Seasonal trends of per- and polyfluoroalkyl substances in river water affected by fire training sites and wastewater treatment plants

Minh A. Nguyen [a], Karin Norström [b], Karin Wiberg [a], Jakob Gustavsson [a], Sarah Josefsson [a,c], Lutz Ahrens [a,*]

[a] Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences (SLU), Box 7050, SE-75007, Uppsala, Sweden
[b] Swedish Environmental Protection Agency, 10648, Stockholm, Sweden
[c] Geological Survey of Sweden, Box 670, SE-75128, Uppsala, Sweden

HIGHLIGHTS

- PFAS levels were impacted by WWTPs and airports in two river catchments.
- PFAS concentrations were significantly correlated to TOC at two sites.
- Seasonal trends of PFASs were impacted by mobilization/dilution processes.
- Average loads of PFASs to Lake Mälaren were dominated by PFHxS and PFOS.

GRAPHICAL ABSTRACT
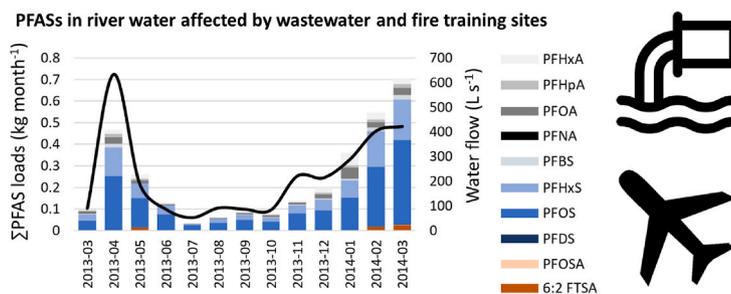
ARTICLE INFO

ABSTRACT

Fire-fighting training areas and wastewater treatment plants (WWTPs) are potential sources of per- and poly-fluoroalkyl substances (PFASs) to the nearby aquatic environment. This study investigated seasonal variations of PFAS levels in two river catchments in Sweden; one impacted by Stockholm Arlanda Airport (Sites 1 and 2), and the other by WWTPs and a military airport (Uppsala) (Sites 3 and 4). $\sum$PFAS concentrations were up to 61 (Sites 1 and 2) and 4 (Sites 3 and 4) times higher compared to the reference site. Distinct different seasonal trends were observed in the two catchments with higher $\sum$PFAS concentrations during the high water flow season at Site 1 compared to the low water flow season, whereas Sites 3 and 4 showed an inverse seasonal trend. This demonstrates that the pollution is mobilized during periods of high flow in the first catchment (Stockholm Arlanda Airport), while it is diluted during high flow in the second catchment (Uppsala). Average annual loads for $\sum$PFASs were estimated at ~5.2 and ~3.7 kg yr^{-1} for the catchment in Uppsala and Stockholm Arlanda Airport, respectively. Thus, both catchments add PFASs to Lake Mälaren, which is Sweden's most important source area for drinking water production.

1. Introduction

Since the 1950s, per- and polyfluoroalkyl substances (PFASs) have been used extensively in various applications such as paper, textile and aqueous fire-fighting foams (AFFFs) (Buck et al., 2011) due to their functional and economic values. High concerns for human health and wildlife have resulted in bans or restrictions of some PFASs due to their extreme persistence, bioaccumulation potential, and toxicity (Giesy et al., 2010; Martin et al., 2003). For instance, perfluorooctanesulfonate (PFOS) has been listed as a persistent organic pollutant (POP) under the Stockholm Convention since 2009 (Stockholm Convention, 2009), and perfluorooctanoate (PFOA) and perfluorononanoate (PFNA) are on the European chemicals agency (ECHA) candidate list (ECHA, 2013) for substances of very high concern. After the bans of many C_8-based PFASs in 2009, the production and applications of PFAS products have shifted towards short-chained PFASs and PFAS precursors (Ahrens, 2011; Martin et al., 2003; Möller et al., 2010). Short-chained perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs) are more mobile and water soluble, whereas long-chained PFCAs and PFSAs are more strongly bound to particles and sediment (Chen et al., 2015; Zhao et al., 2014, 2016). Thus, short-chained PFCAs and PFSAs are more mobile and, for example, pose a higher risk for groundwater contamination (Sharma et al., 2016), while long-chained PFCAs and PFSAs have a higher potential to accumulate in sediments and food webs (Chen et al., 2015; Zhao et al., 2014, 2016).

PFASs can be emitted from point sources, such as firefighting training sites (Dauchy et al., 2017; Houtz et al., 2013) and wastewater treatment plants (WWTPs) (Ahrens et al., 2015; Becker et al., 2008), or derive from diffuse sources (e.g. atmospheric deposition, surface run-off, dispersal from contaminated sediments) (Kim and Kannan, 2007; Taniyasu et al., 2013; Zhao et al., 2014). After the release of PFASs into the environment, they can distribute in terrestrial (Baduel et al., 2017; Filipovic et al., 2015) and aquatic environments (Filipovic et al., 2013; Möller et al., 2010; Sharma et al., 2016). Since the turn-over time of river water is short (Allaby, 1998), levels of pollutants in rivers respond to changes in hydrology or pollution source strength quickly. There are only a few studies published about seasonal changes of PFASs in the aquatic environment (Ahrens et al., 2015; Gago-Ferrero et al., 2017; Zhao et al., 2015; Zhu et al., 2015) and the impact on drinking water source areas (Banzhaf et al., 2017; Gyllenhammar et al., 2015; Hu et al., 2016). More studies are needed on the impact of PFAS point sources on drinking water reservoirs during different seasons.

The aim of this study was to investigate seasonal changes and spatial distribution of PFASs in two catchments potentially impacted by point sources. Surface water samples were collected monthly over a period of one year in two catchments in Sweden, including i) Uppsala catchment area, impacted by a fire training facility at a military airport and WWTPs, and ii) Stockholm Arlanda Airport catchment area, impacted by a fire training facility. The selected study areas are of particular interest because the catchment water is discharged into Lake Mälaren, which is the largest drinking water source in Sweden, serving ~2 million people (~20% of the Swedish population).

2. Materials and methods

2.1. Chemicals

The target analytes ($n = 12$) included the PFCAs with a perfluorocarbon chain length of C_5–C_{10} (i.e. perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), and perfluoroundecanoic acid (PFUnDA)), C_4, C_6, C_8, and C_{10} PFSAs (i.e. perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluorooctanesulfonic acid (PFOS), and perfluorodecanesulfonic acid (PFDS)), 6:2 fluorotelomer sulfonate (6:2 FTSA), and perfluorooctanesulfonamide (PFOSA). Two mass-labelled

internal standards (ISs) were used [$^{13}C_4$]-PFOS and [$^{13}C_4$]-PFOA to correct for sample preparation losses. All reference compounds were purchased from Wellington Laboratories, Ontario, Canada. More details about the analyzed PFASs are given in Table S1 in the Supporting Information (SI).

2.2. Sampling

Water samples were collected monthly at five different locations in Sweden, from February 2013 to March 2014 (Fig. 1; Table S2 in SI). Two of the sampling sites (Sites 1 and 2) were located in the Märsta River, which drains the catchment of Stockholm Arlanda Airport (Sweden's main airport), with Site 1 located ~3 km downstream the main fire-fighting training area and Site 2 located ~5 km downstream Site 1, with no other obvious PFAS point sources located between them. PFAS-containing AFFFs were frequently used at the fire-fighting training area at the Stockholm Arlanda Airport from the 1980s to 2011 (Ahrens et al., 2015; Norström et al., 2015). In 2011, the PFAS-containing AFFFs were replaced by fluorine-free AFFFs (Moussol FF 3/6, Dr. Richard Sthamer GmbH & Co. KG, Hamburg, Germany) (Ahrens et al., 2015). However, due to long term usage of fluorine-containing AFFF, surrounding areas have been contaminated with PFASs (Ahrens et al., 2015).

The second catchment area is located in the municipality of Uppsala (population ~200 000 inhabitants), with three sampling sites in the Fyris River (Fig. 1). Site 3 was located just downstream a military airport (Ärna-Uppsala Airport), where PFAS-containing AFFF was used at the fire training site until 2003 (Gyllenhammar et al., 2015). Site 4 was located downstream of Site 3 and downstream the main WWTP of Uppsala (160 000 population equivalents, Kungsängsverket WWTP). Site 5 was a reference site, located in a relatively pristine area upstream of Uppsala city and thus upstream of Sites 3 and 4. The reference site is, however, impacted by a small WWTP located ~20 km upstream (6400 population equivalents), and also by residential on-site sewage treatment facilities (OSSFs) discharges (Gago-Ferrero et al., 2017).

Samples were collected in pre-cleaned (methanol) 1 L polypropylene (PP) bottles, and the bottles were rinsed three times with river water prior to sampling. Directly after sampling, the bottles were stored dark at 4 °C until analysis, which was conducted within four weeks from sampling. Duplicate samples were taken at Site 4 during three consecutive months (March, April, May 2013). Water temperature, total organic carbon (TOC) and pH data were obtained from the SLU database (SLU, 2022), which reports from one site in the Märsta River (at the river outlet in Märsta) and at three sites in the Fyris River (Klastorp, Vindbron and Lena Kyrka), while water flow data were collected from the Swedish Meteorological and Hydrological Institute (SMHI, 2022) (detailed data and sampling location information is included in Table S2 in SI). Seasonal flow patterns during February 2013 to April 2014 could be seen for all streams and rivers included, with low flow values during March and July–October 2013 and higher flows from November 2013 until spring flood. During spring flood event (April 2013 and February–March 2014), flows for all streams reached their highest values.

2.3. PFAS analysis

Water samples were filtered using pre-cleaned (heated to 400 °C overnight) glass microfiber filters (Whatman GF/C; diameter 47 mm, 1.2 µm pore size) to remove particles. The filters were extracted with 5 mL methanol for 30 min in ultrasonic bath, and the extracts were then combined with the filtered water before further treatment. Thus, the analysis included the total amount of PFASs in the water (dissolved + particulate). Each sample was spiked with 30 ng absolute IS ($^{13}C_4$-PFOS and $^{13}C_4$-PFOA), followed by solid phase extraction (SPE) using Oasis weak anion exchange (WAX) cartridges (Waters, 150 mg, 6 mL, 30 µm) as described previously (Ahrens et al., 2015; ISO, 2009). All samples were analyzed using high performance liquid chromatography (HPLC, Shimadzu CBN-20A, Japan) coupled to negative electrospray ionization
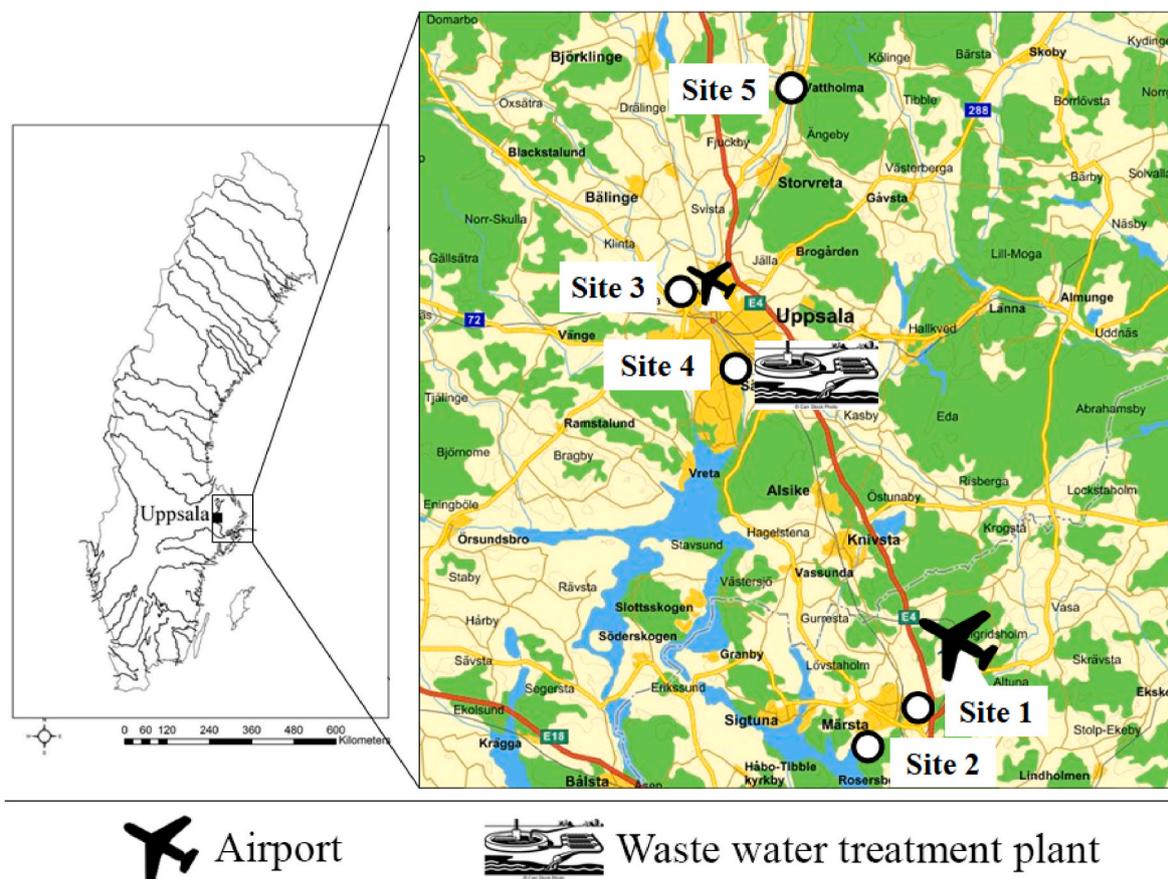
Fig. 1. Locations of the five sampling sites in the Stockholm-Uppsala region in Sweden, with four located nearby airports and wastewater treatment plants (1–4) and one reference site (5).

tandem mass spectrometry (ESI-MS/MS, API 4000, AB Sciex, Foster City, CA, USA). The isotope dilution method was applied for quantification of the individual PFASs. The method detection limits (MDLs) were calculated from batch measurements (3 × standard deviation (σ)/sample volume). The MDLs ranged from 0.1 to 25 ng L^{-1} (Table S3 in SI). The average standard deviation of the duplicate samples was generally below 20%. Details about the instrumental method and analytical performance are given elsewhere (Ahrens et al., 2015).

2.4. Data treatment and statistical analysis

Loads of PFASs (kg month^{-1}) for each site were calculated by using average monthly flow (L s^{-1}) and concentrations of PFASs (ng L^{-1}) (Table S4 in SI). Loads of PFASs (kg yr^{-1}) for the Fyris and Märsta River were calculated using average yearly flow (L s^{-1}) and concentrations of PFASs (ng L^{-1}) at Site 4 and Site 2, respectively, i.e. the sites furthest downstream. Pearson correlation was used for statistical evaluation to assess relationships between concentrations of PFASs and environmental parameters (water flow and TOC content). In the statistical analyses, all included variables were log$_{10}$ transformed to reduce the skewness of data. Individual PFASs with detection frequencies <50% (per site) were not included in the statistical analyses.

3. Results and discussion

3.1. Impact of fire training sites and WWTPs on PFASs in river water

Ten out of the 12 analyzed PFASs were detected in at least one sample from the five sampling sites. The ΣPFAS concentrations in the river water at the 5 sites ranged from 0.86 to 620 ng L^{-1} (average 130 ±

160 ng L^{-1}; median 23 ng L^{-1}; $n = 67$). The highest average ΣPFAS concentrations were found in the area of Stockholm Arlanda Airport at Site 1 (390 ± 110, $n = 13$, ~3 km from the airport fire-fighting training area) and further downstream at Site 2 (220 ± 70 ng L^{-1}, $n = 14$). The overall average ΣPFAS concentration in the catchment impacted by Stockholm Arlanda Airport (300 ± 120 ng L^{-1} at Site 1 and 2; $n = 27$) was a factor of 16 higher than in the Uppsala municipality area (19 ± 13 ng L^{-1} as an average for Sites 3 and 4; $n = 28$). The lowest average ΣPFAS concentration was found at the reference site (Site 5; 6.4 ± 8.7 ng L^{-1}; $n = 14$; Fig. 2 and Table S5 in SI). A previous seasonal trend study of PFAS levels in the same catchment in Uppsala with less frequent sampling ($n = 4$ over one year), but with more sampling sites downstream the main WWTP ($n = 7$) showed a clear impact from the main WWTP on the river water levels of PFASs with gradually lower values downstream the plant (Gago-Ferrero et al., 2017). Alltogether, these observations demonstrate a substantial impact from PFAS-related activities at airports (i.e. Stockholm Arlanda Airport and Ärna-Uppsala Airport) and from WWTP effluents (Uppsala community) on the levels of PFASs in the receiving catchment with levels above typical background levels (Site 5; Fig. 2 and Table S5 in SI). It should, however, be noted that Gago-Ferrero et al. (2017) concluded that although PFAS levels were elevated downstream WWTPs, the elevation was less distinct than for most other substance groups studied (e.g. pharmaceuticals), demonstrating that PFASs has additional sources and entry pathways into the aquatic environment than e.g. pharmaceuticals.

The ΣPFAS concentrations at Sites 1 and 2 (on average 390 ± 110; $n = 13$; and 220 ± 70 ng L^{-1} at Site 2; $n = 14$) showed comparable levels to those reported in previous studies on PFASs in surface water located nearby AFFF contaminated sites, with $\sum$PFAS concentrations ranging from a couple of hundreds to thousands ng per liter (Ahrens et al., 2015;
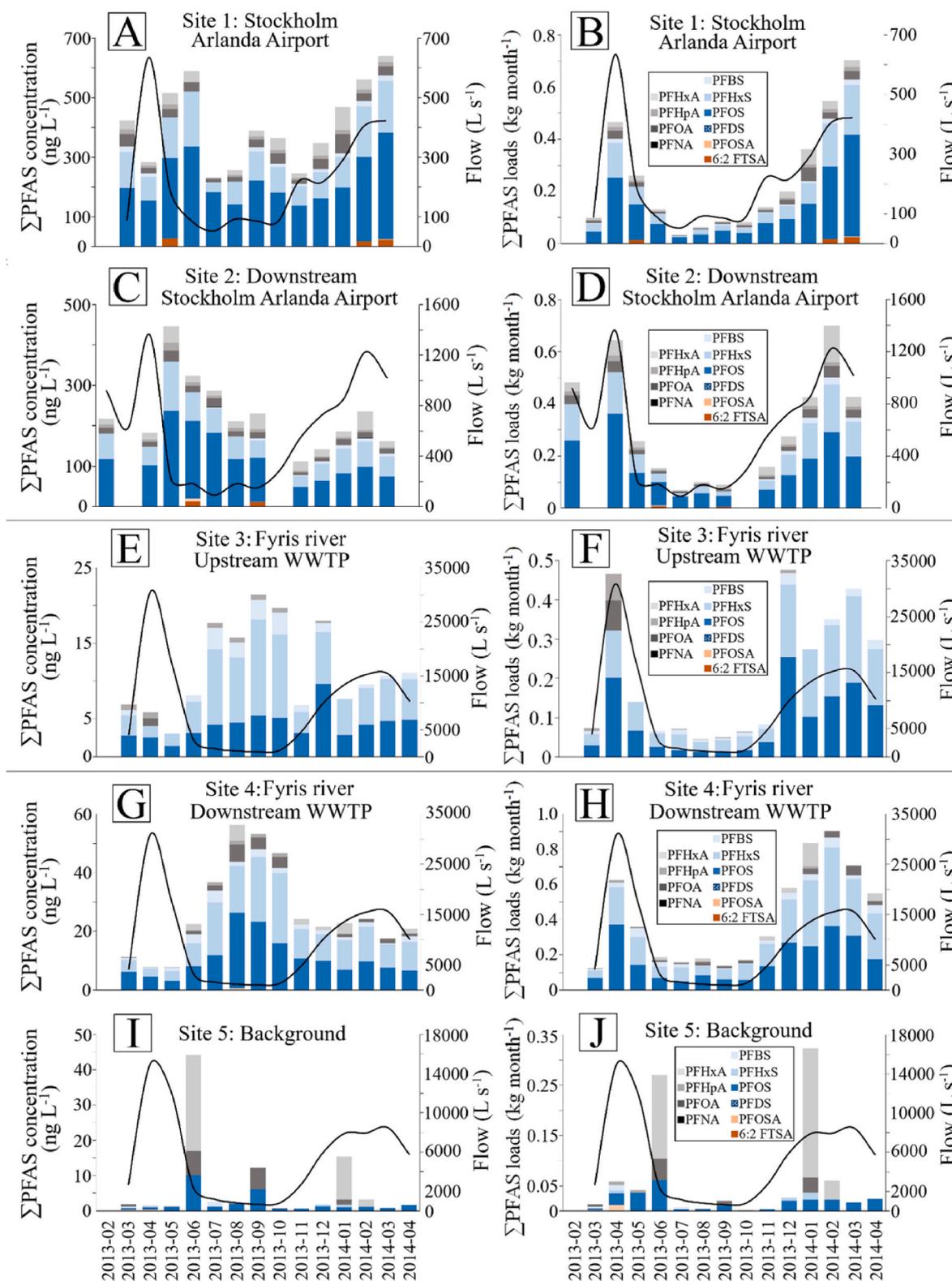
Fig. 2. ΣPFAS concentrations (ng L⁻¹) and loads (kg month⁻¹) plotted against flow (L s⁻¹) at A-B) Site 1 (Märsta River ~3 km downstream Stockholm Arlanda Airport), C-D) Site 2 (Märsta River ~8 km downstream Stockholm Arlanda Airport), E-F) Site 3 (Fyris River, upstream WWTP), G-H) Site 4 (Fyris River, downstream WWTP), and I-J) Site 5 (Fyris River, background site) from February 2013 to April 2014.

Kärrman et al., 2011; Solla et al., 2012). The PFAS composition profiles at the sites affected by the fire-fighting training area at Stockholm Arlanda Airport (Sites 1 and 2) were dominated by PFOS (~52% of the ΣPFAS concentration), followed by PFHxS (~26%), PFHxA (~9.0%) and PFOA (~6.9%) (Fig. 3). Similar predominance of PFOS (~36% of the

ΣPFAS) and PFHxS (29%) were reported previously for surface water sampled near the same airport (Ahrens et al., 2015). The composition profiles observed in the current study also agree with those found in other studies conducted in catchments near fire-fighting training areas in France and Canada (Awad et al., 2011; Dauchy et al., 2017). The
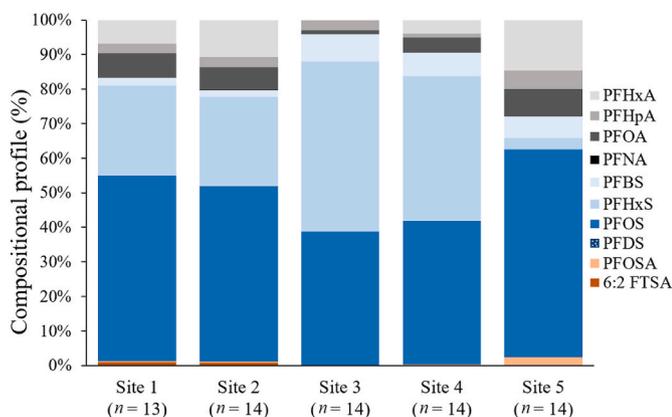
Fig. 3. Average composition profile of detected PFASs at Sites 1–5.

precursor 6:2 FTSA had a low contribution to the $\sum$PFAS at Sites 1 and 2 (~0.8%) and negligible contribution at Sites 3 and 4 (Fig. 3). This suggests that PFHxA detected at Sites 1 and 2 (6.9–11% of the $\sum$PFAS) may originate from degradation of 6:2 FTSA, which has been detected frequently at AFFF impacted fire training areas previously (Backe et al., 2013; Houtz et al., 2016; Schultz et al., 2004). The degradation of 6:2 FTSA to PFHxA has been suggested in a previous study by Wang et al. (2011).

The $\sum$PFAS concentrations in the Fyris River found in this study (average 11 ± 5.0 ng L^{-1} at Site 3; $n = 14$ and 26 ± 15 ng L^{-1} at Site 4; $n = 14$) were comparable to other outgoing water from WWTPs in Sweden or surface water impacted by WWTP effluents in other countries (Llorca et al., 2012; Swedish EPA, 2019). The $\sum$PFAS concentrations in effluent water of 9 WWTPs in Sweden (Ryaverket, Nolhaga, Umeå, Henriksdal, Gässlösa, Ellinge, Bollebygd, Borlänge and Bergkvara) ranged from 14 to 136 ng L^{-1} (Swedish EPA, 2019). In other countries, $\sum$PFAS concentrations in surface water impacted by WWTP effluents ranged from non-detected up to 2900 ng L^{-1} (average 180 ng L^{-1}) in Spain (Llorca et al., 2012) and from non-detected up to 88 ng L^{-1} (average 21 ng L^{-1}) in Germany (Llorca et al., 2012). In comparison to sites impacted mainly by application of AFFFs, the WWTP-impacted Site 4 showed a different composition profile, with PFHxS (~42%) and PFOS (~41%) being equally dominant. Generally, there was a higher percentage of short-chained PFASs (e.g., average of PFHxS 42% and PFBS 6.7% of the $\sum$PFASs; $n = 14$) in comparison to the highly AFFF impacted sites (Sites 1 and 2; average PFHxS 26% and PFBS 2.1%; $n = 27$) (Fig. 3). If assuming the AFFF impacted sites reflect historical PFAS sources and that WWTPs reflect more recent inputs, these observations confirm a shift from C$_8$-based PFASs towards more short-chained species, which was also suggested in other studies (Ahrens, 2011; Martin et al., 2003; Möller et al., 2010).

3.2. Seasonal trends of PFAS concentrations in river water

The PFAS concentrations showed distinct but different seasonal trends at the sampling sites (Fig. 2). At the site most impacted by AFFFs (Site 1, Stockholm Arlanda airport), $\sum$PFAS concentrations were a factor of 1.5 higher during the spring flood events (April 2013 and Feb–March 2014), with on average 490 ± 150 ng L^{-1} compared to the low flow season (July–October 2013), with on average 310 ± 50 ng L^{-1} (Fig. 2A). PFASs concentrations at this site tended to follow the changes in river water flow, i.e. PFAS concentrations were higher when the flow was higher (Fig. 2A). One reason for this may be the mobilization of PFASs during periods of high flow. For example, during the spring flood period, snow melt and elevated groundwater table can result in a mobilization of PFASs from contaminated upper soil layers near the fire training area and subsequent subsurface flow to the nearby water systems. Previous studies have shown that PFASs associated to soil can be

mobilized by surface runoff (Kim and Kannan, 2007) and sub-surface groundwater transport (Ahrens et al., 2015; Houtz et al., 2013) and subsequently transported into streams and rivers. However, during the extreme high water flow event in April 2013, the $\sum$PFAS concentration in water at Site 1 decreased from March to April from 410 ng L^{-1} to 320 ng L^{-1}, whereas the $\sum$PFAS concentration one month later (May 2013) was higher with 420 ng L^{-1} (Fig. 2A). Also at Site 2, the PFAS concentration increased in May compared to April (Fig. 2C). The delayed increase of PFAS levels one month after the water flow peak could be an indication that the mobilization of PFASs was delayed due to the slow transport of the water in the PFAS contaminated soil. The slow mobilization of PFASs from groundwater has also been observed in a previous study (Filipovic et al., 2015) at a pristine catchment area where leaching of PFASs into the nearby stream water was found to originate from PFASs in soil from the atmospheric deposition years to decades ago.

Seasonal trends in the Fyris River (Sites 3 and 4) were clearly different from Site 1, with lower $\sum$PFAS concentrations (two-fold for Site 3 and three-fold for Site 4) during high flow season (spring flood, April 2013 and Feb–March 2014). The average $\sum$PFAS concentration was 8.5 ± 2.8 ng L^{-1} at Site 3 and 17 ± 7.8 ng L^{-1} at Site 4 compared to the low flow season (July–October 2013) with an average $\sum$PFAS concentration of 18 ± 2.0 ng L^{-1} at Site 3 and 47 ± 8.6 ng L^{-1} at Site 4 (Fig. 2E and G; Table S5 in SI). Gago-Ferrero et al. (2017) measured 44 organic micropollutants (pharmaceuticals, PFASs, illicit drugs, artificial sweeteners, pesticide, stimulants, and personal care products) in Fyris River during one year (every third months; $n = 4$) and reported a similar seasonal pattern, with higher levels in September and on average > 10 times lower levels in March (Gago-Ferrero et al., 2017). One reason for lower concentrations during periods of high flow might be dilution during high flow events without extra inputs of pollution. Thus, more or less constant inputs from the sewage treatment facilities (WWTPs and OSSFs) appear to be main sources. The $\sum$PFAS concentrations were significantly negatively correlated with the water flow at Sites 3 and 4 ($p < 0.05$ and $p < 0.001$, respectively; Fig. 4 and Table S6 in SI), i.e. both up- and downstream the main WWTP. A significant negative correlation was found also for Site 2 ($p < 0.05$), while no significant correlation was found for Site 1 (Fig. S1 in SI). Another reason for the differences observed between Fyris River (Sites 3 and 4) and Arlanda Airport (particularly Site 1) might be that the Fyris River is impacted by a constant flow of PFAS-contaminated groundwater, which is more dominant during the summer when the flow in Fyris River is low.

Site 2, located downstream Site 1, displayed seasonal trends with similarities to both Site 1, on one hand, and Sites 3 and 4, on the other hand (Fig. 2C). The PFAS concentrations tended to follow the flow, with concentration peaks when flow was at maxima, similar to Site 1. However, concentrations were, on average, higher during low flow season, although not as markedly as for Sites 3 and 4. The average $\sum$PFAS concentration during low flow season (July–October 2013) at Site 2 was 240 ± 18 ng L^{-1}, while during high flow season (spring flood April 2013 and Feb–March 2014), it was 200 ± 18 ng L^{-1}.

The seasonal trends of PFAS concentrations at the background Site 5 were less distinct than at Sites 1–4 with an average $\sum$PFAS concentration of 3.4 ng L^{-1} ($n = 8$) during high flow season (March–May 2013 and December 2013 to March 2014) and 3.7 ng L^{-1} ($n = 5$) during low flow season (July–November 2013), except June 2013, with a $\sum$PFAS concentration of 44 ng L^{-1} (Fig. 2).

The TOC content and ΣPFAS concentrations were significantly positively correlated at Site 1 ($R = 0.59$, $p < 0.05$), while negatively correlated at Site 4 ($R = -0.81$, $p < 0.001$) (Table S6 in SI; no significant correlation at Sites 2 and 3). Positive correlation between PFAS and TOC levels in river water has been demonstrated previously (Nguyen et al., 2017; Pereira et al., 2018) and indicates binding to organic matter and co-transport of organic matter and PFASs. This difference could potentially be attributed to differing compositional profiles at Sites 1 and 4. At Site 1, the fraction of PFASs with a perfluorocarbon chain of 8 or longer was higher (54%) than at Site 4 (44%) (Fig. 3). PFASs with longer

A Site 2 (downstream Stockholm Arlanda Airport)

$y = -0.21x + 2.9$
$R = -0.61$
$p < 0.05$

B Site 3 (Fyris river, upstream WWTP)

$y = -0.29x + 2.1$
$R = -0.73$
$p < 0.05$

C Site 4 (Fyris river, downstream WWTP)

$y = -0.42x + 2.9$
$R = -0.80$
$p < 0.001$
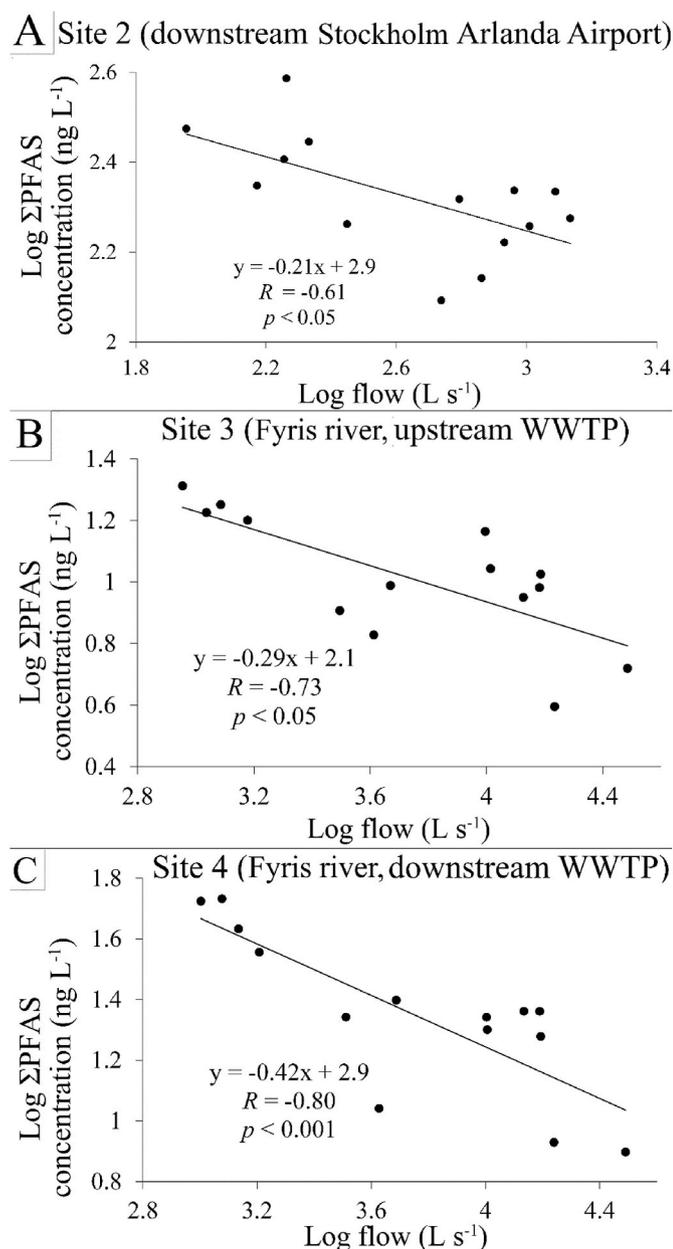
Fig. 4. Log flow ($L\ s^{-1}$) plotted against log ΣPFAS concentration (ng L^{-1}) at A) Site 2 (downstream Stockholm Arlanda Airport), B) Site 3 (Fyris River, upstream WWTP), C) Site 4 (Fyris River, downstream WWTP). For Site 1, see Fig. S1 in SI.

perfluorocarbon chains sorb more efficiently to organic carbon and particles, and are more likely to be co-transported and mobilized together with organic matter in the catchment (Arp et al., 2006; Du et al., 2014; Guelfo and Higgins, 2013; Higgins and Luthy, 2006; Zhao et al., 2016)). Short-chained PFASs, on the other hand, have higher potential to dissolve in water than long-chained PFASs (Zhao et al., 2016), thus the short-chained PFASs have higher potential to be mobilized and transported into the aquatic environment. Although the PFAS composition profiles varied between the sites in this study, the PFAS patterns were similar during the different seasons and more data are needed to elucidate the transport mechanisms of PFASs.

3.3. PFAS loads into the drinking water source area Lake Mälaren

Märsta River (Sites 1 and 2) and Fyris River (Sites 3–5) are two out of

twelve main tributaries for Lake Mälaren (Persson, 2001), which is the third largest lake in Sweden (14 km^3) (SMHI) and also the main drinking water source in Sweden, serving ~2 million inhabitants. Thus, to assure safe drinking water, it is necessary to monitor and prevent chemical pollution. ∑PFAS loads (kg $month^{-1}$) showed a common seasonal trend at all sites except at the reference site (Fig. 2), which is not surprising considering the importance of the flow for the load. The average load of ΣPFASs during low flow season was 0.094 ± 0.047 kg $month^{-1}$ ($n = 15$), while during high flow season it was 0.58 ± 0.16 kg $month^{-1}$ ($n = 12$) for Sites 1 to 4 (Fig. 2B, D, 2F, 2H).

The average annual load (kg yr^{-1}) of PFASs was calculated for Märsta River (Site 2, $n = 12$) and Fyris River (Site 4, $n = 14$) using seasonal load data. The average annual load of ∑PFASs to Lake Mälaren from these two rivers was estimated to be ~5.2 kg yr^{-1} for Fyris River and ~3.7 kg yr^{-1} for Märsta River (Fig. 2). Albeit Märsta River has a significantly lower water flow (average flow from February 2013 to March 2014: 600 ± 430 L s^{-1}) compared to Fyris River (average 9300 ± 8600 L s^{-1}), the annual ∑PFASs load from Märsta River was only 29% lower than that of Fyris River due to the high PFAS contamination level of Märsta River. The compounds with the highest contributions to ΣPFAS loads in Märsta and Fyris rivers were PFOS (1.8 kg yr^{-1} and 2.2 kg yr^{-1}, respectively) and PFHxS (0.98 kg yr^{-1} and 2.2 kg yr^{-1}, respectively). The estimated annual load of Σ_{12}PFASs from Märsta River in the current study (3.7 kg yr^{-1}, February 2013 to April 2014) was in the same range as in a previous study from the same location (5.3 kg yr^{-1}) but during a different time period and with a lower sampling frequency ($n = 2$; March and December 2011) (Ahrens et al., 2015). The results show the long-term impact of PFAS-contaminated soil at fire training sites, even long after the use of PFAS-containing AFFF ceased at Stockholm Arlanda Airport in 2011 (Ahrens et al., 2015).

The contribution of the Fyris and Märsta rivers to Lake Mälaren was calculated using the total loads from the two rivers ($\sum$PFASs 5.2 kg yr^{-1} + 3.7 kg yr^{-1}) and the water volume of Lake Mälaren (~14 km^3). The PFAS input per year through these two source pathways would be equivalent to a concentration of 0.64 ng L^{-1} assuming no degradation, uptake, sedimentation etc. This value corresponds to ~0.7% of the $\sum_{11}$PFASs water guideline value in Sweden (90 ng L^{-1}; Swedish Food Agency, 2016). Besides the riverine contribution from these two sources, PFAS pollution in Lake Mälaren also derives from many other sources, such as stormwater, effluents from sewage treatment plants, landfills, other rivers and direct atmospheric deposition (Malnes et al., 2022; Rehrl et al., 2020). The residence time of the water in Lake Mälaren is 2.8 years (Kvarnäs, 2001) and PFASs are extremely persistent, which means that they will circulate in the water, sediment and biota in the lake and eventually end up in the Baltic Sea (Ahrens et al., 2010; Filipovic et al., 2013; Helsinki Commission - Baltic Marine Environment Protection Commission, 2010).

4. Conclusions

ΣPFAS concentrations were up to 61 and 4 times higher at the sites impacted by WWTPs and a military airport (Uppsala), and Stockholm Arlanda Airport, respectively, compared to the reference site. This shows that airport fire-fighting training areas and WWTPs are important point sources for PFASs. Distinct different seasonal trends were observed in the two catchments showing that the release and mobilization of PFASs from contaminated areas is a complex process depending on factors such as levels and composition profiles of the PFAS contamination, hydrological events/conditions, topography, soil type and permeability (or non-permeability) of the upper surface soil layer. The average annual load of $\sum$PFASs to Lake Mälaren from the two studied rivers was estimated to be ~5.2 kg yr^{-1} for Fyris River and ~3.7 kg yr^{-1} for Märsta River. The results show that both rivers add PFASs to Lake Mälaren, which is the main drinking water source in Sweden, serving ~2 million inhabitants. A better understanding of the sorption and re-mobilization of PFASs in soil is needed to predict the release of PFASs from PFAS

contaminated soil and groundwater over time and space. In addition, the remediation of the contaminated areas and implementation of treatment technologies for removal of PFAS is needed to reduce the risk of PFASs exposure for humans and the environment.

Author statement

Minh A. Nguyen: Methodology, Data curation, Visualization, Validation, Writing - Original draft preparation. **Karin Norström**: Supervision, Writing - Review & Editing. **Karin Wiberg**: Conceptualization, Supervision, Writing - Review & Editing. **Jakob Gustavsson**: Methodology, Data curation. **Sarah Josefsson**: Supervision, Writing - Review & Editing. **Lutz Ahrens**: Conceptualization, Supervision, Validation, Writing - Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2022.136467.

References

Ahrens, L., 2011. Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. J. Environ. Monit. 13, 20–31.

Ahrens, L., Gerwinski, W., Theobald, N., Ebinghaus, R., 2010. Sources of polyfluoroalkyl compounds in the North Sea Baltic Sea and Norwegian Sea: evidence from their spatial distribution in surface water. Mar. Pollut. Bull. 60, 255–260.

Ahrens, L., Norström, K., Viktor, T., Cousins, A.P., Josefsson, S., 2015. Stockholm Arlanda Airport as a source of per- and polyfluoroalkyl substances to water, sediment and fish. Chemosphere 129, 33–38.

Allaby, M., 1998. A Dictionary of Ecology. Oxford University Press, Oxford.

Arp, H.P.H., Niederer, C., Goss, K.-U., 2006. Predicting the partitioning behavior of various highly fluorinated compounds. Environ. Sci. Technol. 40, 7298–7304.

Awad, E., Zhang, X., Bhavsar, S.P., Petro, S., Crozier, P.W., Reiner, E.J., Fletcher, R., Tittlemier, S.A., Braekevelt, E., 2011. Long-term environmental fate of perfluorinated compounds after accidental release at toronto airport. Environ. Sci. Technol. 45, 8081–8089.

Backe, W.J., Day, T.C., Field, J.A., 2013. Zwitterionic, cationic, and anionic fluorinated chemicals in aqueous film forming foam formulations and groundwater from U.S. Military bases by nonaqueous large-volume injection HPLC-MS/MS. Environ. Sci. Technol. 47, 5226–5234.

Baduel, C., Mueller, J.F., Rotander, A., Corfield, J., Gomez-Ramos, M.-J., 2017. Discovery of novel per- and polyfluoroalkyl substances (PFASs) at a fire fighting training ground and preliminary investigation of their fate and mobility. Chemosphere 185, 1030–1038.

Banzhaf, S., Filipovic, M., Lewis, J., Sparrenbom, C.J., Barthel, R., 2017. A review of contamination of surface-, ground-, and drinking water in Sweden by perfluoroalkyl and polyfluoroalkyl substances (PFAS). Ambio 46, 335–346.

Becker, A.M., Gerstmann, S., Frank, H., 2008. Perfluorooctane surfactants in waste waters, the major source of river pollution. Chemosphere 72, 115–121.

Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., De Voogt, P., Jensen, A. A., Kannan, K., Mabury, S.A., Van Leeuwen, S.P.J., 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. Integrated Environ. Assess. Manag. 7, 513–541.

Chen, X., Zhu, L., Pan, X., Fang, S., Zhang, Y., Yang, L., 2015. Isomeric specific partitioning behaviors of perfluoroalkyl substances in water dissolved phase, suspended particulate matters and sediments in Liao River Basin and Taihu Lake, China. Water Res. 80, 235–244.

Convention, Stockholm, 2009. Stockholm Convention on Persistent Organic Pollutants (POPs).

Dauchy, X., Boiteux, V., Bach, C., Rosin, C., Munoz, J.-F., 2017. Per- and polyfluoroalkyl substances in firefighting foam concentrates and water samples collected near sites impacted by the use of these foams. Chemosphere 183, 53–61.

Du, Z., Deng, S., Bei, Y., Huang, Q., Wang, B., Huang, J., Yu, G., 2014. Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents—a review. J. Hazard Mater. 274, 443–454.

ECHA, 2013. In: E.C. (Ed.), Inclusion of Substances of Very High Concern in the Candidate List for Eventual Inclusion in Annex XIV in: Agency. ED/69/2013, Helsinki.

Filipovic, M., Berger, U., McLachlan, M.S., 2013. Mass balance of perfluoroalkyl acids in the Baltic Sea. Environ. Sci. Technol. 47, 4088–4095.

Filipovic, M., Laudon, H., McLachlan, M.S., Berger, U., 2015. Mass balance of perfluorinated alkyl acids in a pristine boreal catchment. Environ. Sci. Technol. 49, 12127–12135.

Gago-Ferrero, P., Gros, M., Ahrens, L., KarinWiberg, 2017. Impact of on-site, small and large scalewastewater treatment facilities on levels and fate of pharmaceuticals, personal care products, artificial sweeteners, pesticides, and perfluoroalkyl substances in recipient waters. Sci. Total Environ. 601–602, 1289–1297.

Giesy, J.P., Naile, J.E., Khim, J.S., Jones, P.D., Newsted, J.L., 2010. Aquatic toxicology of perfluorinated chemicals. Rev. Environ. Contam. Toxicol. 202, 1–52.

Guelfo, J.L., Higgins, C.P., 2013. Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-Impacted sites. Environ. Sci. Technol. 47, 4164–4171.

Gyllenhammar, I., Berger, U., Sundström, M., McCleaf, P., Eurén, K., Eriksson, S., Ahlgren, S., Lignell, S., Aune, M., Kotova, N., Glynn, A., 2015. Influence of contaminated drinking water on perfluoroalkyl acid levels in human serum – a case study from Uppsala, Sweden. Environ. Res. 140, 673–683.

Helsinki Commission - Baltic Marine Environment Protection Commission, 2010. Hazardous Substances in the Baltic Sea: an Integrated Thematic Assessment of Hazardous Substances in the Baltic Sea.

Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments. Environ. Sci. Technol. 40, 7251–7256.

Houtz, E.F., Higgins, C.P., Field, J.A., Sedlak, D.L., 2013. Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil. Environ. Sci. Technol. 47, 8187–8195.

Houtz, E.F., Sutton, R., Park, J.-S., Sedlak, M., 2016. Poly- and perfluoroalkyl substances in wastewater: significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. Water Res. 95, 142–149.

Hu, X.C., Andrews, D.Q., Lindstrom, A.B., Bruton, T.A., Schaider, L.A., Grandjean, P., Lohmann, R., Carignan, C.C., Blum, A., Balan, S.A., Higgins, C.P., Sunderland, E.M., 2016. Detection of poly- and perfluoroalkyl substances (PFASs) in U.S. Drinking water linked to industrial sites, military fire training areas, and wastewater treatment plants. Environ. Sci. Technol. Lett. 3, 344–350.

ISO, 2009. Water Quality – Determination of Perfluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA) – Method for Unfiltered Samples Using Solid Phase Extraction and Liquid Chromatography/mass Spectrometry. ISO/DIS25101 (ISO/ TC147/SC2/WG56).

Kärrman, A., Elgh-Dalgren, K., Lafossas Møskeland, T., 2011. Environmental levels and distribution of structural isomers of perfluoroalkyl acids after aqueous fire-fighting foam (AFFF) contamination. Environ. Chem. 8, 372–380.

Kim, S.-K., Kannan, K., 2007. Perfluorinated acids in air, rain, snow, surface runoff, and lakes: relative importance of pathways to contamination of urban lakes. Environ. Sci. Technol. 41, 8328–8334.

Kvarnäs, H., 2001. Morphometry and hydrology of the four large lakes of Sweden. Ambio 30, 467–474.

Llorca, M., Farré, M., Picó, Y., Müller, J., Knepper, T.P., Barceló, D., 2012. Analysis of perfluoroalkyl substances in waters from Germany and Spain. Sci. Total Environ. 431, 139–150.

Malnes, D., Ahrens, L., Köhler, S., Forsberg, M., Golovko, O., 2022. Occurrence and mass flows of contaminants of emerging concern (CECs) in Sweden's three largest lakes and associated rivers. Chemosphere 294, 133825.

Martin, J.W., Mabury, S.A., Solomon, K.R., Muir, D.C.G., 2003. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (Oncorhynchus mykiss). Environ. Toxicol. Chem. 22, 196–204.

Möller, A., Ahrens, L., Surma, R., Westerveld, J., Wielen, F.v.d., Ebinghaus, R., Voogt, P. d., 2010. Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed. Environ. Pollut. 158, 3243–3250.

Nguyen, M.A., Wiberg, K., Ribeli, E., Josefsson, S., Futter, M., Gustavsson, J., Ahrens, L., 2017. Spatial distribution and source tracing of per- and polyfluoroalkyl substances (PFASs) in surface water in Northern Europe. Environ. Pollut. 220, 1438–1446.

Norström, K., Viktor, T., Cousins, A.P., Rahmberg, M., 2015. Risks and Effects of the Dispersion of PFAS on Aquatic, Terrestrial and Human Populations in the Vincinity of International Airports. IVL report, p. 2232. https://www.ivl.se/download/18 .343dc99d14e8bb0f58b76d0/1445517746360/B2232.pdf (access date: 2020-08-21.

Pereira, H.C., Ullberg, M., Kleja, D.B., Gustafsson, J.P., Ahrens, L., 2018. Sorption of perfluoroalkyl substances (PFASs) to an organic soil horizon - effect of caption compsition and pH. Chemosphere 207, 183–191.

Persson, G., 2001. Phosphorus in tributaries to Lake mälaren, Sweden: analytical fractions, anthropogenic contribution and bioavailability. Ambio 30, 486–495.

Rehrl, A.L., Golovko, O., Ahrens, L., Köhler, S., 2020. Spatial and seasonal trends of organic micropollutants in Sweden's most important drinking water reservoir. Chemosphere 249, 126168.

Schultz, M.M., Barofsky, D.F., Field, J.A., 2004. Quantitative determination of fluorotelomer sulfonates in groundwater by LC MS/MS. Environ. Sci. Technol. 38, 1828–1835.

Sharma, B.M., Bharat, G.K., Tayal, S., Larssen, T., Becanova, J., Karaskova, P., Whitehead, P.G., Futter, M.N., Butterfield, D., Nizzetto, L., 2016. Perfluoroalkyl substances (PFAS) in river and ground/drinking water of the Ganges River basin: emissions and implications for human exposure. Environ. Pollut. 208, 704–713.

Solla, S.R.d., Silva, A.O.D., Letcher, R.J., 2012. Highly elevated levels of perfluorooctane sulfonate and other perfluorinated acids found in biota and surface water downstream of an international airport, Hamilton, Ontario, Canada. Environ. Int. 39, 19–26.

Swedish EPA, 2019. Miljöövervakning Av Utgående Vatten & Slam Från Svenska Avloppsreningsverk. Report, Swedish environmental protection agency (access date: 2020-08-21). http://www.diva-portal.se/smash/get/diva2:1343079/FULLTEXT01.pdf.

SLU, 2022. Department of Aquatic Sciences and Assessment. Swedish University of Agricultural Sciences. https://www.slu.se/institutioner/vatten-miljo/datavardskap/ (access date: 2022-05-03).

SMHI, 2022. Swedish meteorological and hydrological institute. http://vattenwebb.smhi.se/ (access date: 2022-05-03).

Swedish Food Agency, 2016. https://www.livsmedelsverket.se/livsmedel-och-innehall/oonskade-amnen/miljogifter/pfas-poly-och-perfluorerade-alkylsubstanser/riskhantering-pfaa-i-dricksvatten. Accessed 2022-05-03.

Taniyasu, S., Yamashita, N., Moon, H.-B., Kwok, K.Y., Lam, P.K.S., Horii, Y., Petrick, G., Kannan, K., 2013. Does wet precipitation represent local and regional atmospheric transportation by perfluorinated alkyl substances? Environ. Int. 55, 25–32.

Wang, N., Liu, J., Buck, R.C., Korzeniowski, S.H., Wolstenholme, B.W., Folsom, P.W., Sulecki, L.M., 2011. 6:2 Fluorotelomer sulfonate aerobic biotransformation in activated sludge of waste water treatment plants. Chemosphere 82, 853–858.

Zhao, X., Xia, X., Zhang, S., Wu, Q., Wang, X., 2014. Spatial and vertical variations of perfluoroalkyl substances in sediments of the Haihe River, China. J. Environ. Sci. 26, 1557–1566.

Zhao, Z., Xie, Z., Tang, J., Sturm, R., Chen, Y., Zhang, G., Ebinghaus, R., 2015. Seasonal variations and spatial distributions of perfluoroalkyl substances in the rivers Elbe and lower Weser and the North Sea. Chemosphere 129, 118–125.

Zhao, P., Xia, X., Dong, J., Xia, N., Jiang, X., Li, Y., Zhu, Y., 2016. Short- and long-chained perfluoroalkyl substances in the water, suspended particulate matter, and surface sediment of a turbid river. Sci. Total Environ. 568, 57–65.

Zhu, Z., Wang, T., Meng, J., Wang, P., Li, Q., Lu, Y., 2015. Perfluoroalkyl substances in the Daling River with concentrated fluorine industries in China: seasonal variation, mass flow, and risk assessment. Environ. Sci. Pollut. Res. 22, 10009–10018.