tree itself is not removed. Besides the long-term applications that do not harm the intact tree, the tree could also be fully removed, as birches are pioneer species that regrow fast and produce biomass quickly. Further assessment is needed to estimate which method would remove more PFASs in the long term or if a combination of both methods yield optimum results.

Spruces have previously demonstrated the ability for metal accumulation and yielded bioaccumulation factors (BAF; $C_{shoot}/C_{soil}$ based on mg $kg^{-1}$ concentrations) of 1-3 for *Zn* (Placek et al., 2016). Besides, the tree is appreciated for its high adaptability (Placek et al., 201). The spruce needles showed similar PFAS concentrations as found in the birch leaves. The needles have proven quite successful PFCA accumulators, accumulating 3-5 different PFCAs. However, while the leaves of birch make up 7% of the tree's total biomass and grow within roughly 6 months, the needles make up 4% of the spruces biomass and grow for 3-7 years. Consequently, birch leaves accumulate PFASs a lot faster (6-14 times faster) and more efficiently. Furthermore, the spruce is a non-deciduous tree and annual removal of the foliage, which usually stays 3-7 years on the healthy tree, could potentially harm or even kill the tree. Therefore, annual harvests of the tree's needles seem not applicable, however, the systematic planting and felling of spruces might be an option.

The bird cherry is a deciduous shrub with moderate growth rate and ornamental flowers (The Moray Council, 2008). It accumulated 8-10 different compounds in its leaves with BCFs >1 for four of those. However, the BCFs scored by mountain ash were usually exceeding those of the bird cherry to a considerable degree. Yet, the mountain ash accumulated not more than five compounds (n = 3) in its leaves. Hence, application might be dependent on the contamination profile, as bird cherry seems to be the better all-rounder, whereas mountain ash demonstrated higher bioconcentration of PFPeA, PFHpA and the PFSAs tested.

While ground elder was more prevalent than the long beechfern, it was not as successful in accumulating PFASs in the same extent as the fern. Particularly PFCAs, that were present (n=4) and highly accumulated in the fern (BCF of 5,450 for PFPeA), could not be detected in the ground elder from the same site, nor at the other sites (in the same diversity; max n=2). The BCFs of strawberries were negligible. Consequently, the long beechfern seems the most promising candidate of the annual plants to be studied further.

The soil and groundwater concentrations at Arlanda airport were corresponding to concentrations found in samples from other AFFF-impacted sites (such as emergency response locations, AFFF lagoons, hangar-related AFFF storage tanks etc.) (Anderson et al., 2016). The median soil concentrations were ranging between 0.7 and 52.5 µg $kg^{-1}$ while the soil concentrations at Arlanda airport were in the range of 5.7-42 µg $kg^{-1}$. Similarly, the median groundwater concentrations ranged from 0.2-4.2 µg $L^{-1}$ (Anderson et al., 2016) and 1.19-34 µg $L^{-1}$ (present study), respectively. After an accidental release of 22,000 L AFFF at Toronto airport, Awad et al. (2011) found long-term PFASs concentrations in a surface water stream ranging from 290 ng $L^{-1}$ for PFOS in 2009 and 690 ng $L^{-1}$ PFOS in 2003 (directly after the spill). Additionally, they observed elevated PFOS/PFOA ratios between 10.1 and 22 which are in correspondence with those found at Arlanda airport (surface water: 23.6; groundwater 8.2 ± 7). Thus, the findings from the present study seem to be applicable to other contaminated sites as well. In contrast, Kärrman et al. (2011) detected seepage water concentrations of 5,100-6,700 ng $L^{-1}$ for 6:2 FTSA and 1,400-2,000 ng $L^{-1}$ for PFOS at Flerland airport in Norway. These levels are several orders of magnitude higher than the concentrations in the surface water found at Arlanda airport but similar to the groundwater concentrations. However, further studies are needed to determine if this range still lies within the uptake capabilities of plants and enables using the full uptake potential that was not reached within this study, or if the concentrations have reached toxic levels and inhibit proper growth.

A BCF >1 is considered to indicate accumulation and is therefore preferable for remediation purposes. However, due to the high concentration of PFASs detected at Arlanda airport and increased plant uptake of PFASs with increasing soil concentrations, BCFs <1 can potentially be considered sufficient for remediation measures. This option is particularly interesting for deciduous or annual plants that seasonally shed their leaves or regrow every summer, as they could be used for long-term removal of PFASs.

# 6 Conclusion

All plants showed PFASs uptake with an affinity for accumulation in the foliage. Consequently, needles and leaves were, irrespective of the species, the most contaminated tissues sampled in this study. The whole tree burden was highest for birch trees in comparison to spruce which makes birches the preferable remediation species. The BCFs were varying a lot for species, substance and tissues so correlation between perfluorocarbon chain length and BCF could be observed.

However, the results confirm previous findings of the high dependency of PFASs uptake on species and substance. Therefore, no generalizations can be made or conclusions drawn for related species. Additionally, no harmful effects of PFASs on plants were observed, so the toxicity threshold remains unknown and the full uptake potential of the plants needs to be investigated further. Moreover, the results indicate that Norway spruce and particularly silver birch are potential candidates for PFASs remediation and that annual ground cover species like the long beechfern have a higher uptake and remediation potential than bushes like bird cherry and mountain ash. While ground cover species enable contaminant removal by mowing, birches provide three removal options; tapping of the sap, annual leaf collection or felling of the tree. Spruce appears to be a satisfactory accumulator, however, felling seems the only option for PFASs removal which requires long-term treatment of decades to centuries. According to the findings, silver birch and long beechfern seem promising candidates for PFASs removal at AFFF-impacted sites.

While the extent of the study was restricted to Arlanda airport, the local vegetation and a time frame of five months, the results still provide a benchmark for further studies and hopefully raise the interest of phytoremediation of PFASs contaminated sites.

# 7 Outlook

Ideally, the results of this study build the foundation for further research on the phytoremediation potential of PFASs and can be beneficial in a pilot remediation project of PFASs at Arlanda airport. The results are applicable for various AFFF-impacted sites with a similar plant species composition, however, more research is needed to determine other suitable species and extend the knowledge of PFASs-plant interaction. Besides, the uptake and toxicity threshold of the investigated species and environmental factors that can affect a plant's performance should be investigated further.

This research project is the first step in a series of investigations that are necessary to evaluate the applicability, revenue and expenses of phytoremediation at Arlanda airport in particular and similar sites in the northern hemisphere. Subsequently, the potential annual PFASs extraction through regular harvests, tapping or felling have to be determined and how these harvests should be performed (extent, machinery, costs). Estimates of feasible duration of remediation projects for dramatic improvements of site conditions should be made and the monetary effort of remediation measures needs to be assessed. A successful remediation could prevent further spread of the contaminated groundwater plume and leaching while protecting adjacent aquifers, connected streams and rivers. Additionally, the fixation of soil by plants effectively prevents aerial transport of PFASs via dust.

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# Appendix

## Groundwater flow

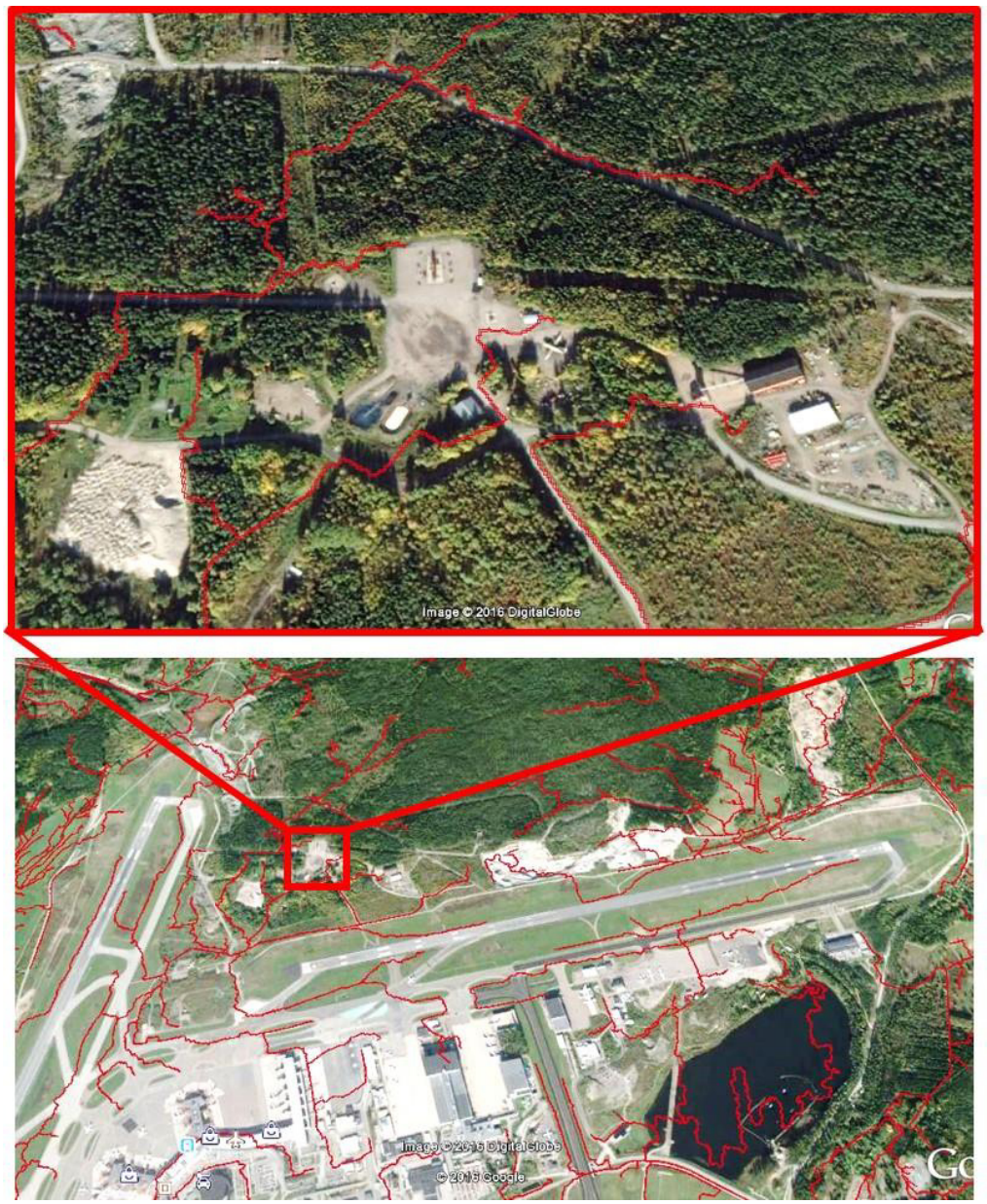


**Figure A1 Groundwater Flow direction at fire training site, Arlanda airport. Map and Aerial photo taken from google.de/maps**

| Blanks | Method Blanks | | | | Solvent Blanks | | | |
|---|---|---|---|---|---|---|---|---|
| | **Water** (***n*** **= 4**) | | **Plant/soil** (***n*** **= 10**) | | **Homogenizer** (***n*** **= 1**) | | **Coffee grinder** (***n*** **= 2**) | |
| | blank [ng $L^{-1}$] | MDLs [ng $L^{-1}$] | blank [ng $g^{-1}$ dw] | MDLs [ng $g^{-1}$ dw] | blank [ng $L^{-1}$] | MDLs [ng $L^{-1}$] | blank [ng $L^{-1}$] | MDLs [ng $L^{-1}$] |
| PFBA | 0.088 | 2.10 | 0.127 | 0.208 | ND | ND | ND | ND |
| PFPeA | 0.0053 | 0.199 | 0.368 | 0.193 | ND | ND | ND | ND |
| PFHxA | ND | 0.269 | 0.091 | 0.139 | ND | ND | ND | ND |
| PFHpA | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| PFOA | ND | 0.269 | 0.002 | 0.003 | ND | ND | ND | ND |
| PFNA | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| PFDA | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| PFUnDA | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| PFDoDA | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| PFTriDA | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| PFTeDA | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| PFHxDA | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| PFOcDA | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| PFBS | 0.0073 | 0.264 | 0.040 | 0.060 | 0.0017 | 0.0093 | ND | ND |
| PFHxS linear | 0.0069 | 0.259 | 0.054 | 0.077 | ND | ND | ND | ND |
| PFHxS branched | 0.184 | 0.269 | 0.006 | 0.010 | ND | ND | ND | ND |
| PFOS linear | 0.123 | 3.23 | 0.047 | 0.040 | ND | ND | ND | ND |
| PFOS branched | 0.031 | 0.967 | 0.020 | 0.021 | ND | ND | ND | ND |
| PFDS | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| 6:2 FTS | 0.071 | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| FOSA linear | ND | 0.269 | ND | 0.017 | 0.0090 | 0.049 | ND | ND |
| FOSA branched | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| MeFOSA | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| EtFOSA | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| MeFOSE | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| EtFOSE | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| FOSAA | ND | 0.269 | ND | 0.017 | 0.014 | 0.075 | ND | ND |
| MeFOSAA | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |
| EtFOSAA | ND | 0.269 | ND | 0.017 | ND | ND | ND | ND |

| **Duplicates** | **Water (*n* = 5)** mean RSD | **Birch sap (*n* = 8)** mean RSD | **Soil (*n* = 6)** mean RSD | **Plants (*n* = 45)** mean RSD |
|---|---|---|---|---|
| PFBA | 7.78 | 12.2 | 4.20 | 28.0 |
| PFPeA | 3.91 | 9.56 | 4.83 | 10.0 |
| PFHxA | 5.90 | 11.4 | 3.71 | 9.41 |
| PFHpA | 5.81 | 13.7 | 4.79 | 34.7 |
| PFOA | 6.43 | 21.5 | 3.63 | 23.1 |
| PFNA | 42.5 | ND | 6.97 | 7.99 |
| PFDA | 13.3 | ND | 13.8 | 11.4 |
| PFUnDA | ND | ND | 8.66 | ND |
| PFDoDA | ND | ND | ND | 94.8 |
| PFTriDA | ND | ND | ND | ND |
| PFTeDA | ND | ND | ND | ND |
| PFHxDA | ND | ND | ND | ND |
| PFOcDA | ND | ND | ND | ND |
| PFBS | 4.98 | 16.3 | 30.0 | 24.0 |
| PFHxS linear | 6.44 | 16.8 | 4.99 | 13.1 |
| PFHxS branched | 8.31 | 47.5 | ND | 36.6 |
| PFOS linear | 4.32 | 13.7 | 13.2 | 18.0 |
| PFOS branched | 5.37 | 47.5 | 29.1 | 27.2 |
| PFDS | ND | ND | ND | ND |
| 6:2 FTS | 6.98 | 22.9 | 171 | 20.8 |
| FOSA linear | 4.81 | 22.5 | 4.30 | 12.9 |
| FOSA branched | 1.97 | ND | 6.92 | ND |
| MeFOSA | ND | ND | 15.0 | ND |
| EtFOSA | ND | ND | ND | ND |
| MeFOSE | ND | ND | 141 | ND |
| EtFOSE | ND | ND | ND | ND |
| FOSAA | ND | ND | 1.98 | ND |
| MeFOSAA | ND | ND | ND | ND |
| EtFOSAA | ND | ND | ND | ND |

Recovery

| **Recovery** | **Groundwater (*n* = 12)** | | **Birch sap (*n* = 21)** | | **Soil (*n* = 18)** | | **Plants (*n* = 97)** | |
|---|---|---|---|---|---|---|---|---|
| | mean | ± SD | mean | ± SD | mean | ± SD | mean | ± SD |
| $^{13}C_4$ PFBA | 32 | 28 | 127 | 143 | 145 | 57 | 28 | 32 |
| $^{13}C_2$ PFHxA | 84 | 20 | 60 | 57 | 118 | 42 | 12 | 12 |
| $^{13}C_4$ PFOA | 110 | 54 | 97 | 92 | 118 | 36 | 23 | 18 |
| $^{13}C_5$ PFNA | 104 | 38 | 93 | 86 | 108 | 43 | 18 | 17 |
| $^{13}C_2$ PFDA | 161 | 38 | 90 | 88 | 116 | 38 | 29 | 20 |
| $^{13}C_2$ PFUnDA | 149 | 34 | 71 | 76 | 98 | 38 | 28 | 18 |
| $^{13}C_2$ PFDoDA | 126 | 32 | 49 | 55 | 111 | 26 | 27 | 16 |
| $^{18}O_2$ PFHxS | 97 | 32 | 94 | 75 | 176 | 40 | 43 | 26 |
| $^{13}C_4$ PFOS | 98 | 64 | 82 | 74 | 156 | 37 | 43 | 29 |
| $^{13}C_8$-FOSA | 145 | 35 | 53 | 57 | 120 | 44 | 36 | 22 |
| $d_3$-*N*-MeFOSA | 59 | 28 | 45 | 46 | 124 | 41 | 103 | 42 |
| $d_5$-*N*-EtFOSA | 37 | 27 | 34 | 40 | 104 | 39 | 27 | 17 |
| $d_7$-*N*-MeFOSE | 92 | 29 | 50 | 54 | 120 | 38 | 26 | 18 |
| $d_9$-*N*-EtFOSE | 87 | 30 | 37 | 41 | 98 | 37 | 25 | 15 |
| $d_3$-*N*-MeFOSAA | 171 | 43 | 92 | 96 | 168 | 56 | 39 | 30 |
| $d_5$-*N*-EtFOSAA | 167 | 43 | 85 | 86 | 158 | 56 | 49 | 34 |

Tree biomass estimations

| | **Birch** | **Spruce** |
|---|---|---|
| Root | 0.125 | 0.26 |
| Trunk | 0.665 | 0.53 |
| Twig | 0.14 | 0.17 |
| Leaf/Needle | 0.07 | 0.04 |
| Total Biomass, 15m tall tree [kg] | 900 | 900 |
| Data from | Johansson, Tord (2007) | Minerbi & Cescatti (2015) |