



# Stockholm Arlanda Airport as a source of per- and polyfluoroalkyl substances to water, sediment and fish



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## ABSTRACT

Fire training facilities are potential sources of per- and polyfluoroalkyl substances (PFASs) to the nearby environment due to the usage of PFAS-containing aqueous fire-fighting foams (AFFFs). The multimedia distribution of perfluoroalkyl carboxylates (PFCAs), perfluoroalkyl sulfonates (PFSAs), perfluorooctane-sulfonamide (PFOSA) and 6:2 fluorotelomer sulfonate (FTSA) was investigated near a fire training facility at Stockholm Arlanda Airport in Sweden. The whole body burden of PFASs in European perch (*Perca fluviatilis*) was  $334 \pm 80 \mu\text{g}$  absolute and was distributed as follows: Gonad > liver  $\approx$  muscle > blood > gill. The bioconcentration factor (BCF) and sediment/water partition coefficient ( $K_d$ ) increased by 0.6–1.7 and 0.2–0.5 log units, respectively, for each additional  $\text{CF}_2$  moiety for PFCAs and PFSAs. PFAS concentrations in water showed no significant decreasing trend between 2009 and 2013 ( $p > 0.05$ ), which indicates that Stockholm Arlanda Airport may be an important source for long-term contamination of the nearby environment with PFASs.

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## 1. Introduction

Aqueous fire-fighting foams (AFFFs) are concentrated liquids designed to extinguish hydrocarbon fuel fires and are used by commercial, public, and military fire-fighting organizations (Paul et al., 2009). Since the 1960s, per- and polyfluoroalkyl substances (PFASs) have been used in AFFFs due to their surface active characteristics to enable the formation of an aqueous film and to resist heat, oil, and water. PFASs have received increasing public attention due to their persistence, bioaccumulative potential, and possible adverse effects on humans and wildlife. As a consequence, perfluorooctane sulfonate (PFOS) and its precursors have been added to the persistent organic pollutants (POPs) list of the Stockholm Convention in May 2009, resulting in global restrictions on its use and production (Paul et al., 2009). After the voluntary phase-out or ban of the  $\text{C}_8$ -based PFASs, such as PFOS, the production shifted to PFAS precursors, due to their higher degradation potential, and to short-chain PFASs (perfluoroalkyl chain length of  $\text{C} < 8$ ), due to their lower bioaccumulation potential (Martin et al., 2003; Möller et al., 2010; Ahrens, 2011). However, PFAS precursors can be (bio)degraded under aerobic and anaerobic conditions to long- and short-chain perfluoroalkyl carboxylates (PFCAs) and perfluoroalkane sulfonates (PFSAs) which are the final

degradation products and extremely persistent in the environment (Rhoads et al., 2008; Wang et al., 2011).

Previous studies have linked the usage of AFFFs at fire training facilities to the contamination of the environment with PFASs (Moody et al., 2002, 2003; Awad et al., 2011; Kärrman et al., 2011; De Solla et al., 2012). PFOS and 6:2 fluorotelomer sulfonate (FTSA) were the dominant PFASs detected at AFFF contaminated sites with maximum concentrations in the  $\text{mg L}^{-1}$  and  $\mu\text{g g}^{-1}$  range for water and fish, respectively (Moody et al., 2003; Awad et al., 2011; Kärrman et al., 2011; De Solla et al., 2012). Once released into the environment, PFASs are subject to various partitioning, degradation, and transport processes depending on their physico-chemical properties and environmental conditions (Ahrens, 2011). The short-chain PFSAs and PFCAs are potentially more water soluble, whereas long-chain PFSAs and PFCAs seem to bind more strongly to particles and accumulate in the food chain (Higgins and Luthy, 2006; Ahrens et al., 2010). However, there is a lack of knowledge of the multimedia distribution of PFASs in the environment. AFFFs are a particularly problematic source of PFASs since high amounts are used in liquid form during a relatively short time period, which increases the potential for the PFASs to be released into the aqueous environment.

The aim of this study was to examine the transport and fate of PFASs in water, sediment and fish near a fire training facility at Stockholm Arlanda Airport. The specific objectives were to (i) determine the concentrations and composition profile of various

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PFASs in the multimedia environment (i.e., water, sediment and fish), (ii) to calculate fish bioconcentration factors (BCF) and the sediment/water partition coefficient ( $K_d$ ) of individual PFASs, and (iii) to investigate the spatial distribution and temporal trends of PFASs in a lake near the fire training facility.

## 2. Materials and methods

### 2.1. Sampling sites

The study was carried out in an area surrounding Stockholm Arlanda Airport, which is the largest airport in Sweden. Stockholm Arlanda Airport is an international airport located ~37 km north-northwest of Stockholm and is used by approximately 19 million people annually (2012). There is a fire training facility located in the north part of the airport area (Fig. 1) where PFOS-containing AFFFs (STHMEX-AFFF 3%, Dr. Richard Sthamer GmbH & Co. KG, Hamburg, Germany) were used frequently from the 1980s until 2003. From 2003, remaining stocks of STHMEX-AFFF 3% were used and then replaced by PFOS-free AFFFs (Presto AFFF and Moussol APS-P, Dr. Richard Sthamer GmbH & Co. KG, Hamburg, Germany); however, these PFOS-free AFFFs still contained other PFASs. According to the manufacturer, the PFOS-free AFFFs contain <10% of PFASs, but further details about the AFFF products are not available. In 2011, Stockholm Arlanda Airport stopped purchasing PFAS-containing AFFFs and a fluorine-free (FF)-AFFF (Moussol FF 3/6, Dr. Richard Sthamer GmbH & Co. KG, Hamburg, Germany) is used instead.

### 2.2. Sampling

Surface water ( $n = 33$ ), sediment ( $n = 3$ ) and fish ( $n = 21$ , European perch (*Perca fluviatilis*)) samples were collected at Lake Halmsjön nearby Stockholm Arlanda Airport between 2009 and 2013 (Fig. 1, and Supplementary Tables S1, S2, S3). Perch tissue samples included muscle tissue ( $n = 18$ ), and blood, liver, muscle, gill and gonad tissues from three individual fish. In addition to the sampling at Lake Halmsjön (sampling site 13,  $n = 13$ , 2009–2013), surface water samples were collected at two reference lakes (sampling sites 1 and 2,  $n = 2$ , 2009), artificial ditches downstream of the fire training facility (sampling sites 5–10,  $n = 6$ , 2011), and various streams in the area surrounding Stockholm Arlanda Airport (sampling sites 3, 4, 11, 12, 14–18,  $n = 12$ , 2011) (for details see Supplementary information).

### 2.3. Chemicals

The target analytes included  $C_6$ – $C_{11}$  PFCAs ( $C_nF_{2n+1}COO^-$ , PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA),  $C_6$ ,  $C_8$ ,  $C_{10}$  PFSAs ( $C_nF_{2n+1}SO_3^-$ ,

PFHxS, PFOS, PFDS), perfluorooctanesulfonamide (PFOSA,  $C_8F_{17}SO_2NH_2$ ) and 6:2 FTSA ( $C_6F_{13}CH_2CH_2SO_3^-$ ) plus [ $^{13}C_4$ ]-PFOS and [ $^{13}C_4$ ]-PFOA as mass-labeled internal standards (IS).

### 2.4. Analysis

The water samples were extracted by solid phase extraction (SPE) according to the ISO/DIS 25101:2009 method using Oasis WAX cartridges (Waters, 150 mg, 6 mL, 30  $\mu$ m) (ISO/DIS25101, 2008). The fish tissue and unsieved sediment samples were extracted based on the solid-liquid extraction method described by Powley et al. (2005). The separation and detection of PFASs were performed by high-performance liquid chromatography (HPLC, UFLC Shimadzu, model CBN-20A, Japan) coupled to a mass spectrometer interfaced with an electrospray ionization source in a negative-ion mode (ESI-MS/MS, API 4000, AB Sciex, Foster City, CA, USA). The isotope dilution method was used for quantification. As standard procedure, laboratory blanks, method detection limits (MDLs), and recoveries were examined. Blank concentrations were <1% of the concentrations measured in the samples. MDLs were in the range of tens to hundreds of picograms per liter and grams, respectively. The recoveries in the sample were typically in the range of 70–110% (for details see Supplementary information).

## 3. Results and discussion

### 3.1. PFAS composition profiles in water, sediment and fish

All 11 target PFASs were detected and quantified in water, sediment and perch tissues (i.e. blood, liver, muscle, gill, gonad). The composition profiles PFASs varied between compartments in Lake Halmsjön (Supplementary Fig. S1). In water, PFOS (~36%), PFHxS (~29%), and PFOA (~20%) were the dominant PFASs, followed by PFHxA (~8%). PFOS was even more predominant in sediment and perch tissues with a contribution of ~86% and ~99%, respectively. This indicates a compound-specific distribution of PFASs in the multi-compartment environment (Martin et al., 2003; Higgins and Luthy, 2006; Ahrens, 2011).

### 3.2. Tissue distribution of PFASs in perch

PFASs were determined in blood, liver, muscle, gill and gonad tissues in perch from Lake Halmsjön. No significant decreasing trend was observed for the PFAS concentrations in muscle tissues between 2009 and 2012 ( $p > 0.05$ , ANOVA), and therefore they are discussed as average values in the following. PFOS was the predominant PFAS in all tissue samples. The highest average  $\Sigma$ PFAS concentrations were detected in blood with  $5900 \pm 900$  ng  $g^{-1}$  ww ( $n = 3$ ), followed by liver ( $3900 \pm 500$  ng  $g^{-1}$  ww,  $n = 3$ ), gill

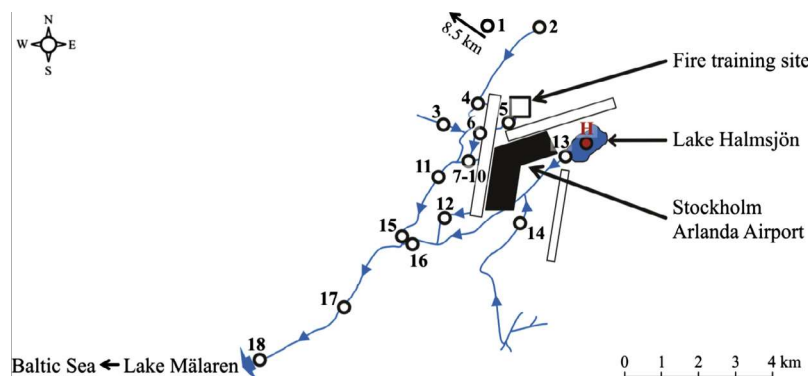


Fig. 1. Sampling sites for water sampling (1–18) and sampling of water, sediment and European perch (*Perca fluviatilis*) (H) at Stockholm Arlanda Airport, Sweden.

( $2100 \pm 700 \text{ ng g}^{-1} \text{ ww}$ ,  $n = 3$ ), gonad ( $1600 \pm 800 \text{ ng g}^{-1} \text{ ww}$ ,  $n = 3$ ) and muscle ( $330 \pm 190 \text{ ng g}^{-1} \text{ ww}$ ,  $n = 21$ ) (Supplementary Fig. S2). Similar to our finding, the PFAS concentrations were highest in blood, followed by kidney > liver > gall bladder > gonads > adipose > muscle tissue in rainbow trouts (*Oncorhynchus mykiss*) exposed in a flow-through system (Martin et al., 2003).

The tissue distribution of individual PFASs in perch varied depending on the functional group and fluorocarbon chain length (Supplementary Fig. S3). Most PFASs were mainly distributed in blood (PFOSA, PFDS and  $C_8$ – $C_{11}$  PFCAs with a contribution of ~77%, ~58%, ~46%, ~49%, ~54% and ~54%, respectively). In contrast, 6:2 FTSA, PFOS, and PFHxS were more distributed in gonad tissue (~76%, ~54%, and ~36% respectively). The compound-specific distribution of PFASs in perch can be influenced by differences in accumulation and elimination of individual compounds (Martin et al., 2003).

### 3.3. Whole body burden of PFASs in perch

The whole body burden distribution was calculated by multiplying the PFAS concentration in the sub-sample with the individual tissue weight. The mean whole body burden in perch of all detected PFASs was estimated to be  $334 \pm 80 \mu\text{g}$  absolute ( $n = 3$ ). PFOS was the predominant compound in all tissue samples with a contribution of ~99% ( $330 \pm 80 \mu\text{g}$  absolute). PFAS whole body burden distribution for the individual tissues decreased in the following order: gonad (54%) > liver (19%)  $\approx$  muscle (17%) > blood (7%) > gill (2%) (Fig. 2). More studies are required to investigate the whole body burden in fish and other species (Ahrens et al., 2009) for a better understanding of the bioaccumulation process of PFASs.

The relatively high body burden in perch in relation to the total body weight (in average,  $1.3 \pm 0.3 \text{ kg}$ ) may have an effect on the physiological functions of the fish. It has been shown that PFOS can be transferred to developing embryos in zebrafish (*Danio rerio*), where a chronic exposure to PFOS can alter the sex ratio, induce histopathological alterations and have a negative effect on reproduction, embryonic growth, and subsequent offspring development (Du et al., 2009). More ecotoxicological studies are needed to investigate the effects of individual PFASs and their mixtures on individual and community/ecosystem level. Recent studies have found a positive correlation of the consumption of PFAS contaminated freshwater fish and PFAS levels in human blood which indicate a risk for human health (Hölzer et al., 2011; Zhao et al., 2011; Zhang et al., 2011). In 2008, Swedavia Swedish Airports restricted

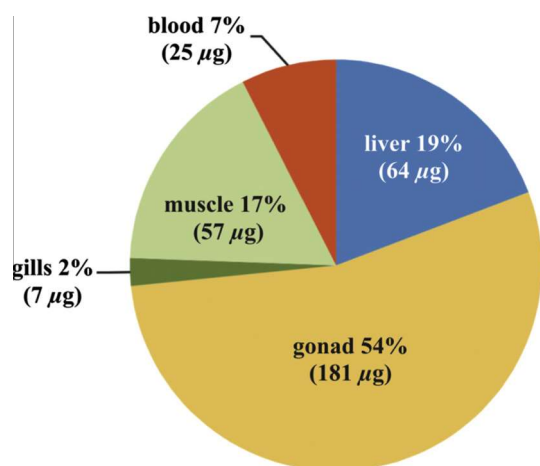


Fig. 2. PFAS whole body burden distribution in percent and  $\mu\text{g}$  per tissue in brackets for European perch (*Perca fluviatilis*) collected from Lake Halmnsjön.

fishing in Lake Halmnsjön due to the high PFOS contamination in the lake.

### 3.4. Fish bioconcentration factors (BCF) and sediment/water partition coefficients ( $K_d$ ) for PFASs

BCF were estimated in various tissues of perch in Lake Halmnsjön, based on the concentrations in water and fish tissue.

$$BCF_{\text{tissue}} = c_{\text{tissue}}/c_{\text{water}} \quad (1)$$

where  $BCF_{\text{tissue}}$  is the bioconcentration factor ( $\text{L kg}^{-1}$ ) based on the tissue concentration,  $c_{\text{tissue}}$  is the concentration of chemical in the tissue of perch ( $\text{ng kg}^{-1} \text{ ww}$ ), and  $c_{\text{water}}$  is the concentration of the target analyte in water ( $\text{ng L}^{-1}$ ). Since the concentrations differed between tissues for perch, the BCFs also varied. Generally, the highest BCF was found for  $BCF_{\text{blood}}$  (maximum  $BCF_{\text{blood}} = 65000$ ), followed by  $BCF_{\text{liver}}$ ,  $BCF_{\text{gill}}$  and  $BCF_{\text{gonad}}$ , whereas the BCF was lower in muscle and whole body (Supplementary Table S3).

Different BCFs were found for individual PFASs depending on the perfluoroalkyl chain length and functional group (Table 1). Highest average  $BCF_{\text{whole body}}$  value was found for PFOS ( $6400 \pm 3600$ ), whereas the  $C_6$  chained PFHxS had an average  $BCF_{\text{whole body}}$  of only  $26 \pm 10$ . For the PFCAs, the  $BCF_{\text{whole body}}$  decreased from an average of  $181 \pm 58$  for PFDA to an average of  $1.0 \pm 0.2$  for PFOA. The influence of the functional group on the BCF can be illustrated for three different PFAS classes (i.e., PFCAs, FOSAs, and PFSAs) by comparing the  $BCF_{\text{whole body}}$  between PFNA, PFOSA and PFOS, which all have a perfluoroalkyl chain length of  $C_8$ . The highest average  $BCF_{\text{whole body}}$  was found for PFOS ( $6400 \pm 3600$ ), whereas the  $BCF_{\text{whole body}}$  for PFOSA was ~5 times lower ( $1200 \pm 900$ ) and the  $BCF_{\text{whole body}}$  for PFNA was more than two orders of magnitude lower ( $48 \pm 8.8$ ). In general, the  $\log BCF_{\text{whole body}}$  values increased by 0.6–1.7 log units for each additional  $CF_2$  moiety and the bioaccumulation of PFOS was 0.7 log units and 2.1 log units higher compared to PFOSA and PFNA, respectively. Overall, the BCF calculated in this study were in the same range as previously reported in rainbow trout (Martin et al., 2003). However, it has to be considered that perch are carnivorous fish and it is not known whether the water phase or the food is the primary route of PFAS uptake.

The distribution of PFASs between water and sediment can be described by the  $K_d$  ( $\text{cm}^3 \text{ g}^{-1}$ ).

$$K_d = c_{\text{sediment}}/c_{\text{water}} \quad (2)$$

where  $c_{\text{sediment}}$  is the concentration of chemical in sediment ( $\text{ng g}^{-1}$  dry weight (dw)) and  $c_{\text{water}}$  is the concentration of the target analyte in water ( $\text{ng cm}^{-3}$ ). Similar as for the BCF, the perfluoroalkyl chain length and functional group had an influence on the  $K_d$  values (Table 1). The  $\log K_d$  for PFOS was  $2.3 \pm 0.3$ , whereas the  $C_6$  chained PFHxS had an average  $\log K_d$  of only  $1.3 \pm 0.4$ . For the PFCAs, the  $\log K_d$  decreased from an average of  $1.2 \pm 0.3$  for PFOA to an average of  $0.8 \pm 0.3$  for PFHxA. In general, the  $\log K_d$  values increase by 0.2–0.5 log units for each additional  $CF_2$  moiety. The highest  $\log K_d$  was calculated for PFOSA with an average of  $3.1 \pm 0.1$ , whereas the  $\log K_d$  of the  $C_8$  chained PFOS was 0.8 log units lower ( $2.3 \pm 0.3$ ). These findings are in agreement with previous reported  $K_d$  values (Higgins and Luthy, 2006; Ahrens et al., 2010), but it is important to bear in mind that the  $K_d$  values can be influenced by environmental factors such as the organic carbon content of sediment, pH and salinity of water (Higgins and Luthy, 2006).

### 3.5. Spatial distribution of PFASs in water around Stockholm Arlanda Airport

The spatial distribution of PFASs was investigated in water around Stockholm Arlanda Airport (Fig. 3).  $\Sigma$ PFAS concentrations

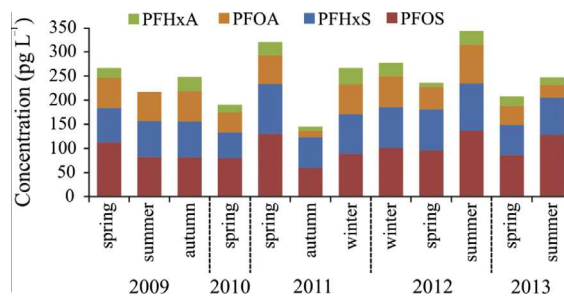
**Table 1**

Whole body bioconcentration factors (BCF,  $L\ kg^{-1}$ ) of European perch (*Perca fluviatilis*) and sediment/water partition coefficients ( $K_d$ ,  $cm^3\ g^{-1}$ ) for PFASs in Lake Halmstön near the Stockholm Arlanda Airport (average values and ranges are given in parentheses; N/A = not available).

	BCF <sub>whole body</sub>	Log BCF <sub>whole body</sub>	$K_d$	Log $K_d$
PFHxA	N/A	N/A	8.3 (4.2–16)	0.8 (0.6–1.2)
PFOA	1.0 (0.9–1.1)	0.0 (−0.07–0.05)	17 (9.7–30)	1.2 (1.0–1.5)
PFNA	48 (42–54)	1.7 (1.6–1.7)	N/A	N/A
PFDA	181 (140–220)	2.3 (2.2–2.4)	N/A	N/A
PFHxS	26 (14–33)	1.4 (1.2–1.5)	23 (10–48)	1.3 (1.0–1.7)
PFOS	6400 (3200–10200)	3.8 (3.5–4.0)	240 (120–450)	2.3 (2.1–2.7)
PFOSA	1200 (170–1800)	3.1 (2.2–3.3)	1300 (1000–1700)	3.1 (3.0–3.2)

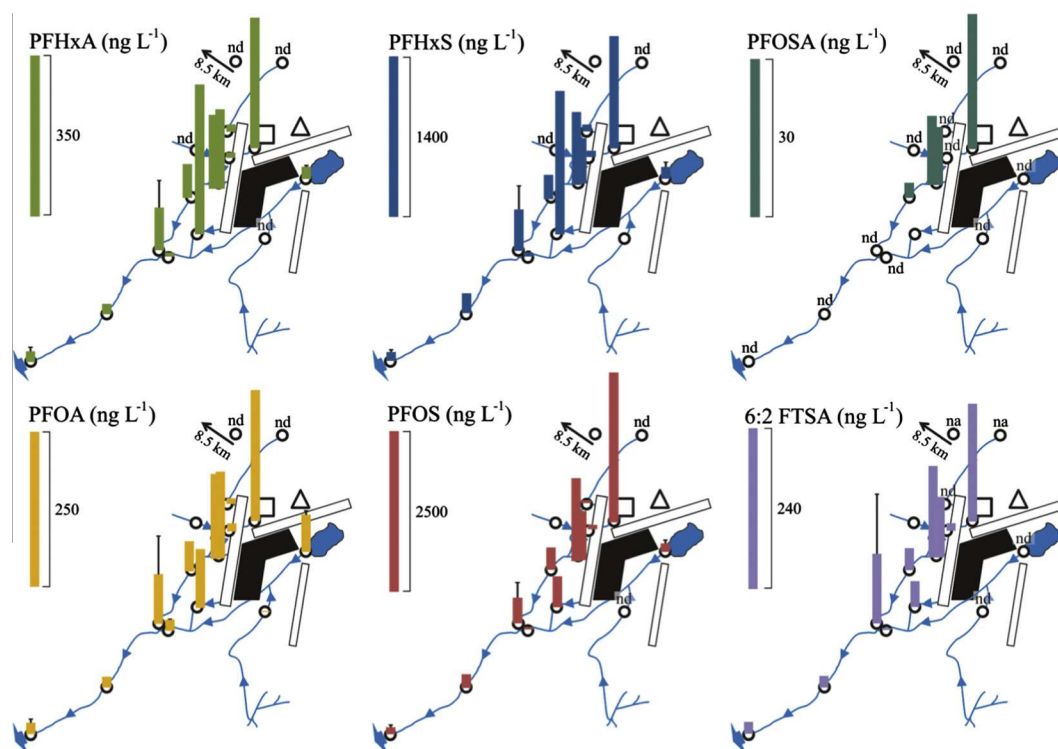
showed a high variability ranging from a few nanograms to several thousands nanograms per liter depending on the location. The highest PFAS concentrations were found in a ditch close to the fire training facility with  $\sim 4000\ ng\ L^{-1}$  for  $\Sigma$ PFASs (sampling site 5, see Figs. 1 and 4). PFOS (2340  $ng\ L^{-1}$ ) was the predominant compound at sampling site 5, followed by PFHxS (980  $ng\ L^{-1}$ ), PFHxA (290  $ng\ L^{-1}$ ), and PFOA (210  $ng\ L^{-1}$ ). The PFAS levels around Stockholm Arlanda Airport were comparable with those found in seepage and surface water contaminated with AFFFs, which ranged from hundreds to a few thousand nanograms per liter (Kärman et al., 2011; De Solla et al., 2012).

The PFOA concentration typically exceeded the PFOS concentration in the aqueous environment (Ahrens, 2011). The PFOS concentration in this study, however, was consistently higher than PFOA with an average PFOS/PFOA ratio of  $6.5 \pm 4.0$ , which confirms the presence of a local contamination source of PFOS in this area (Naile et al., 2010).  $\Sigma$ PFAS concentration in the two reference lakes (sampling sites 1 and 2) and two reference streams (sampling sites 3 and 14) were much lower ( $<10\ ng\ L^{-1}$ ) than at the contaminated sampling site 5 (4000  $ng\ L^{-1}$ ) indicating that the Stockholm Arlanda Airport is the dominating source of PFASs in this region. With increasing distance from the fire training facility, the  $\Sigma$ PFAS



**Fig. 4.** Temporal trends of PFASs (with a contribution  $>5\%$ ) in water in Lake Halmstön south of Stockholm Arlanda Airport between 2009 and 2013.

concentrations decreased along the stream towards the outlet into the Lake Mälaren (sampling site 18) by a factor of 10–50, i.e. from 4000 to a few hundred nanograms per liter. The same decrease was observed for individual PFASs (Fig. 3). The decreasing water concentrations with increasing distance from the source can be explained by the dilution effect and the partitioning as described in the previous chapter 3.4.



**Fig. 3.** Spatial distribution of PFASs in water around Stockholm Arlanda Airport, Sweden (note: nd = not detected; na = not available).

PFOS water concentrations at sampling sites 5, 9, and 10 were above the Estimated No-Effects Value (ENEV) of 491 ng L<sup>-1</sup> for aquatic organisms (used by Environment Canada and calculated from the NOEC of 49100 ng L<sup>-1</sup> for *Chironomus tentans* (MacDonald et al., 2004) divided by the safety factor of 100). In addition, for almost all sampling sites (i.e., sampling sites H, 1, 3–13, and 15–18) PFOS concentrations were above the proposed Annual Average Environmental Quality Standard (AA-EQS) of 0.65 ng L<sup>-1</sup>, but always below the proposed Maximum Acceptable Concentration (MAC-EQS) of 36000 ng L<sup>-1</sup> under the Water Framework Directive (WFD) of the European Union (EU) (EU, 2011).

To estimate the yearly PFAS fluxes (kg year<sup>-1</sup>) from the catchment to Lake Mälaren, the PFAS concentration at the river outlet to Lake Mälaren (sampling site 18) was multiplied by the yearly water flow of 18 million m<sup>3</sup> year<sup>-1</sup> (Water Information System Sweden (VISS), <http://www.viss.lansstyrelsen.se/>). It should be noted that the estimated yearly PFAS fluxes are subject to uncertainties due to the possible variations in PFAS concentrations in the river throughout the year, which was not covered in our sampling. The yearly PFAS fluxes were estimated to be approximately 5.3 kg year<sup>-1</sup> for ∑PFASs, divided into 2.6 kg year<sup>-1</sup> for PFOS, 1.7 kg year<sup>-1</sup> for PFHxS, 0.6 kg year<sup>-1</sup> for PFHxA, and 0.4 kg year<sup>-1</sup> for PFOA. The PFAS fluxes estimated in this study were considerably lower than the PFAS fluxes estimated for the major European rivers (McLachlan et al., 2007; Möller et al., 2010), which is not surprising considering the relatively low water flow of the catchment.

### 3.6. Temporal trends of PFASs in water

Temporal and seasonal trends were investigated in Lake Halmsjön (sampling site 13) over a time period of five years (2009–2013). ∑PFASs ranged from 146–344 ng L<sup>-1</sup> with PFOS (59–137 ng L<sup>-1</sup>), PFHxS (54–104 ng L<sup>-1</sup>), PFOA (13–80 ng L<sup>-1</sup>), and PFHxA (8.2–34 ng L<sup>-1</sup>) as the dominant compounds (Fig. 4). PFAS concentrations in the two reference lakes (sampling sites 1 and 2) north of Stockholm Arlanda Airport were two orders of magnitude lower, clearly indicating a contamination of Lake Halmsjön from the airport. However, no direct stream connects the fire training facility with Lake Halmsjön, indicating a sub-surface transport of PFASs into the lake. It is interesting to note that the PFAS composition profile close to the point source at the fire training facility (sampling site 5) was different compared to Lake Halmsjön. The contribution of PFOS decreased (60% vs. 40%), whereas the contribution of PFHxS (24% vs. 32%) and PFOA (5% vs. 19%) increased in Lake Halmsjön compared to sampling site 5. The changed composition profile can be explained by the higher sorption potential of PFOS to particles compared to PFHxS and PFOA (Higgins and Luthy, 2006). 6:2 FTSA displayed highest concentrations near the fire training facility (176 ng L<sup>-1</sup>, sampling site 5), but was not detected in Lake Halmsjön. It is likely that 6:2 FTSA is biotransformed to primarily 5:3 acid (F(CF<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>COOH), PFPA, and PFHxA during the sub-surface transport into Lake Halmsjön (Wang et al., 2011).

Although no PFOS- or PFAS-containing AFFFs were purchased after 2003 and 2011, respectively, the PFAS concentrations in Lake Halmsjön showed no significant decreasing trend between 2009 and 2013 ( $p > 0.05$ , ANOVA) (Fig. 4). It is interesting to note that not even PFOS showed a significant decreasing temporal trend ( $p > 0.05$ , ANOVA) despite the phase-out of PFOS-containing AFFFs from 2003. It is interesting to note that the average ∑PFAS concentrations were slightly higher in summer (296 ng L<sup>-1</sup>) compared to spring, autumn and winter periods (254 ng L<sup>-1</sup>, 209 ng L<sup>-1</sup> and 272 ng L<sup>-1</sup>, respectively) (Fig. 4). The low water flow conditions during the dry summer season (0.3 m<sup>3</sup> s<sup>-1</sup>) may diminish the dilution capacity of the river compared to the spring, autumn

and winter periods (0.7–0.9 m<sup>3</sup> s<sup>-1</sup>). However, the PFAS concentrations were relatively constant over time and no significant seasonal trend was observed ( $p > 0.05$ , ANOVA). This indicates that PFASs are still leaching out from the contaminated soil or are slowly transported from contaminated groundwater at the fire training facility. Previous studies have reported elevated PFAS concentrations even after several years of decommissioning of the fire training facility (Moody et al., 2002, 2003). Ultimately, the continued presence of PFASs in Lake Halmsjön may reflect a long-term impact of the AFFF contaminated fire training facility on the nearby environment.

### 3.7. Implications

PFASs are transported from the contaminated area at Arlanda airport through the watercourse towards Lake Mälaren. The contamination of Lake Mälaren is of concern since the water is used by ~2 million people in the Stockholm area as drinking water. The outgoing fluxes into Lake Mälaren from Arlanda airport of ∑PFAS fluxes are estimated to be ~5.3 kg year<sup>-1</sup>, of which PFOS represents approximately 50% (2.6 kg year<sup>-1</sup>). This can be compared to the estimated atmospheric deposition of PFOS to Lake Mälaren (1.5–5.3 kg year<sup>-1</sup>), based on the measured concentration in precipitation on the Swedish west coast (2.2–7.7 ng L<sup>-1</sup>) (Woldegiorgis et al., 2006), the average annual precipitation rate at Arlanda (0.6 m<sup>3</sup> m<sup>-2</sup>, average 1979–2012, SMHI database, <http://luftwebb.smhi.se/>) and the total surface area of Lake Mälaren (1140 km<sup>2</sup>). PFASs may also enter the lake through other pathways, such as riverine inflow and via stormwater and effluent water from municipal and private treatment plants, but the magnitude of such releases is not known.

PFAS concentrations in the water phase of Lake Halmsjön did not show a decreasing trend over a time period of five years (2009–2013) which indicates that Stockholm Arlanda Airport may be an important source for long-term contamination of the nearby environment with PFASs. PFASs can sediment or bioaccumulate in the food chain depending on their chain length and functional group (see field-based  $K_d$  and BCF in Table 1). Generally, shorter-chained PFASs (perfluoroalkyl chain length of C < 8) are mainly transported in the water phase, whereas longer-chained PFASs (perfluoroalkyl chain length of C ≥ 8) have a higher potential to partition to particles and accumulate in the food chain. More studies on the whole body burden of PFASs in different species are needed for a better toxicology and risk assessment. In addition, the ecotoxicological and human impact of other PFASs (e.g., shorter chain PFASs) needs to be investigated (Möller et al., 2010) and more research on the multimedia distribution of PFASs is needed for a better understanding of the fate of PFASs in the environment. PFAS-containing AFFFs are used worldwide by commercial, public, and military fire-fighting organizations. Although most airports are now using PFOS-free AFFFs, many of these AFFF products still contain high amounts of PFASs. Alternative fluorine-free FF-AFFFs are available to be used against hydrocarbon-fuel fires (Schaefer et al., 2008), but due to the lack of legal restrictions, PFAS-containing AFFFs are still being used or stockpiled and pose a potential threat for the environment, for example for human drinking water reservoirs.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.03.136>.

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