# SCREENING FOR PER- AND POLYFLUOROALKYL SUBSTANCES IN VARIOUS PLANT TISSUES

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## Introduction

Per- and polyfluoroalkyl substances (PFASs) are commonly known for their persistence, toxicity and bioaccumulative nature[1]. Their ability to repel water and resist fires made PFASs key constituents in a wide range of products such as firefighting forms, ski waxes, coating of nonstick kitchen ware and in dirt and water repellent sprays[2–4]. Fire training sites have been reported as important point sources of PFASs to their surrounding environments[5]. Many studies have been carried out to improve our understanding of the distribution and fate of PFASs in water, soil and living organisms in areas impacted by fire training sites/events. However, few studies have investigated PFAS uptake and distribution in plants, despite their potential as a remediation technique or possible route of exposure through food.
The aim of this study is to assess the distribution of different PFASs in plant species growing at fire training sites at Arlanda Airport Stockholm. The specific objectives were to (i) determine PFAS distribution in the soil, groundwater and different plant species; (ii) investigate the PFAS distribution profiles in different plant tissues i.e. leaves, twigs, stems and roots, and (iii) access the total tree burden of PFASs in two plant species.

## Materials and methods

A total of 26 PFASs were investigated which including $C_4$, $C_6$, $C_8$, $C_{10}$ perfluoroalkane sulfonates (PFSAs) (PFBS, PFHxS, PFOS, PFDS), $C_{3\text{-}13}$, $C_{15}$, $C_{17}$ perfluoroalkyl carboxylates (PFCAs) (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, PFOcDA), perfluorooctane sulfonamides (FOSAs) (FOSA, MeFOSA EtFOSA), perfluorooctane sulfonamidoethanols (FOSEs) (MeFOSE, EtFOSE), perfluorooctane sulfonamidoacetic acids (FOSAAs) (FOSAA, MeFOSAA, EtFOSAA) and fluorotelomer carboxylate (6:2 FTSA). For the mass labelled internal standards, $^{13}C_4$ 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, and $d_5$-N-Et-FOSAA were used. The samples were collected from a fire training site at Arlanda airport in Stockholm, Sweden. This fire training site was established in 1987 with the runoff collection facility constructed in 1997 and ceased using PFOS containing AFFFs in 2010[6]. Two sampling campaigns were performed, on 22nd March 2016 and 30th June 2016, at three locations south (< 500 m) of the fire training site. Plant tissue samples from seven different plant species were collected (i.e. silver birch (*Betula pendula*), bird cherry (*Prunus padulus*), mountain ash (*Sorbus aucuparia*), ground elder (*Aegopodium podagraria*), long beechfern (Phegopteris connectilis) and wild strawberry (*Fragaria vesca*)) into plastic zip lock bags ($n$ = 44). Grab samples for surface water ($n$ = 1) and groundwater ($n$ = 3) were collected in 1 L polypropylene (PP) bottles. Composite soil samples ($n$ = 6) were collected from the three sites near the ground water wells.
The soil and plant tissue samples were extracted with solid-liquid extraction in methanol and cleaned up using ENVI-carb[7]. Preparation of water samples was performed using solid-phase extraction as described elsewhere[7]. Instrumental analysis was performed using ultra performance liquid chromatography (UPLC) coupled with a tandem mass spectrometer (MS/MS). Blanks and duplicates were included in each batch of samples for purposes of quality assurance and control.

## Results and discussion:

*PFAS distribution in the soil, ground water and different plant species*
Of the 26 analyzed PFASs, 13 could be detected in ground- and surface water and 17 could be detected in soil. The closer the sampling site was to the fire training site, the higher the measured PFAS concentration. Groundwater contained $\Sigma_{26}$PFAS concentration ranging from 1200 ng $L^{-1}$ (site 1) to 3400 ng $L^{-1}$ (site 3). The

surface water in the ditch nearby the sampling site contained 650 ng $L^{-1}$ for $\Sigma_{26}$PFASs. The $\Sigma_{26}$PFAS concentrations in the surface water is lower than measured in 2011 (~4000 ng $L^{-1}$), probably due to the fact that PFAS-containing PFASs have not been used at the site and the PFAS concentration has been diluted over time[6]. Dominant PFASs were PFOS (48%), PFHxS (11%), PFHxA (4%) and PFOA (2%). $\Sigma_{26}$PFAS concentrations in the soil ranged from 16 ng $g^{-1}$ (site 1) to 160 ng $g^{-1}$ (site 3).

Of the 26 analyzed PFASs, 10 were detected in the plants. PFAS uptake greatly varied among the different plant species. In the foliage, the $\Sigma_{26}$PFAS uptake decreased as follows: Birch (12–97 ng $g^{-1}$ ww) > spruce (14–94 ng $g^{-1}$ ww) > bird cherry (4.3–21 ng $g^{-1}$ ww) > ground elder (0.89–23 ng $g^{-1}$ ww). Short chained PFCAs, especially PFPeA (on average 24% of $\Sigma_{26}$ PFAS) and 6:2 FTSA (on average 50% of $\Sigma_{26}$ PFAS), were the most dominant PFASs in plants (**Figure 1**). Since these PFASs are highly water soluble and mobile, they are taken up through the transpiration stream and can accumulated in the plant tissue[8].

In comparison to foliage, twigs had lower PFAS concentration levels. However, like the foliage, twigs from birch had the highest concentration (5.3–40 ng $g^{-1}$ ww) > spruce (4.1–4.2 ng $g^{-1}$ ww) > mountain ash (0.15–0.78 ng $g^{-1}$ ww). PFSAs like PFHxS (on average, 12% of $\Sigma_{26}$PFASs) and PFOS (on average, 14% of $\Sigma_{26}$ PFASs) together with 6:2 FTSA (on average 55% of $\Sigma_{26}$ PFAS) were the most dominant PFASs.

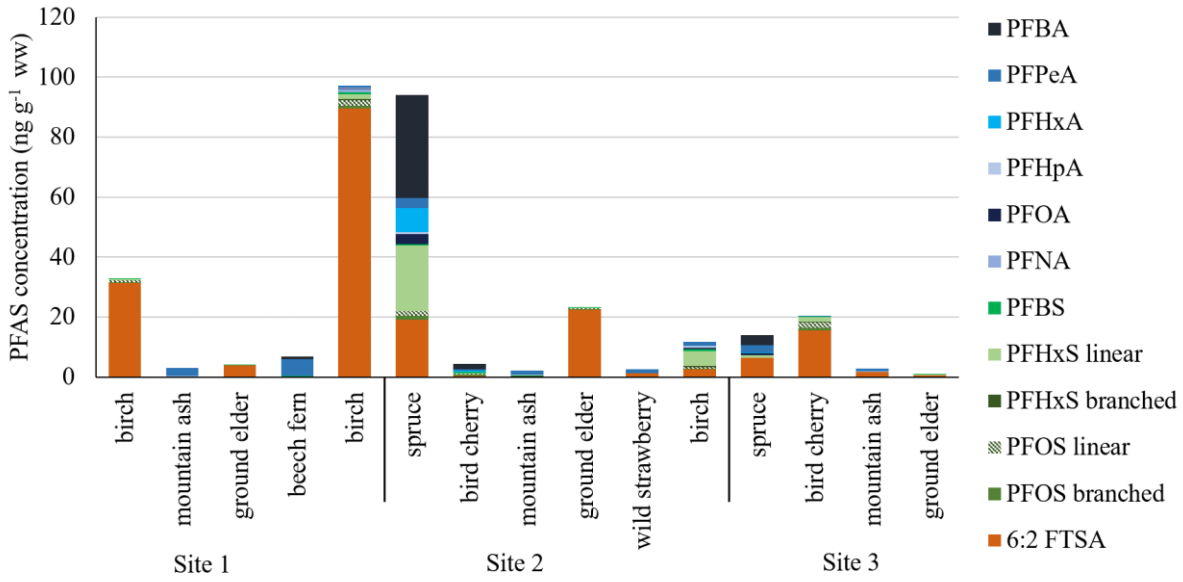


**Figure 1:** Detected individual PFASs in foliage of the investigated plant species from three different sites.

*PFAS distribution in different plant tissues*

Leaves/needles, twigs, stem and roots were analysed separately in birch and spruce to better understand the distribution of PFASs in the different plant tissues. The leaves (12 – 97 ng $g^{-1}$ ww) contained the highest $\Sigma_{26}$PFAS concentrations followed by twigs (5.3 – 49 ng $g^{-1}$ ww), stem (0.37 – 31 ng $g^{-1}$ ww) and roots (2.6 – 6.2 ng $g^{-1}$ ww). A similar trend was observed in spruce.

Analysis of tree core samples from both plant species revealed that heartwood (core without bark) contained 3 times higher $\Sigma_{26}$PFAS concentrations in comparison to sapwood (core with bark). Sapwood from birch contained 0.37–11 ng $g^{-1}$ ww, while heartwood contained 0.93 – 31 ng $g^{-1}$ ww for $\Sigma_{26}$PFASs. Spruce contained 1.3 ng $g^{-1}$ ww in the sapwood and 4.3 ng $g^{-1}$ ww in the heartwood for $\Sigma_{26}$PFASs. This pattern of PFAS distribution in the two tree core tissues could be due to the construction of a runoff trapping unit and the change to using PFOS-free AFFF that has reduced recontamination.

*PFAS tree burden*

Birch had higher mean total tree burden for $\Sigma_{26}$ PFASs (1.5–11 mg, $n$ = 3) in comparison to spruce (0.26 and 1.8 mg, $n$ = 2). This is probably because birch has a higher wood density[7]. PFAS burden in birch was highest in the trunk (14 – 88%) > foliage (8 – 63%) > twigs (4 –26%) > roots (1– 4%). A similar trend was observed in birch with 53%, 20%, 20% and 23% PFAS burden in trunk, foliage, twigs and roots, respectively. Birch also accumulated most of the PFASs in the aboveground biomass (96–99%), while spruce had much higher PFAS concentration in the roots (23 %).

From this study, it can be concluded that plants at contaminated sites take up PFASs. However, PFAS uptake and composition profiles among plants varied with plant species, plant tissues and soil and groundwater PFAS concentrations. Phytoremediation of PFASs using plants is a promising technique with proper optimization. Therefore, further research on how to increase plant PFAS uptake is required.

**Acknowledgements:**
The authors acknowledge SGI and Swedavia for the financial support

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