



Analysis of ultra-short chain perfluoroalkyl substances in Swedish environmental waters

Ingrid Ericson Jogsten, Leo Yeung
Örebro universitet, Forskningscentrum Människa-Teknik-Miljö (MTM)

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| Report authors Ingrid Ericson Jogsten, Örebro university Leo Yeung, Örebro university | Responsible publisher Örebro university Postal address Fakultetsgatan 1, 701 82 Örebro, Sweden Telephone 019-30 12 09 |
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| Summary The purpose of this study was to investigate the environmental occurrence of ultra-short chain perfluoroalkyl substances (PFASs) in Swedish water samples. So far established protocols have focused on measuring PFASs with a carbon chain length of four or more carbons. In this study, perfluoroalkyl sulfonates of chain lengths of two, perfluoroethane sulfonate (PFEtS), and three, perfluoropropane sulfonate (PFPrS), carbons have been measured using a newly established instrumental method employing supercritical fluid separation (SFC) coupled to tandem mass spectrometry detection. A total of 26 samples were analysed, including ground water, surface water, rain water and snow. The sample locations included military and civilian airports, a former hard chromium plating facility, the vicinity of a hazardous waste management facility and background areas (lake surface water, rain and snow). Results show that both PFPrS and PFEtS could be detected in environmental samples using SFC separation coupled to triple quadrupole detection. Out of the 26 samples analysed, the ultra-short-chain PFPrS could be detected and quantified in 22 samples. The concentrations for PFPrS in all the samples ranged between 0.93 ng/l to 39 000 ng/l. The ultra-short-chain PFPEtS could be quantified in all of the 26 samples, with a concentration range between 0.07 and 5 700 ng/l. The highest concentrations represents highly contaminated ground water samples collected from a military airport. In the samples, PFPrS had a relative contribution to total PFAS concentration of 6 and 10 %, indicating the importance of measuring these compounds in environmental samples. | |

Sammanfattning

Syftet med denna studie var att undersöka huruvida ultrakorta perfluorerade alkylsubstanser (PFASs) förekommer i prov från svenska vatten. Dagens metoder för att analysera PFASs fokuserar på ämnen som har en kolkedja om minst fyra kol. I denna studie har ultrakorta perfluoralkylsulfonater analyserats, mer specifikt perfluorpropansulfonat (PFPrS, C3) och perfluoretansulfonat (PFEtS, C2), med hjälp av en ny separationsmetod som använder superkritisk vätskekromatografi kopplad till masspektrometrisk detektion.

Totalt har 26 vattenprov analyserats omfattande grundvatten, ytvatten, regnvatten och snö. De olika provplatserna har varierat från civila och militära brandövningsplatser, vid en före detta anläggning för hårdkromplätering, omkring en anläggning för farligt avfall, samt bakgrundsprover i form av regnvatten, snö och ytvatten från en sjö. Med den nya metoden kunde de ultrakorta PFAS-ämnena PFPrS och PFEtS uppmätas i prover från svenska vatten för första gången. PFPrS kunde mätas i 22 av totalt 26 prov, och PFEtS kunde mätas i samtliga prov. Halterna för PFPrS varierade mellan 0.93 ng/l till 39 000 ng/l, medan koncentrationen för PFEtS varierade mellan 0.07 och 5 680 ng/l. De högsta halterna härstammar från brandövningsplatser inom ett militärt flygplatsområde. I dessa prover uppgår PFPrS till 6 respektive 10% av totalhalten PFAS, vilket pekar på vikten av att inkludera även ultrakorta PFAS i mätningar av PFAS i miljöprover.

Background

The ubiquitous distribution of perfluoroalkyl substances (PFASs) has been documented worldwide in different environmental samples including humans. Due to their unique properties of repulsion to both oil and water, PFASs have been used for over half a century in a multitude of various products in both industrial and commercial applications. More than 3000 PFASs are estimated to be used on the global market (KEMI, 2015). In Sweden, severe PFAS contamination in drinking water has resulted in elevated blood PFAS concentrations in residents living in contaminated areas (Gyllenhammar). In many cases, the use of aqueous film forming-foams (AFFFs) at both civil and military airports has resulted in this contamination, as PFASs are one of the active ingredients in AFFFs. According to a nationwide survey, it was estimated that 30 % of the Swedish population has their closest drinking water source contaminated with these substances (Livsmedelsverket, 2014). A guideline value for safe use of drinking water set by the Swedish Food Agency is the sum of eleven PFASs including perfluoroalkylated sulfonates (PFASs; C4, C6, C8), perfluoroalkylated carboxylates (PFCAs; C4-C10) and 6:2 fluorotelomer sulfonate. This is set to 90 ng/L, while the health based limit, based on the tolerable daily intake, is set to 900 ng/L.

In the US, Barzen-Hansen et al. (2015) showed the presence of ultra-short chain PFASs, perfluoropropane sulfonate (PFPrS) and perfluoroethane sulfonate (PFEtS), in five AFFFs. In ground water samples from eleven US military bases, PFEtS was detected in eight out of eleven samples ranging from 11-7 500 ng/L, while PFPrS was detected in all samples, ranging from 19-63 000 ng/L). Conventional reversed-phase LC using C18 column is not suitable to chromatograph these ultra-short chain PFAS, because they are highly polar; ion-exchange column has been demonstrated useful for separating these ultra-short chain PFAS, although requiring longer analysis time and broad chromatographic peaks for these compounds (Taniyasu et al., 2008). The chemical structures of PFPrS and PFEtS are depicted in Figure 1.

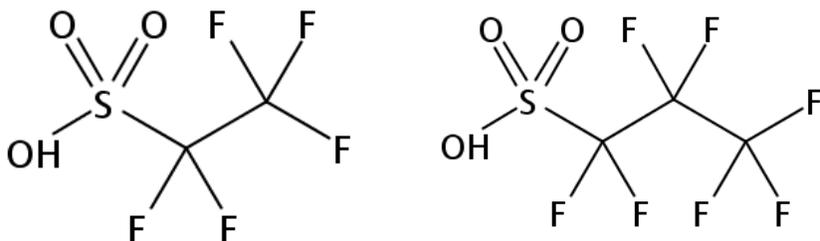


Figure 1. Chemical structures of perfluoroethane sulfonate and perfluoropropane sulfonate.

Aim

The objective of this study was to investigate the environmental occurrence of the ultra-short chain PFASs in Swedish environmental water samples using a new analytical approach (Yeung et al., 2017) employing supercritical fluid chromatography (SFC) for the chromatographic separation of these compounds.

Project administration and coordination

This project has been performed at Örebro University with the project leader responsible for the contact with the Swedish Environmental Protection Agency. Sample collection, preparation and instrumental analysis including data interpretation have been performed by Örebro University.

The following persons have been involved in the project:

Ingrid Ericson Jogsten, Assistant professor

Malin Kvist, student

Maria Björnsdotter, Ph D student

Leo Yeung, Associate professor

Materials and methods

Samples

Environmental samples including surface water, ground water, rain water and snow was included in the study. The samples originated from various locations with suspected PFAS contamination as well as background samples, including civil and military airports, run off from a hazardous waste management site, a former hard chromium plating facility and background samples (lake surface water, rain water and snow). All samples were collected in polyethylene containers. Surface water samples were collected from areas around Sätenäs airport, a creek near Ronneby civil and military airport and Revingehed military training field. Also two high contaminated ground water samples from a military airport had been collected previously and was provided from an environmental consultant company. Note that the storage conditions of these samples are unknown as well as the location. Three ground water samples were collected from former Iggesund hard chromium plating facility, now undergoing remediation. Samples were collected by Golder Associates and sent with ice-packs. Surface water samples from Fortum Waste Solution hazardous waste management facility waste treatment's water outlet and samples following creeks further downstream and nearby lakes were also collected (Figure 2). Surface water samples from areas around two civil airports, Arlanda and Axamo airports (Figure 5), were also included in the study. In addition, one snow and one rain water sample with believed low contamination were collected from Södra Lindhult, Örebro, Sweden. All samples were stored refrigerated until further processing and ultrasonicated before extraction to prevent adsorption during storage.

Extraction and chemical analysis

A volume of 5 to 500 ml water was concentrated using established protocols from the ISO25101 method (ISO, 2009). All samples were filtered using GF/B filters from Whatman, prior to concentration.

Isotopically labeled internal standards were added to monitor the recovery during sample preparation. Solid phase extraction (SPE) Oasis Weak Anion Exchange (WAX) cartridges (Waters Corporation, Milford, USA) were preconditioned with 4 mL 0.1% sodium hydroxide in methanol followed by 4 mL methanol and finally 4 mL of MilliQ water. Water samples were loaded on to the cartridges at a rate of 1 drop per second. Washing of cartridges was performed using 4 mL sodium acetate buffer solution (pH 4), before drying of cartridges. After elution with methanol, fraction not analysed, targeted compounds were eluted with 4 mL 0.1 % ammonium hydroxide in methanol. The extract was reduced in volume by nitrogen evaporation and samples were split to different fractions for analysis using both ultra performance liquid chromatography (UPLC) and ultra performance convergence chromatography (UPC2)

Table 1. Perfluoroalkyl substances (PFASs), their abbreviations, mass transitions for mass spectrometry detection and chromatographic separation method.

| Compound name | Abbreviation | 1 st MRM transition | 2 nd MRM transition | Separation method | Method detection limit (ng/L) |
|--|--------------|--------------------------------|-----------------------------------|-------------------|-------------------------------|
| Perfluorobutanoic carboxylic acid | PFBA | 212.97 > 169.00 | - | UPLC | 2,7 |
| Perfluoropentanoic carboxylic acid | PFPeA | 262.97 > 219.00 | | UPLC | 0.03 |
| Perfluorohexanoic carboxylic acid | PFHxA | 312.97 > 269.00 | 312.97 > 118.95 | UPLC | 0.50 |
| Perfluoroheptanoic carboxylic acid | PFHpA | 362.97 > 319.00 | 362.97 > 168.97 | UPLC | 0.67 |
| Perfluorooctanoic carboxylic acid | PFOA | 412.97 > 369.00 | 412.97 > 168.97 | UPLC | 0.14 |
| Perfluorononanoic carboxylic acid | PFNA | 462.99 > 419.00 | 462.99 > 219.00 | UPLC | 0.24 |
| Perfluorodecanoic carboxylic acid | PFDA | 512.97 > 469.00 | 512.97 > 219.00 | UPLC | 0.09 |
| Perfluoroundecanoic carboxylic acid | PFUnDA | 562.97 > 268.99 | 562.97 > 519.00 | UPLC | 0.06 |
| Perfluorododecanoic carboxylic acid | PFDoDA | 612.97 > 569.00 | 612.97 > 168.96 | UPLC | 0.92 |
| Perfluorotridecanoic carboxylic acid | PFTTrDA | 662.90 > 619.00 | 662.90 > 168.96 | UPLC | 1.0 |
| Perfluorotetradecanoic carboxylic acid | PFTeDA | 712.90 > 669.00 | 712.90 > 168.97 | UPLC | 0.01 |
| Perfluorohexadecanoic carboxylic acid | PFHxDA | 812.90 > 769.00 | 812.90 > 168.96 | UPLC | 0.40 |
| Perfluorooctadecanoic carboxylic acid | PFOcDA | 912.90 > 869.00 | 912.90 > 168.96 | UPLC | 0.40 |
| 4:2 fluorotelomer sulfonate | 4:2FTS | 327.00 > 307.00 | 329.00 > 81.00 | UPLC | 2.4 |
| 6:2 fluorotelomer sulfonate | 6:2FTS | 427.00 > 407.00 | 427.00 > 81.00 | UPLC | 0.13 |
| 8:2 fluorotelomer sulfonate | 8:2FTS | 527.00 > 507.00 | 527.00 > 80.00 | UPLC | 0.03 |
| Perfluoroethane sulfonic acid | PFEtS | 198.80 > 79.80 | - | SFC | 0.06 |
| Perfluoropropane sulfonic acid | PFPrS | 248.90 > 80.00 | - | SFC | 0.43 |
| Perfluorobutane sulfonic acid | PFBS | 298.90 > 79.96 | 298.90 > 98.90 | UPLC | 0.94 |
| Perfluoropentane sulfonic acid | PFPeS | 348.90 > 79.96 | 348.90 > 98.96 | UPLC | 0.86 |
| Perfluorohexane sulfonic acid | PFHxS | 398.90 > 79.96 | 398.90 > 98.90 | UPLC | 0.04 |
| Perfluoroheptane sulfonic acid | PFHpS | 448.97 > 79.96 | 448.97 > 98.90 | UPLC | 2.0 |
| Perfluorooctane sulfonic acid | PFOS | 498.97 > 79.96 | 498.97 > 98.96 498.97 > 169.03 | UPLC | 0.16 |
| Perfluorononane sulfonic acid | PFNS | 548.90 > 79.96 | 548.90 > 98.96 | UPLC | 0.02 |
| Perfluorodecane sulfonic acid | PFDS | 598.97 > 79.96 | 598.97 > 98.90 | UPLC | 0.02 |
| Perfluorododecane sulfonic acid | PFDoDS | 698.90 > 79.96 | 698.90 > 98.90 | UPLC | 0.07 |

coupled to tandem mass spectrometric detection using a Xevo TQ-S (Waters Corporation, Milford, USA). Both chromatographic systems were operated in negative electrospray ionization mode. Gradient separation with UPLC was performed using a 100 mm C18 BEH column (1.7 μ m, 2.1 mm) with 2 mM ammonium acetate mobile phases in water and methanol. Supercritical carbon dioxide mixed with 0.1% ammonium hydroxide was used for supercritical separation on a 150 mm Acquity UPC² Torus DIOL

(3.0 mm × 150 mm, 1.7 μm) column with an injection volume of 2.0 μL. The flow rate was set to 1.3 mL/min for 8 minute gradient separation with supercritical CO₂ and 0.1%NH₄OH in MeOH (co-solvent) mobile phases (initial 5% co-solvent increased to 40 %). The active back pressure regulator (ABPR) was at 1500 psi and the column temperature kept at 40°C.

Multiple reaction monitoring (MRM) was used to monitor both quantification and qualification ions. Note that for perfluorobutane carboxylic acid (PFBA), perfluoropropane sulfonic acid (PFPrS) and perfluoroethane sulfonic acid (PFEtS) only one MRM transition was monitored.

Validation of instrumental method and quality assurance and quality control

Linearity for the instrumental method using supercritical fluid chromatography was assessed by injecting an eight point calibration curve from 0.1 to 100 ng/mL. Linear regression analysis showed good linearity for each analyte (C₂-C₁₄ PFASs; R² > 0.99). The relative standard deviation of repeatability of 5 consecutive of standards was at most 20% at 0.2 ng/mL level and at most 5% at 10 ng/mL level. The instrumental LOQs of target analytes ranged from 0.1-0.5 ng/mL and the method detection limits are reported in Table 1. The instrumental LOQ (amount on column) is 2.5-12.5 times lower compared to the ion exchange column (C₅ and C₆ PFCAs similar instrumental LOQs) but 10 times higher compared to UPLC-MS/MS. Isotopically labelled internal standards were used to monitor potential loss of analytes during extraction. Average recoveries of internal standards ranged between 62 to 117 %, with the majority of internal standards within the 50-120% range and only 12 out of 448 internal standards lower than 20 % or higher than 150%. Blank samples of MilliQ water were extracted with every sample batch analysed and the average of these blanks (detected peaks or baseline peaks) multiplied by three was used as the method detection limit (MDL). To ensure reproducibility for the extraction a spiked sample was prepared for each batch of samples and extracted with the same procedure as the samples, the relative standard deviation was then calculated. For most (18) compounds the RSD was below 10 %, while PFNS, PFTDA and PFHxDA was below 20%; RSD for PFDS and PFTrDA was 26 and 32 % respectively, while PFOcDA and PFDoDS was above 60%.

Results and discussion

In a total of 26 environmental water samples, ultra-short chain perfluoroalkyl sulfonates (PFSAs) could be detected in all samples. Perfluoropropanesulfonate was detected in 22 out of 26 samples with a concentration range from 0.93 to 39 000 ng/L, and a method detection limit (MDL) of 0.45 ng/L. The shortest chain compound, PFEtS, was detected in all samples, ranging from 0.07 ng/L to 5 700 ng/L, having a MDL of 0.06 ng/L. Average concentrations for PFPrS and PFEtS were 2 200 ng/L and 280 ng/L, respectively, while median concentrations were 7.7 ng/L for PFPrS and 0.74 ng/L for PFEtS, illustrating the large variation in contamination at various sampling sites. Concentrations for all PFASs measured in these samples, including ultra-short chain compounds, are given in the Appendix. Most samples are clearly dominated by PFSAs, with PFOS as major component although the contribution of PFOS to sum of all measured compounds varies from 1 to 87%.

The two most contaminated samples were ground water samples originating from fire drill sites at a military airport. These two samples showed distinct dissimilar patterns with regards to distribution of PFSAs, as illustrated in Figure 1.

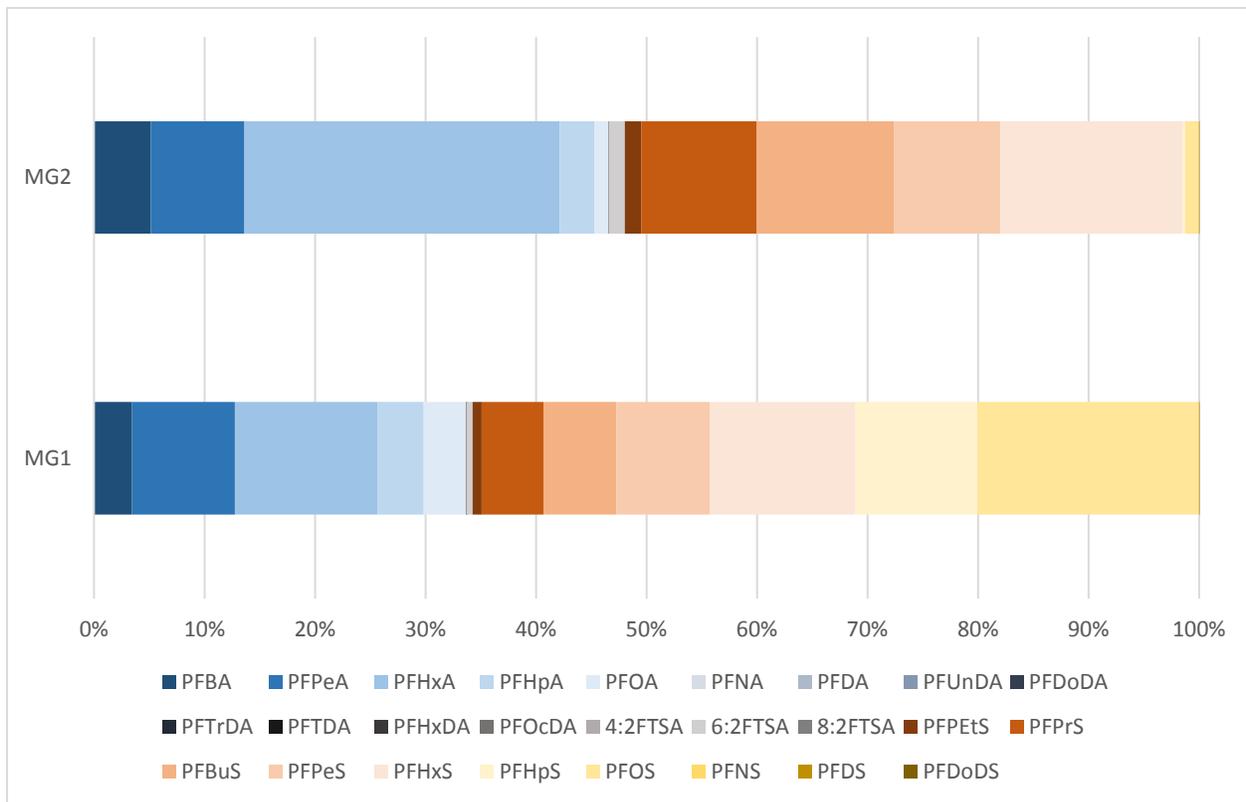


Figure 1. Homologue distribution of perfluoroalkyl sulfonates (PFASs) in ground water samples from a military airport.

The difference in homologue distribution between these samples could be the result of different AFFF formulations used at the different sites although no information is available on specific content of AFFF formulations used at this site. Total PFAS concentrations reached 700 000 ng/L in sample MG1 and 110 000 ng/L in sample MG2. High concentrations of ultra-short chain compounds were also measured in these samples; PFETs had a concentration of 1600 ng/L and 5700 ng/L in sample MG1 and MG2, respectively, while PFPrS could be detected at 39 000 ng/L in MG1 and 11 000 ng/L in MG2. Also seen in Figure 1 is the relative contribution of ultra-short chain compounds. Especially PFPrS has a high relative contribution to the total PFAS concentration of 5.6% and 10% in sample MG1 and MG2, respectively.

In the US, Barzen-Hansen and Fields (2015) reported concentrations for PFETs ranging from 11-7 500 ng/L, with detection in 8 out of 11 samples, while PFPrS concentrations ranged from 19 to 63 000 ng/L, and was detected in all 11 samples. In the same study, these compounds were also measured in aqueous film forming foams. Regards environmental occurrence, a limited number of studies have reported their occurrence in snow, rain and tap water³⁻⁵ at low concentrations (Kwok, et al., 2010, Taniyasu, et al., 2008, Mak, et al., 2009).

A total of ten samples from the surrounding area of Fortum Waste Solution hazardous waste management facility were also analyzed. Sampling points are depicted in Figure 2. Figure 3 illustrates PFASs concentrations of 24 measured compounds in surface water samples in this area. Sample E1 is from a nearby lake not connected to the outlet from the facility, neither is sample E2. However, this sample might be affected by landfill from a smaller local water treatment facility, as was discovered during sampling. Directly at the outlet of waste management facility is sample E3, with samples E4 to E8 following creeks further downstream, and sample E9 and E10 in connected lakes. Noteworthy is that across the road from

sample 10 is a skid pad where local bus companies have had fire drills (personal communication Maria Björnsdotter). Next to the waste management facility are also other industrial sites making the contamination of the area complex. Elevated concentrations of PFOS (up to 750 ng/g) has been reported from Lake Söderhavet (SWECO, 2016).



Figure 2. Sampling points in the area around Fortum Waste Solutions hazardous waste management facility.

PFASs could be detected in all samples from the area. PFOS was the dominating compound (10-370 ng/L), followed by PFBS detected at a concentration of 250 ng/L. The concentration range of the ultra-short chain compounds was for PFPrS from below the MDL to 34 ng/L and for PFEtS from 0.33 to 5.8 ng/L.

Perfluoroalkyl carboxylic acids from C4 to C9 were detected in all samples, while PFNA and PFDA were detected in nine and eight out of the ten samples, respectively. Remaining long chain perfluorocarboxylic acids (PFCAs) and fluorotelomer sulfonates were under their respective detection limit in all samples. Sample E2, not connected to the facility's outlet, had the lowest concentrations of PFASs (Figure 3) with a similar contribution of both PFCAs and perfluoroalkyl sulfonic acids (PFSAs). All other samples were clearly dominated by PFSAs.

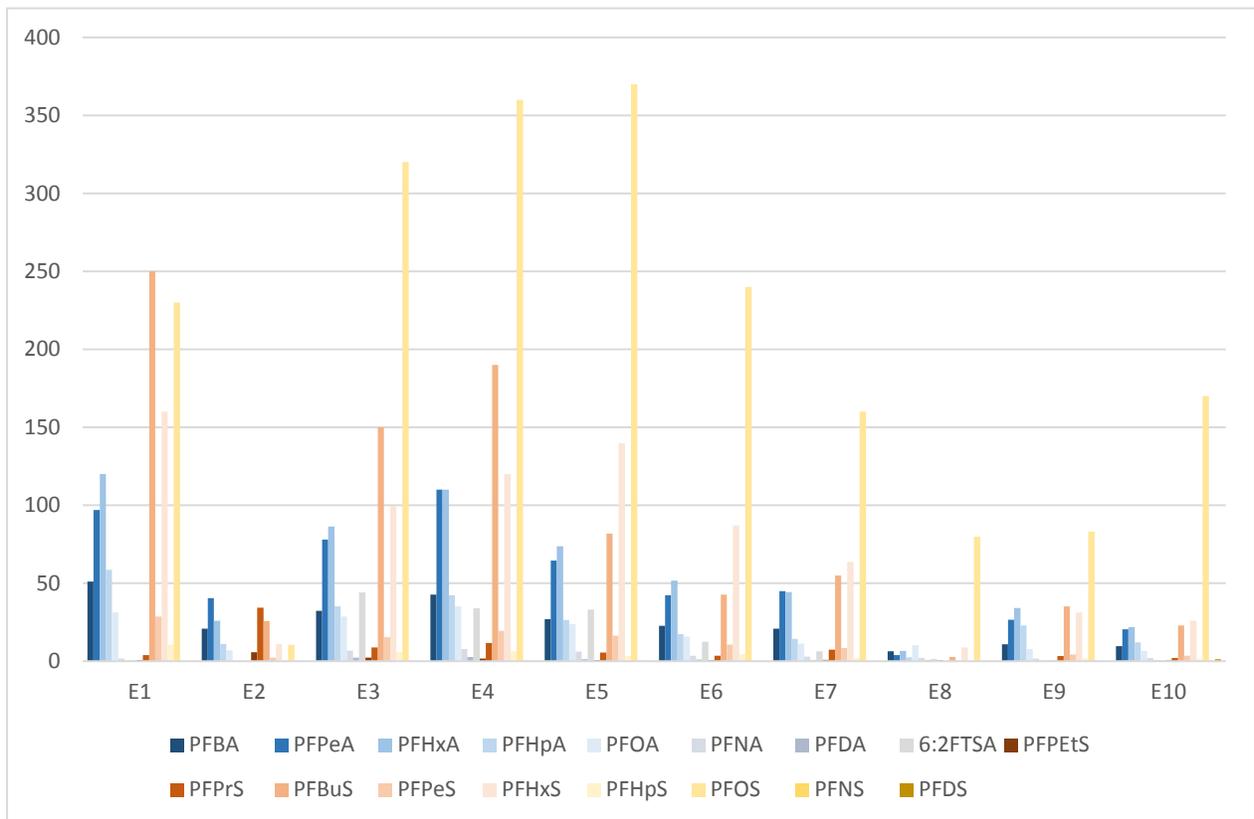


Figure 3. PFASs concentrations in ten sampling points around the Fortum Waste Solution hazardous waste management facility. Note that compounds below or close to the MDL have been removed for illustration purposes.

Homologue profiles (Figure 4) indicate similar source of PFASs for samples collected from the outlet and further downstream. Sample E1 is collected on the opposite side of the facility while E2 is collected in an area where sewage sludge from a local waste water treatment plant have been deposited. The area thus has several possible sources of PFASs with sample E10 possibly affected by the skid pad across the road from the sampling point.

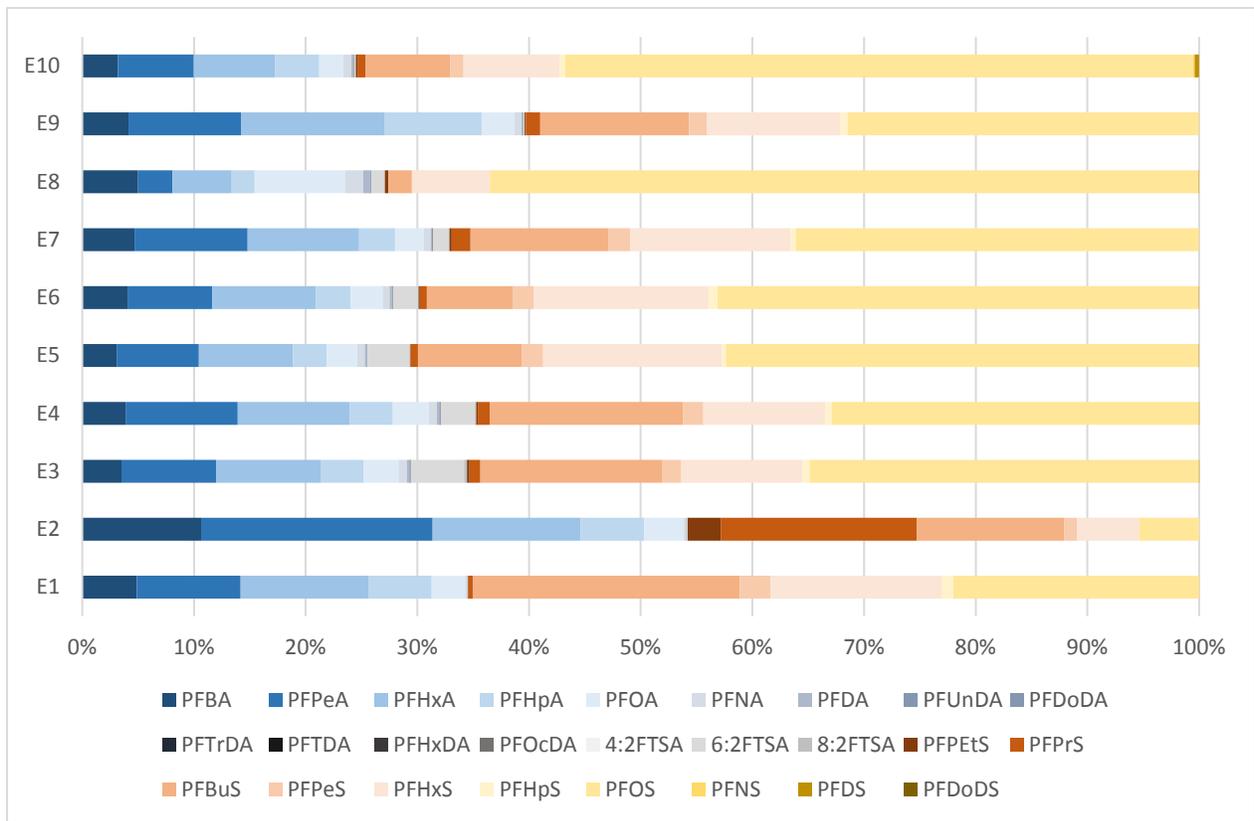


Figure 4. Homologue distribution of perfluoroalkyl carboxylic acids (in blue), flurotelomer sulfonic acids (in grey) and perfluoroalkyl sulfonic acids (in orange scale) in samples from the area around the Fortum Waste Solution hazardous waste management facility.

PFAS surface water contamination at areas around civil and military firefighting training sites

Contamination around both civil and military Swedish airport has been reported previously (Ahrens et al., 2015, Filipovic et al.,) with subsequent contamination of drinking water and resulting elevated blood PFAS concentration in populations in these areas (Gyllenhammar et al., 2015). Included in this study were samples collected close to civil airports of Arlanda and Axamo civil airports, a sample from Revingehed military training ground (Södra Skånska regementet P7), and samples from military airports; Klintabäcken (Blekinge flygflottilj F17), Vissbäcken and outlet 4 (Skaraborgs flygflottilj F7 Såtenäs. PFASs is the dominating compound class in samples from areas close to both civil and military airports, with a contribution to total PFASs measured of 69% (Axamo ditch) to 88 % (Klintabäcken). At civil airports PFSA concentrations were similar at sampling sites close to Arlanda airport and Sandserydsån close to Axamo airport, with sumPFASs at 250 and 240 ng/L, respectively. Closer to fire drill sites at Axamo airport concentrations of PFASs were clearly elevated, especially in a sample from the fire pond with sum PFASs measured to 22 000 ng/L, while the concentration in Axamo ditch was 1 300 ng/L. Concentrations for ultra-short chain compounds in these samples range from 0.08 to 17 ng/L for PFPEtS, and from 0.93 to 190 ng/L for PFPrS. Comparisons with concentrations from earlier Swedish studies are not possible for the ultra-short chain compounds. Concentrations of other PFASs, such as PFOS are similar to what has been documented by Ahrens, et al. (2015), Filipovic, et al. (2015) and others with ranges of below 100 ng/L to a few thousand ng/L.



Figure 5. Sampling points for surface waters around Axamo airport.

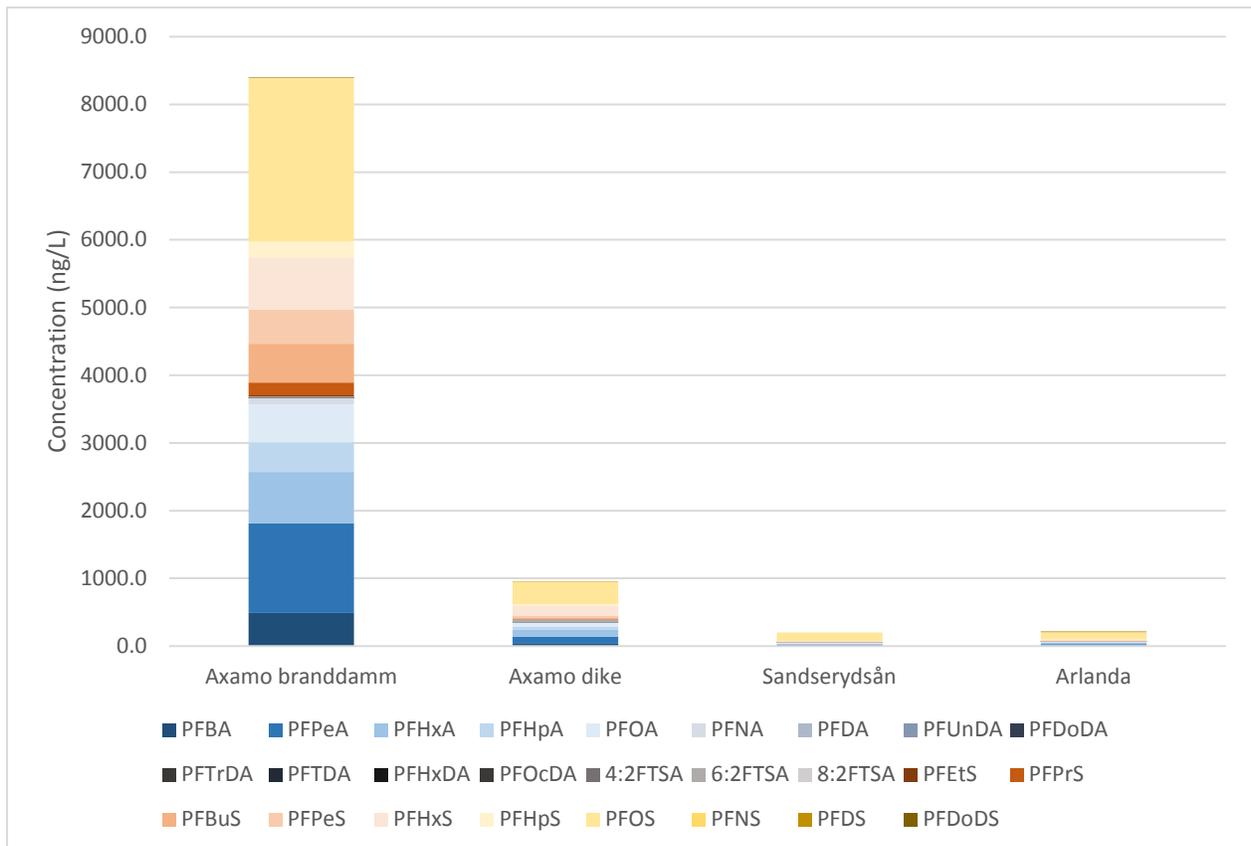


Figure 6. Comparison of different PFASs measured in surface water samples collected from areas around civil airports.

These high concentration samples from Axamo airport (Figure 5) are suspected to be close to fire drill sites and origin of contamination, while the other samples represents creeks further away from the source of contamination. Homologue distribution for these samples are seen in Figure 7, showing fairly similar profiles at the actual airport. Noteworthy is that concentrations of PFPrS are higher than PFDA and PFNA in all these samples, with PFDA and PFNA being included in guidelines for safe use of drinking water as recommended by the Swedish Food Agency (Livsmedelsverket, 2016) while PFPrS is not included in these guidelines.

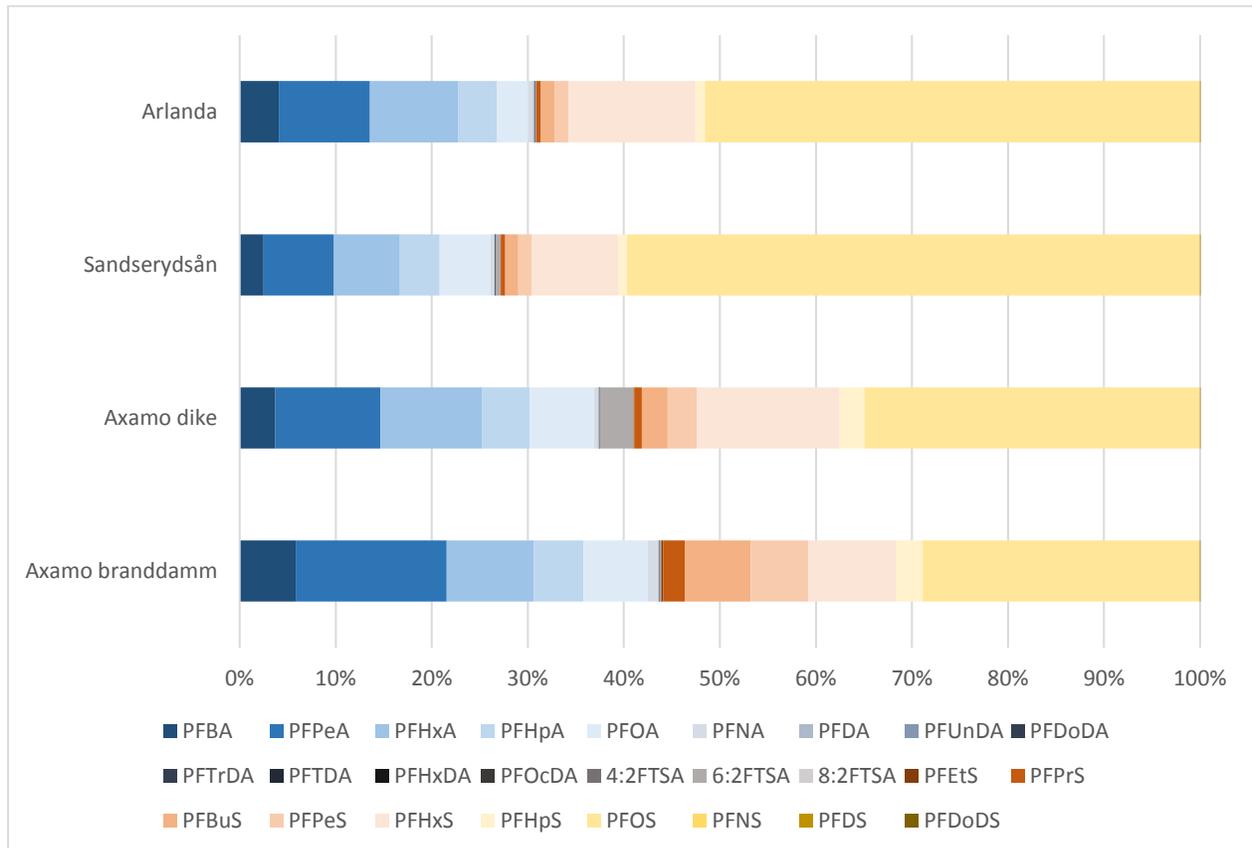


Figure 7. Homologue distribution of perfluoroalkyl carboxylic acids (in blue), flurotelomer sulfonic acids (in grey) and perfluoroalkyl sulfonic acids (in orange scale) in surface water samples around civil airports.

All samples from military airports and training grounds represent samplings points for surface waters, mainly creeks, downstream the contamination source. Sum PFAS concentrations from Revingehed was the lowest measured at 66 ng/L, followed by 410 ng/L in Klintabäcken. Both samples from either side of Skaraborgs military airport, outlet 4 (1 500 ng/L), and Vissbäcken (3 400 ng/L) are elevated compared to other surface water samples outside military airports included in this study. The ultra-short chain compounds in these samples had concentration ranges of <MDL to 76 ng/L for PFPrS and from 0.07 to 9.3 ng/L for PFETS. The homologue pattern of PFSAs are shown in Figure 7, indicating the presence of ultra-short chain PFASs although to a small extent compared to other PFASs.

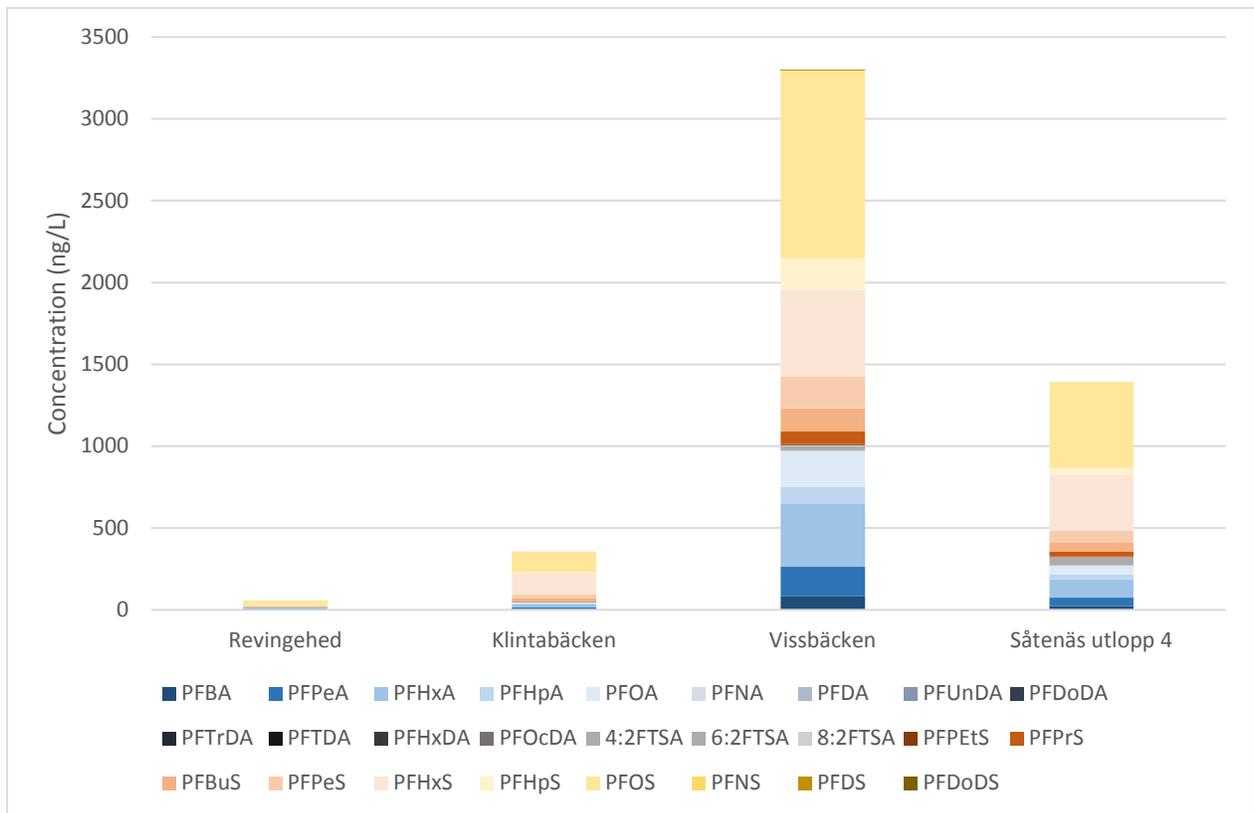


Figure 8. Perfluoroalkyl substances in surface water samples around military firefighting training facilities.

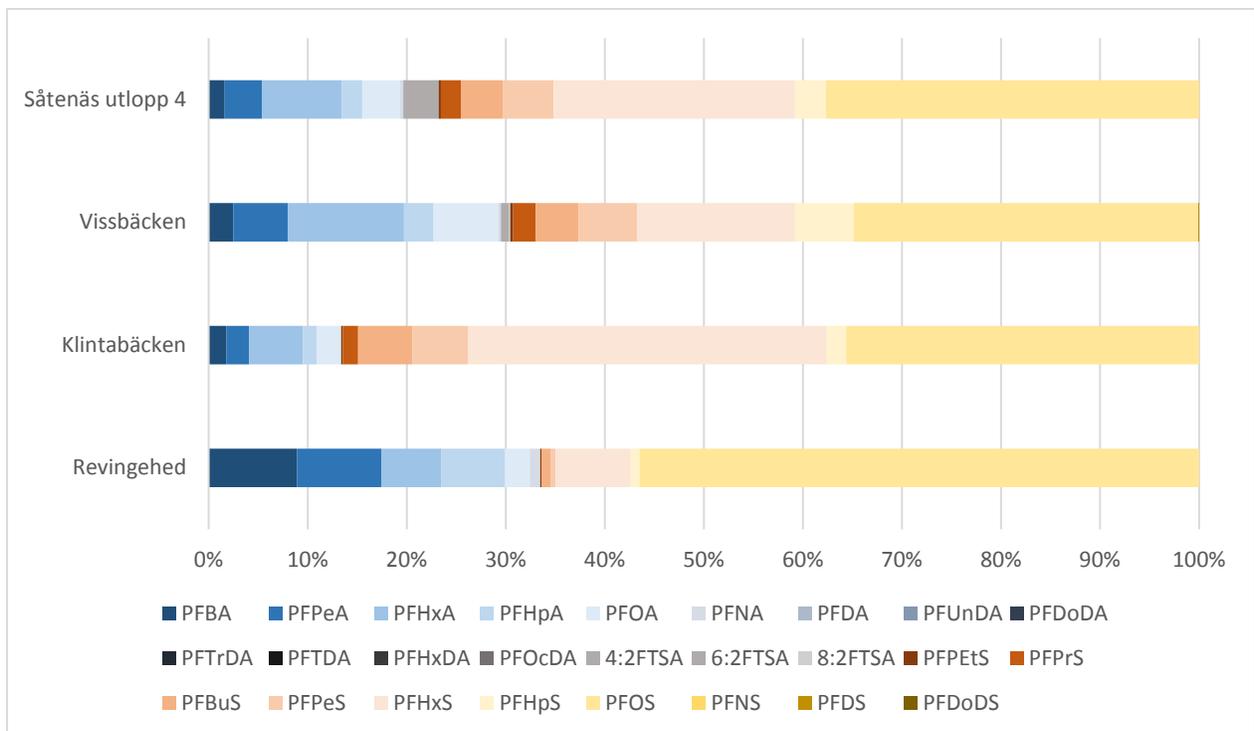


Figure 9. Homologue pattern for perfluoroalkyl sulfonates from samples close to military airports in Sweden.

Summary

Ultra-short chain compounds could be detected in all samples included in the study. PFEtS was detected in all 26 samples in a concentration range of 0.07 to 5 700 ng/L, while PFPrS was detected in 22 out of 26 samples with concentrations ranging from below the method detection limit up to 39 000 ng/L. The contribution of PFPrS varies in the samples from 0.4% to 17%. Concentrations of ultra-short chain compounds were in the low ng/L range in a limited number of background samples included in the study. Additional sampling from non-contaminated sites is needed for a better understanding of the occurrence of PFPrS and PFEtS in such sites, including drinking water samples. Although not measured in drinking water, PFPrS alone exceeds the 90 ng/L safety limit in three samples. PFOS is the only compound with an annual average environmental quality standard (AA-EQS) available (0.65 ng/L) for all other compounds no such limits exists. Although not bioaccumulative, the ultra-short chain compounds are highly polar and persistent and will be distributed in the environment. Further, current water treatment methods suffer from earlier breakthrough of these compounds in comparison with more efficient removal of longer chain PFASs (Appelman et al., 2013).

Conclusion and recommendations

Further analysis of water samples not only from sites with potential or known contamination is needed to see the extent of the distribution of ultra-short chain perfluoroalkyl substances in Swedish environmental waters. Included in this survey was ultra-short chain perfluoroalkyl sulfonic acids in samples with potential PFOS contamination. Future studies should also include ultra-short chain perfluoroalkyl carboxylic acids from both contaminated and non-contaminated sites. Using a new analytical approach such measurements are possible using supercritical fluid chromatography for their separation. Especially the C3 compound, perfluoropropane sulfonate, was detected in high proportions compared to sum of all measured PFASs as well as in elevated concentrations in this study indicating a potential need for its inclusion in guideline values for safe drinking water. Precursor compounds for the ultra-short chain compounds would also be of interest in future monitoring studies as the C4 precursor for sulfonates, perfluoro-1-butane-sulfonamide (FBSA), has been documented with high detection frequency (32 out of 33 samples) in fish from North America (Chu, S. et al., 2016).

References

- Livsmedelsverket, 2014. PFAA i råvatten och dricksvatten. Resultat av en kartläggning, september 2014.
- Barzen-Hanson, K. A., & Field, J. A., 2015. Discovery and implications of C2 and C3 perfluoroalkyl sulfonates in aqueous film-forming foams and groundwater. *Environmental Science and Technology Letters*, 2(4), 95-99.
- S. Taniyasu, et al., 2008. Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C2-C4) in precipitation by liquid chromatography-tandem mass spectrometry: comparison to patterns of long-chain perfluorinated acids (C5-C18), *Anal. Chim. Acta.* 619, 221–230. doi:10.1016/j.aca.2008.04.064.
- Yeung, W. Y., Stadey, C. and Mabury, S., 2017. Simultaneous analysis of perfluoroalkyl and polyfluoroalkyl substances including ultrashort-chain C2 and C3 compounds in rain and river water samples by ultra performance convergence chromatography. *Journal of Chromatography A*, 1522, 78–85.
- ISO, 2009. ISO25101. Water quality — Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) — Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry.
- Kwok, K. Y., et al., 2010. Flux of perfluorinated chemicals through wet deposition in Japan, the United States, and several other countries, *Environ. Sci. Technol.* 44 (2010) 7043–7049. doi:10.1021/es101170c.
- Mak, Y. L., Taniyasu, S, Yeung, LW, Lu, G, Jin, L, Yang, Y, Lam, PK, Kannan, K, Yamashita, N., 2009. Perfluorinated compounds in tap water from China and several other countries, *Environ. Sci. Technol.* 43, 4824–4829.
- SWECO Environment AB, Cederborg, D., Nordqvist, S., Keiter, S., 2016. Provtagning och analys av abborre i Söderhavet 2015. Slutrapport 2016-02-05.
- Ahrens L, Norström K, Viktor T, Cousins AP, Josefsson S., 2015. Stockholm Arlanda Airport as a source of per- and polyfluoroalkyl substances to water, sediment and fish. *Chemosphere*, 129:33-8. doi: 10.1016/j.chemosphere.2014.03.136. Epub 2014 May 10.
- Gyllenhammar, et al., 2015. Influence of contaminated drinking water on perfluoroalkyl acid levels in human serum—A case study from Uppsala, Sweden. *Environmental Research* 140: 673–683.
- Filipovic M, Woldegiorgis A, Norström K, Bibi M, Lindberg M, Österås AH, 2015. Historical usage of aqueous film forming foam: a case study of the widespread distribution of perfluoroalkyl acids from a military airport to groundwater, lakes, soils and fish. *Chemosphere*, 129:39-45. doi: 10.1016/j.chemosphere.2014.09.005.
- Livsmedelsverket, 2016. Riskhanteringsrapport: Risker vid förorening av dricksvatten med PFAS. 2016-02-29.
- Appleman TD., Dickenson, E., Bellonac, C., Higgins, C., 2013. Nanofiltration and granular activated carbon treatment of perfluoroalkyl acids. *Journal of Hazardous Materials* 260, 740-746.
- Chu, S., Letcher, R., McGoldrick, DJ., Backus, SM., 2016. A New Fluorinated Surfactant Contaminant in Biota: Perfluorobutane Sulfonamide in Several Fish Species. *Environ. Sci. Technol.* 2016, 50, 669–675.

| | LOD | MG1 | MG2 | Arlanda | Sandse-rydsån | Axamo ditch | Axamo fire pond | Revinge- hed | Klinta- bäcken | Viss- bäcken | Outlet 4 | I1 | I2 | I3 | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---------|------|--------|--------|---------|---------------|-------------|-----------------|-----------------|-------------------|-----------------|-------------|-------|-------|------|------|------|------|------|-------|------|------|-------|------|------|
| | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L |
| PFBA | 2.67 | 24000 | 5500 | 8.5 | 4.8 | 35 | 490 | 5.0 | 6.4 | 82 | 22 | 16 | 14 | 230 | 51 | 21 | 32 | 43 | 27 | 23 | 21 | 6.3 | 11 | 9.6 |
| PFPeA | 0.03 | 65000 | 9100 | 20 | 14 | 104 | 1300 | 4.8 | 8.2 | 180 | 52 | 6.4 | 5.0 | 43 | 97 | 41 | 78 | 110 | 64 | 42 | 45 | 3.9 | 27 | 21 |
| PFHxA | 0.5 | 90000 | 31000 | 19 | 13 | 100 | 7600 | 3.4 | 19 | 390 | 110 | 12 | 8.4 | 110 | 120 | 26 | 86 | 110 | 74 | 52 | 44 | 6.7 | 34 | 22 |
| PFHpA | 0.67 | 29000 | 3400 | 8.3 | 8.0 | 47 | 430 | 3.6 | 5.1 | 98 | 29 | 4.5 | 5.0 | 33 | 59 | 11 | 35 | 42 | 26 | 17 | 14 | 2.6 | 23 | 12 |
| PFOA | 0.14 | 26000 | 1300 | 6.8 | 10 | 64 | 560 | 1.4 | 8.4 | 220 | 53 | 14 | 31 | 70 | 31 | 7.0 | 29 | 35 | 24 | 16 | 11 | 10 | 7.8 | 6.5 |
| PFNA | 0.24 | 990 | 8.6 | 1 | 0.75 | 3.7 | 91 | 0.60 | 0.30 | 8.8 | 3.8 | 4.2 | 1.4 | 15 | 1.7 | 0.4 | 6.8 | 7.9 | 6.1 | 3.5 | 2.8 | 2.0 | 1.7 | 2.1 |
| PFDA | 0.09 | 73 | 2.3 | 0.32 | <LOD | 1.5 | 10 | <LOD | <LOD | 0.80 | 0.90 | <LOD | <LOD | 4.1 | 0.2 | <LOD | 2.2 | 2.6 | 1.4 | 1.2 | 0.6 | 0.8 | 0.2 | 0.5 |
| PFUnDA | 0.06 | 1.4 | 1.4 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | 0.30 | 0.30 | <LOD | <LOD | 0.86 | <LOD | <LOD | 0.9 | 1.0 | 0.6 | 0.4 | 0.2 | 0.1 | 0.1 | 0.2 |
| PFDoDA | 0.92 | 0.6 | 0.5 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| PFTrDA | 1.02 | 0.2 | 0.3 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | 0.08 | <LOD | 0.34 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| PFTDA | 0.01 | 0.5 | 0.4 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | 1.4 | 0.01 | 0.01 | 0.02 | 0.02 | <0.01 | 0.1 | 0.03 | <0.01 | 0.01 | 0.01 |
| PFHxDA | 0.4 | 2.3 | 2.4 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| PFOcDA | 0.4 | <LOD | 0.5 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| 4:2FTSA | 2.39 | 5.6 | 23 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | 0.01 | 0.02 | 0.01 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| 6:2FTSA | 0.13 | 3700 | 1600 | <LOD | 0.93 | 33 | 17 | <LOD | <LOD | 25 | 49 | 5.1 | 5.6 | 17 | 0.6 | 0.3 | 44 | 34 | 33 | 13 | 6.3 | 1.6 | 0.4 | 0.5 |
| 8:2FTSA | 0.03 | 36 | 3.8 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | 5.6 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | 2.2 | 1.2 | 0.2 | 0.2 | 0.3 | <LOD | <LOD | <LOD |
| PFPEtS | 0.06 | 5700 | 1600 | 0.08 | 0.08 | 0.62 | 17 | <LOD | 0.56 | 9.3 | 3.0 | 0.69 | 0.78 | 1.5 | 0.61 | 5.8 | 2.2 | 1.6 | 0.63 | 0.65 | 0.82 | 0.38 | 0.32 | 0.45 |
| PFPrS | 0.43 | 39000 | 11000 | 0.98 | 0.93 | 7.7 | 190 | 0.07 | 5.5 | 76 | 29 | 9.1 | 12 | 23 | 3.8 | 34 | 8.8 | 12 | 5.6 | 3.5 | 7.5 | <LOD | 3.4 | 2.2 |
| PFBuS | 0.94 | 46000 | 13000 | 2.98 | 2.6 | 25 | 570 | 0.50 | 20 | 140 | 58 | 1600 | 1900 | 95 | 250 | 26 | 150 | 190 | 82 | 43 | 55 | 2.7 | 35 | 23 |
| PFPeS | 0.86 | 59000 | 10000 | 2.98 | 2.8 | 29 | 500 | 0.30 | 20 | 200 | 72 | 14 | 19 | 53 | 29 | 2.2 | 15 | 19 | 16 | 11 | 8.5 | <LOD | 4.3 | 3.6 |
| PFHxS | 0.04 | 92000 | 18000 | 28.4 | 18 | 150 | 1000 | 4.4 | 140 | 650 | 400 | 110 | 160 | 250 | 160 | 11 | 100 | 120 | 140 | 87 | 64 | 8.8 | 31 | 26 |
| PFHpS | 1.95 | 77000 | 230 | 2.32 | 2.3 | 23 | 1000 | 0.50 | 7 | 220 | 48 | 8.6 | 110 | 79 | 11 | <LOD | 6.1 | 6.5 | 3.4 | 4.6 | 2.1 | <LOD | 1.8 | 1.5 |
| PFOS | 0.16 | 140000 | 1400 | 147 | 160 | 640 | 15000 | 42 | 180 | 1100 | 520 | 11000 | 13000 | 3600 | 230 | 10 | 320 | 360 | 370 | 240 | 160 | 80 | 83 | 170 |
| PFNS | 0.02 | 0.2 | 0.1 | 0.1 | 0.24 | 0.24 | 6.8 | <LOD | <LOD | 2.0 | 0.20 | 0.02 | <LOD | 2.2 | 0.07 | <LOD | 0.49 | 0.52 | 0.40 | 0.21 | 0.15 | 0.1 | 0.08 | 0.4 |
| PFDS | 0.02 | 0.1 | 0.3 | 0.04 | <LOD | 0.03 | 0.08 | <LOD | <LOD | 0.30 | <LOD | <LOD | <LOD | 0.04 | <LOD | <LOD | 0.07 | 0.07 | 0.16 | 0.11 | <LOD | 0.04 | <LOD | 1.2 |
| PFDoDS | 0.07 | 0.1 | 0.3 | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD |
| SumPFAS | - | 700000 | 110000 | 250 | 240 | 1300 | 29000 | 66 | 420 | 3400 | 1450 | 13000 | 15000 | 4600 | 1000 | 200 | 900 | 1100 | 880 | 560 | 440 | 130 | 260 | 300 |