

Fate of perfluoroalkyl acids in the aquatic
environment with a focus on mass balance studies

Marko Filipovic



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Till Amira, Miomir och Bojan
världens bästa familj. Utan ert
stöd och kärlek hade mina
drömmar aldrig varit ändlösa.

Abstract

Perfluoroalkyl substances (PFASs) are man-made chemicals. Their unique properties make them beneficial for a wide range of industrial and consumer product applications, such as in aqueous film forming foam (AFFF), durable water repellent clothing, hydraulic oils and food packaging materials. Perfluoroalkyl acids (PFAAs), a class of PFASs, are highly persistent in the environment, and long chain PFAAs are bioaccumulative and toxic. International regulation and voluntary actions by the industry have been implemented and led to a recent reduction of primary emissions of PFAAs to the environment. However, point sources such as AFFF training sites as well as diffuse sources continue to contaminate water bodies, soil and biota. Reducing environmental pollution with PFAAs has therefore become a regulatory priority. Designing successful measures to reduce the PFAA contamination requires an understanding of the sources, transport and fate of PFAAs in the environment.

Four scientific publications are included in this PhD thesis, which aimed at increasing the holistic understanding of the fate of PFAAs in aquatic systems. This was achieved by chemical trace analysis combined with mass balance modeling. The following topics were covered: Dispersion and fate of PFAAs from an AFFF-impacted site (**Paper I**), recirculation of PFAAs in the aquatic environment with focus on waste water treatment plants (WWTPs, **Paper II**), mass balance of PFAAs in the Baltic Sea (**Paper III**) and transport and fate of PFAAs in two pristine boreal stream catchments (**Paper IV**).

Results from **Paper I** showed that AFFF-impacted sites at a former military airfield, which was abandoned for more than 30 years, continue to be point sources of PFAAs to recipients. The sum of PFAAs in the ground water and surface waters ranged from 740 to 51000 ng L⁻¹ and <0.5 to 79 ng L⁻¹, respectively. PFOS in muscle tissue of European perch from a nearby lake ranged from 77 to 370 ng g⁻¹ wet weight, representing among the highest values reported worldwide for fish muscle. In **Paper II** the relative importance of environmental recirculation of PFAAs versus new releases from the technosphere was investigated for PFAAs in WWTP influents. It was shown that tap water can be an important source of PFAAs to WWTPs in areas with elevated environmental levels. This needs to be taken into account when calculating emissions via WWTP effluents. PFAA mass balances over the WWTPs suggested that PFHxA and PFOA were formed from precursor compounds within

the plants. Assembled PFAA mass balances for the Baltic Sea (**Paper III**) showed that river inflow and atmospheric deposition were the dominant input pathways, while wastewater treatment plant (WWTP) effluents discharging directly into the Baltic Sea made a minor contribution. The inputs of PFAAs were estimated to be higher than the outputs, suggesting a current increase of the PFAA inventory in the Baltic Sea. Also the mass balance study of PFAAs in two remote stream catchments presented in **Paper IV** revealed that inputs dominated over outputs for both catchments, indicating that a considerable portion of the PFAAs deposited from the atmosphere is retained in soil or in deep ground water and may be released to surface and marine water environments in the future.

Sažetak

Perfluoralkilne tvari (PFASs) su umjetne kemikalije. Zbog svojih jedinstvenih svojstava široko su primjenjive u industriji i izradi proizvoda krajnje potrošnje kao što su pjena za gašenje požara (AFFF), voodootporna odjeća, hidraulična ulja i pakiranja za hranu. Perfluoralkilna kiselina (PFAAs) iz skupine perfluoralkilnih tvari iznimno je dugotrajna u okolišu, a dugolančane PFAAs su bioakumulativne i otrovne. Poduzeta međunarodna regulativa i dobrovoljne akcije vodile su nedavno smanjenoj primarnoj emisiji PFAAs u okoliš. Unatoč tome, primarni izvori, kao što su mjesta na kojima se provode treninzi za gašenje požara i difuzni izvori i dalje zagađuju vode, tlo i biotu. Zbog toga, smanjenje onečišćenja okoliša izazvanog PFAAs predstavlja regulatorni prioritet. Stvaranje uspješnih mjera kojima bi se smanjilo onečišćenje izazvano PFAAs zahtijeva razumijevanje izvora, prijenosa i sudbine tih tvari u okolišu.

U ovaj doktorat uključena su četiri znanstvena članka kojima je cilj povećati sveukupno razumijevanje sudbine PFAAs u vodenim sustavima. To je postignuto kemijskom analizom elemenata u tragovima u kombinaciji s modeliranjem masene ravnoteže. Obradene su sljedeće teme: Širenje i sudbina PFAAs na područjima zahvaćenim AFFF (**Članak I**), ponovna cirkulacija PFAAs u vodenom okolišu s naglaskom na postrojenja za pročišćavanje otpadnih voda (**Članak II**), masena ravnoteža PFAAs u Baltičkom moru (**Članak III**) te prijenos i sudbina PFAAs u dva udaljena sjeverna vodena toka (**Članak IV**).

Rezultati iz **Članka I** pokazali su da su područja zahvaćena AFFF na bivšem vojnom aerodromu napuštenom prije 30 godina i dalje je glavni izvor PFAA zagađenja okolisa. Zbroj PFAAs u podzemnim i površinskim vodama kreće se u rasponu od 740 do 51000 ng L⁻¹ i <0.5 do 79 ng L⁻¹. PFOS u mišićnom tkivu grgeča iz obližnjeg jezera kreće se od 77 do 370 ng g⁻¹ mokre težine, predstavljajući jednu od najviših vrijednosti u svijetu za riblje mišiće. **Članak II** istražuje relativnu važnost ponovne cirkulacije PFAAs imajući na umu novu emisiju PFAAs iz tehnosfere u postrojenjima za pročišćavanje otpadnih voda. Cirkulacija/kruženje u okolišu može se pojaviti kada PFAAs iz sustava pitke voda (rijeka, bunara i jezera) odlaze u otpadne vode. Prikazano je kako voda iz slavine može biti važan izvor PFAAs sustavima za pročišćavanje otpadnih voda u područjima s povišenim razinama zaštite okoliša. To se treba uzeti u obzir pri računanju emisije putem strojeva koji se

koriste za pročišćenje otpadnih voda. Masena ravnoteža PFAA u postrojenjima za pročišćavanje otpadnih voda upućuje na to da su PFHxA i PFOA stvoreni kao prethodni spojevi unutar postrojenja. Prikupljene masene ravnoteže PFAA za Baltičko more (**Članak III**) pokazale su da su pritoke rijeka i atmosfersko taloženje dominantni ulazni putovi, dok postrojenja za pročišćenje otpadnih voda pridonose tek u manjoj mjeri. Ulaz PFAAs je procijenjen višim od izlaza, što objašnjava trenutno povećanje sadržaja PFAA u Baltičkom moru. Masena ravnoteža PFAAs u dva udaljena riječna toka predstavljena u **Članku IV** otkriva da ulaz dominira nad izlazom za oba riječna toka, što upućuje na značajan udio PFAAs koji je iz atmosfere zadržan u tlu ili podzemnim vodama te može biti ispušten u područja površinskih voda i mora.

Sammanfattning

Perfluorerade alkylsyror (PFAA) är kemikalier som är producerade av människan. Deras unika egenskaper gör att de kan användas i många olika industriella applikationer. PFAAs används i brandsläckningsskum, vattenavvisande kläder, hydrauliska oljor och matförpackningar.

PFAAs har visat sig vara persistenta i miljön, och långkedjiga PFAA-homologer har visat sig vara bioackumulerbara samt ha en toxisk verkan. Reglering på internationell nivå tillsammans med initiativ från industrin har lett till minskning av direkta utsläpp. Punktkällor som brandövningsplatser samt andra diffusa källor fortsätter att förorena omgivande vattendrag, jordlager och fauna. Den utbredda föroreningen av PFAAs har därför blivit prioriterad för reglering. För att förstå utsläppen av PFAAs i miljön, hur de transporteras samt deras öde i miljön, är det viktigt att utföra studier som belyser dessa områden.

Denna doktorsavhandling inkluderar fyra vetenskapliga publikationer. Syftet med de underliggande studierna var att öka den holistiska förståelsen av PFAAs rörelse i akvatiska system. Studierna gjordes genom att kombinera kemiska analysmetoder med modellering. Följande studier genomfördes; Transport och spridning av PFAAs från en brandövningsplats (**Paper I**), recyklering av PFAAs i den akvatiska miljön med fokus på vattenreningsverk (**Paper II**), massbalans av PFAAs i Östersjön (**Paper III**), transport och öde av PFAAs i två pristina vattendrag (**Paper IV**).

Resultat från (**Paper I**) visade att brandövningsplatser vid en flygplats som inte har varit i bruk i mer än 30 år, fortfarande är punktkällor av PFAAs till omgivande vattendrag. Summan av PFAAs koncentrationer i grundvattnet och ytvattnet sträckte sig från 740 till 51000 ng L⁻¹ och <0.5 till 79 ng L⁻¹ i respektive vattendrag. Koncentrationen av PFOS i muskelvävnad från aborre i en av sjöarna var 77 till 370 ng g⁻¹ våtvikt. Dessa värden representerar några av de högsta uppmätta koncentrationerna i världen. I **Paper II** testades betydelsen av PFAAs från recirkulering i miljön i jämförelse med nya utsläpp från teknosfären. Recirkulering av PFAAs i miljön kan förekomma då PFAAs i inkommande vatten till reningsverk kommer från dricksvatten.

Denna studie visar att dricksvatten kan vara en påtaglig källa av PFAAs till vattenreningsverk i områden med förhöjda halter av PFAAs i miljön. Detta

måste tas hänsyn till när man beräknar emissioner med utgående vatten från vattenreningsverk. Massbalanser av PFAAs i reningsverken visar att PFHxA och PFOA bildades av prekursorämnena i vattenreningsverken. I **Paper III** beräknades massbalanserna av PFAAs i Östersjön, beräkningarna visar att floder och atmosfärisk nederbörd var de viktigaste källorna medan utsläppen från vattenreningsverk var markant lägre. Importen av PFAAs estimerades vara högre än exporten, varför vi tror att PFAAs mängden i Östersjön kommer att öka över tid. Vidare gjordes en mass balans av PFAAs i två avlägsna avrinningsområden (**Paper IV**). Resultaten visar att importen av PFAAs dominerar över exporten från båda avrinningsområdena. Detta indikerar att en stor del av PFAAs som kommer ner via nederbörd kommer att ansamlas i jorden eller i grundvattnet. Dessa PFAAs kan vid senare tillfälle komma att släppas ut till floder som rinner ut i marina vatten.

Abbreviations

General abbreviations

AFFF	Aqueous film forming foam
BB	Bothnian Bay
BP	Baltic Proper
BS	Bothnian Sea
GoF	Gulf of Finland
GoR	Gulf of Riga
HBE	High bound estimate
HPLC	High performance liquid chromatography
IS	Internal standard
Kd	Sediment/water distribution coefficient
LBE	Low bound estimate
MDL	Method detection limit
SQL	Method quantification limit
RIS	Recovery internal standard
SPE	Solid phase extraction
UPLC	Ultra performance liquid chromatography

Target compounds

PFBA	Perfluorobutanoic acid
PFPeA	Perfluoropentanoic acid
PFHxA	Perfluorohexanoic acid
PFHpA	Perfluoroheptanoic acid
PFOA	Perfluorooctanoic acid
PFNA	Perfluorononanoic acid
PFDA	Perfluorodecanoic acid
PFUnDA	Perfluoroundecanoic acid
PFDoDA	Perfluorododecanoic acid
PFBS	Perfluorobutane sulfonic acid
PFHxS	Perfluorohexane sulfonic acid
PFOS	Perfluorooctane sulfonic acid
PFDS	Perfluorodecane sulfonic acid
PFAAs	Perfluoroalkyl acids
PFASs	Per- and polyfluoroalkyl substances
PFCA	Perfluoroalkyl carboxylic acids
PFSA	Perfluoroalkane sulfonic acids

List of papers

I. 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

Marko Filipovic, Andreas Woldegiorgis, Karin Norström, Momina Bibi, Maria Lindberg, Ann-Helen Österås (2015). *Chemosphere* 129, 39-45

II. Are perfluoroalkyl acids in waste water treatment plant effluents the result of primary emissions from the technosphere or of environmental recirculation?

Marko Filipovic, Urs Berger (2015). *Chemosphere* 129, 74-80

III. Mass balance of perfluoroalkyl acids in the Baltic Sea

Marko Filipovic, Urs Berger, Michael McLachlan (2013). *Environmental Science & Technology* 47 (9), 4088-4095

IV. Mass balance of perfluorinated alkyl acids in a pristine boreal catchment

Marko Filipovic, Hjalmar Laudon, Michael McLachlan, Urs Berger (Submitted to *Environmental Science & Technology*)

Publications outside this thesis

V. Perfluoroalkyl acids in selected waste water treatment plants and their discharge load within the Lake Victoria basin in Kenya

Florah Chirikona, Marko Filipovic, Seline Ooko, Francis Orata (2015). *Environmental Monitoring and Assessment*, doi. 10.1007/s10661-015-4425-6

VI. Application of a novel solid-phase-extraction sampler and ultra-performance liquid chromatography quadrupole-time-of-flight mass spectrometry for determination of pharmaceutical residues in surface sea water

Jörgen Magnér, Marko Filipovic, Tomas Alsberg (2010). *Chemosphere* 80 (11), 1255-1260

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Contribution to papers

I, Marko Filipovic, made the following contributions to the papers presented in this thesis:

Paper I

I initiated the study. The coordination of the sampling was done by WSP and data analysis was performed by IVL. I was responsible for evaluation of the results within the manuscript and took the lead role in authoring the paper.

Paper II

I initiated, planned and designed the study. I coordinated the fieldwork, performed all the experimental work and data analysis and took the lead role in authoring the paper.

Paper III

I participated in the planning and design of the study. I performed all the data collection and data analysis and took the lead role in authoring the paper.

Paper IV

I participated in the planning and design of the study. I coordinated the sampling, which was done by colleagues from SLU. I performed all experimental work and data analysis and took the lead role in writing the paper.

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1. Introduction

1.1 Per – and polyfluoroalkyl substances (PFASs)

Per- and polyfluoroalkyl substances (PFASs) is a generic name for a large group of aliphatic substances that contain one or more carbon atoms on which all hydrogens have been replaced by fluorine, i.e. they contain the perfluoroalkyl moiety C_nF_{2n+1} . The terminological difference between poly- and perfluoroalkyl substances is that in “poly” not all carbons in the aliphatic chain are fully fluorinated, whereas for “per” all H atoms in the molecule are replaced with F atoms (apart from those in functional groups).

In this thesis one subgroup of PFASs, the so called perfluorinated alkyl acids (PFAAs) were studied. PFAAs can be divided into several subgroups, whereof perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) are the most important ones in terms of production volumes and uses. PFCAs and PFSAs are also the most well studied classes of PFASs.

PFCAs contain an alkyl chain with typically three to fifteen fully fluorinated carbon atoms attached to a carboxylic acid functional group. The chemical structure of PFCAs is thus $C_nF_{2n+1}COOH$. The most commonly analyzed PFCA is perfluorooctanoic acid (PFOA, $n=7$). All PFCAs that were included in this thesis are presented in Figure 1.

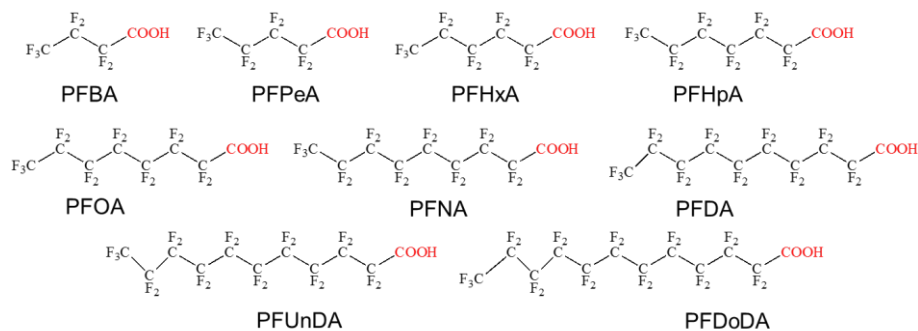


Figure 1. Nine perfluorinated carboxylic acids commonly analyzed in the environment.

PFSAs contain an alkyl chain with four to ten fully fluorinated carbon atoms attached to a sulfonic acid functional group. The chemical structure of PFSAs is $C_nF_{2n+1}SO_3H$. The most commonly analyzed PFSA is perfluorooctane sulfonic acid (PFOS, $n=8$). Perfluorooctane sulfonamide (FOSA) is a derivative of PFOS with the structure $C_8F_{17}SO_2NH_2$. FOSA is not a PFSA, but it can be biotransformed to PFOS. All PFSAs that were included in this thesis as well as FOSA are presented in Figure 2.

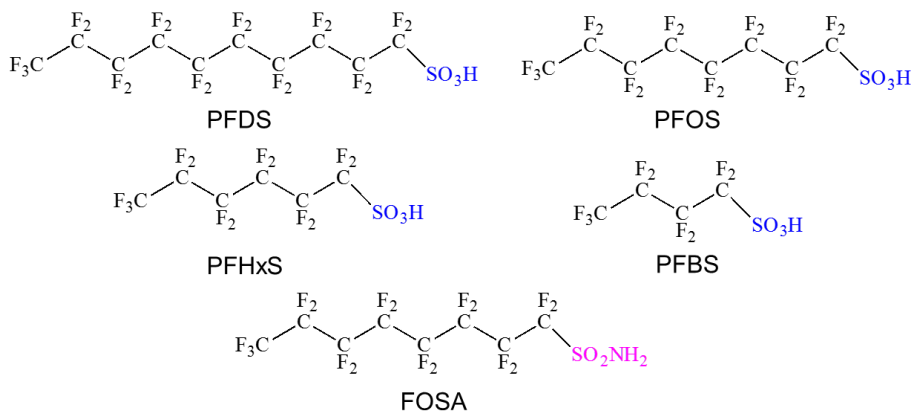


Figure 2. Four perfluoroalkane sulfonic acids and FOSA commonly analyzed in the environment.

In addition to PFAAs there are other groups of PFASs that can be transformed to PFAAs in the environment, e.g. by biodegradation or atmospheric oxidation.^{2,3} These PFASs are commonly called precursor compounds. FOSA is one example for such precursors, as it can be transformed in the environment both to PFOS and to PFOA.

1.2 A brief history of fluorine chemistry

A short summary of the history of fluorine chemistry and recent PFAA research is given in Figure 3. The element fluorine was discovered by Henri Moissan in 1886.⁴ More than 50 years later, in 1938, the fluorine chemistry took a big step forward in a laboratory of the DuPont Company, when Dr. Roy J Plankett in the search of a new refrigerant developed the fluoropolymer polytetrafluoroethylene (PTFE).⁵ PTFE was registered in 1945 and became one of the best known trademarks of the DuPont Company known as Teflon®. The high-volume production of PTFE was eventually made possible by using PFOA as a polymerization aid.

During the same period of time, Patsy Sherman at the 3M Company accidentally synthesized a new perfluorinated compound, PFOS. PFOS became a key ingredient of another famous trademark registered as Scotchgard® by 3M.⁶ These two trademarks introduced the perfluoroalkyl acids (PFAAs) into mainstream consumer products. In the early 1940s, during World War II, the Manhattan project required new inert materials for separation of uranium isotopes via gas diffusion from their corrosive hexafluorides.⁷ Fluorinated materials were uniquely suited for the task. The Manhattan project gave great momentum to the development of new fluorine based chemicals. Ever since, the fluorine industry has grown exponentially and a large variety of poly- or perfluorinated organochemicals have become ingredients in the products of everyday life. The success story of per- and polyfluoroalkyl substances (PFASs) started thus with the accidental synthesis of new chemicals and chemists serendipitously discovering the extraordinary physical-chemical properties of these new materials.

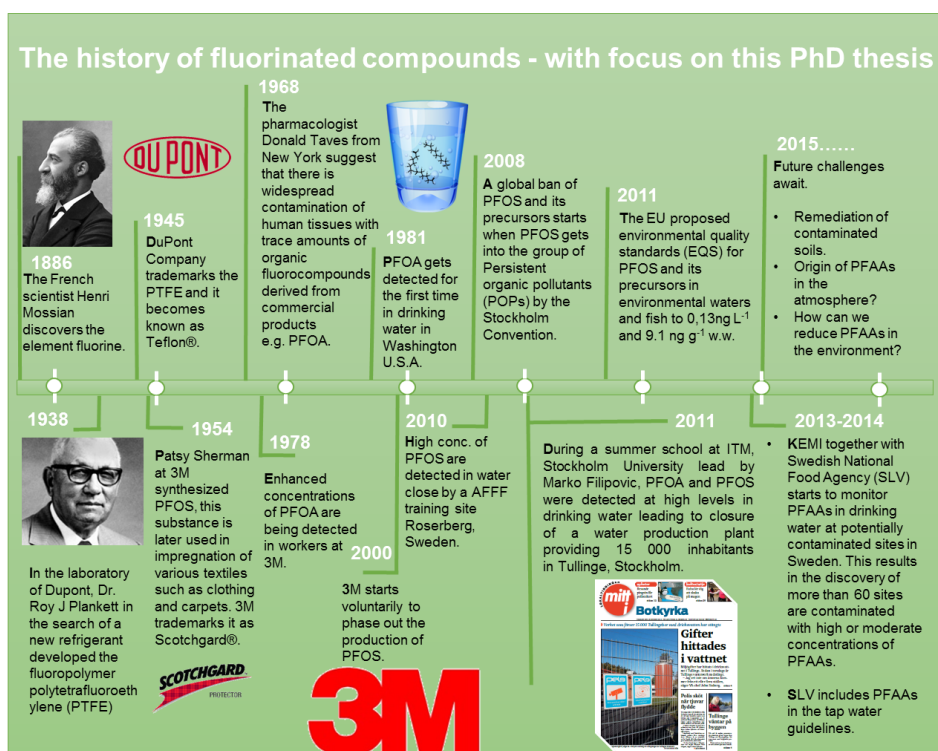


Figure 3. A brief view of the history of fluorine chemistry and recent water research focusing on PFAAs in Sweden. References for year: 1968,⁸ 1978, 1981 (Personal communication Robert C. Buck), 2000,⁹ 2008,¹⁰ 2010, 2011 (I),¹¹ 2011 (II),¹² 2013/2014.¹³

1.3 Production processes of per- and polyfluoroalkyl substances

There are two major industrial processes for production of PFASs, known as electrochemical fluorination (**ECF**) and **telomerization**. These processes are used among the different manufacturers and lead to varying purity of the PFAS products. In order to understand the results presented in this study an overview of these processes is needed.

ECF was developed in the 1940s by Joseph Simons at 3M.¹⁴ In the chemical production of PFOA and PFOS by ECF a raw material (octanoyl fluoride and octane sulfonyl fluoride, respectively) undergoes electrolysis in presence of anhydrous HF (Figure 4). The reaction drives towards total replacement of H atoms with F. The harsh conditions of ECF lead to the formation of free radicals resulting in cleavage of C-C bonds, which leads to production of a mixture of linear and branched isomers and shorter-chain homologues of the resulting PFASs among other chemicals. The branched/linear ratio of ECF produced PFOA and PFOS varies between 30:70 and 20:80, depending on the control of the process.

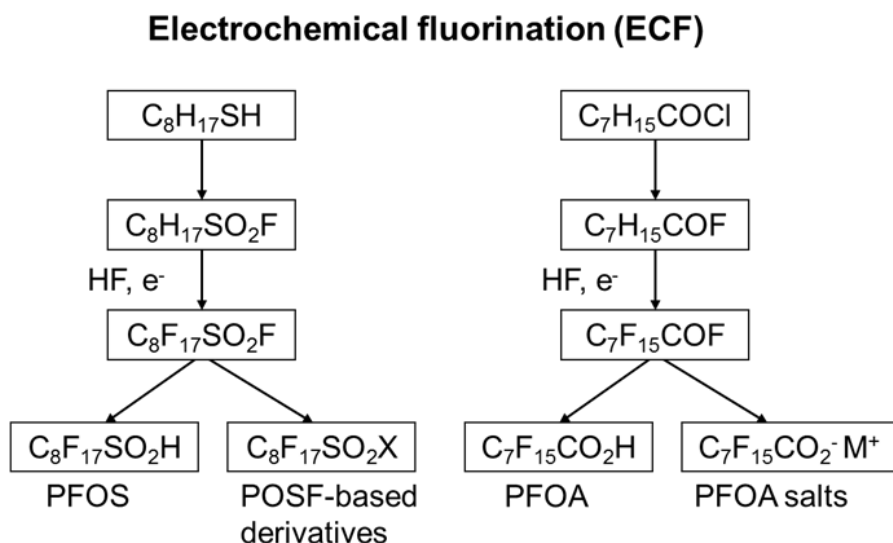


Figure 4. Simplified illustration of the ECF synthesis process of PFOS, POSF derivatives, PFOA and its salts. Adopted from Buck et al. (2011).¹

Telomerization is the second widely used method for PFAS manufacturing (Figure 5). In contrast to ECF, which produces a mixture of branched and linear isomers and homologues, the telomerization process is a high purity process which yields only linear chain products. The initial step of telomerization is a reaction between pentafluoroethyl iodide (telogen) and tetrafluoroethylene (taxogen), which produces a mixture of perfluoroalkyl iodides with an even number of C atoms (Telomer A). Telomer A is then reacted with ethylene to produce n:2 fluorotelomer iodide (Telomer B).

Telomer A and Telomer B are intermediates in the production of fluorinated surfactants and polymers. Telomer B can then further be hydrolysed for production of n:2 fluorotelomer alcohols (FTOHs), which are used in the production of surface coatings for, e.g., textiles and food packaging materials.

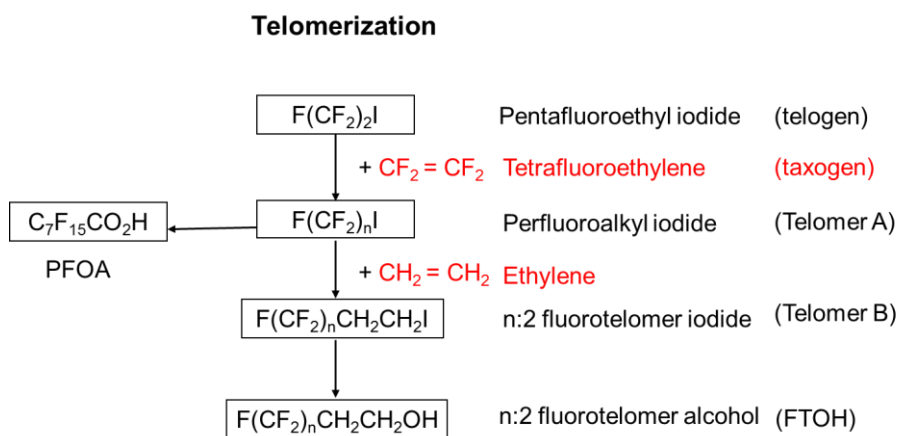


Figure 5. Simplified illustration of the telomerization process for synthesis of PFOA and fluorotelomer alcohols (FTOHs). Adopted from Buck et al. (2011).¹

1.4 PFAS production volumes and usage areas

The first industries producing PFASs were established in the USA. However, in 1971 3M opened the first PFOS production facility in Europe located in Antwerp, Belgium. The world-wide cumulative historic production of PFCAs between the 1970s and 2015 has been estimated to range between 2610 and 21400 tonnes.^{15,16} The historical production of PFSA based products from 1970 to 2002 was estimated to be 122 500 tonnes.¹⁷ The unique physical-chemical properties of PFASs (e.g., surface activity, thermal and chemical stability)¹⁸ make them favorable for application in a wide range of consumer products.

PFAAs are used in everyday products such as water resistant outdoor clothing,¹⁹ non-stick cookware, paper coatings and fire-fighting foams. They are also used in a wide range of industrial applications such as the production of semiconductors, the metal plating industry and the production of fluoropolymers.²⁰

1.5 PFAA properties and environmental fate

When an aliphatic carbon chain is perfluorinated, the chemical properties of the compound change dramatically. The C-F bond is the strongest single bond known in organic chemistry, which makes the perfluorinated compounds extraordinary stable against hydrolysis, photolysis, microbial and thermal degradation.¹⁸ A further unique physical-chemical property of PFAAs is the strong surface activity (water and oil repellence). Despite the water repellent properties, PFAAs are relatively well soluble in water, with a better solubility for PFCAs compared to PFSAs with the same number of carbon atoms. E.g., PFOA (3.4 g L^{-1}) is significantly more water soluble compared to PFOS (0.57 g L^{-1}). Laboratory studies have shown that PFCAs have low pKa values probably around 1,²¹ which causes a major fraction of PFCAs to be ionized and non-volatile under environmental conditions. PFSAs have even lower pKa values <0 .²¹

Once released to the environment PFAAs may partition into water, biota, soil, sediment and/or the atmosphere. Based on the properties described above, modelling studies have predicted that PFCAs and PFSAs will mostly be distributed to environmental waters.^{22,23} In water PFAAs will equilibrate with sediment and potentially bioaccumulate in aquatic biota.

PFAAs are frequently detected in atmospheric deposition despite their low volatility. There are several hypothesized pathways for PFAAs to the atmosphere. First, PFAAs could be transferred on aerosols via sea spray from surface waters to the atmosphere;²⁴ second, PFAAs could be emitted bound to airborne particles; third, PFAAs in the atmosphere may be attributed to degradation of (semi-)volatile precursor compounds such as FTOHs.²⁵ Wet or dry atmospheric deposition will lead to PFAA release to soil. PFAAs may then bind to organic carbon in the topsoil with compound-specific binding affinities. However, eventually the PFAAs will migrate down through the soil column into the groundwater, whereby shorter chain PFAAs will migrate faster compared to longer chain PFAAs.²⁶

1.6 PFAA toxicity

PFAA toxicity has predominantly been assessed for PFOA and PFOS and potential effects have intensively been studied. Some of the observed effects of PFOA and PFOS in rodents are carcinogenicity, immune toxicity, hormonal effects and hepa-toxicity.²⁷ Studies have also shown that some PFASs are potential endocrine disruptors and affect the function of thyroid hormone and of estrogen and androgen *in vitro*.²⁸ Wielsøe et al. have shown in an *in vitro* study with a cell line representing the human liver that PFAAs (in particular PFOA and PFOS) induce oxidative stress including DNA damages.²⁹

In breast cancer patients from Greenland significantly higher serum levels of PFHxS, PFOS, FOSA and PFOA were observed compared to controls. PFOS and FOSA were found as significant risk factors.³⁰ Several prospective studies have recently been done in Denmark on PFAAs and human toxicity. In one of the studies on women FOSA was also found as a potential breast cancer risk factor.²⁸ In another study no association between plasma concentrations of PFOS and PFOA and the risk of prostate, bladder, pancreatic, or liver cancer was observed.³¹

Toxicological studies which have investigated the association between exposure to PFOA and PFOS and human fetal growth have shown inconsistencies in their results.³² Exposure to high PFOS and PFOA concentrations was associated with decreased average birth weight in most studies, but only some results were statistically significant.

1.7 European regulation on PFOS and PFOA

Between 2000 and 2002 the 3M Company voluntarily phased out the production of PFOS-based chemicals, based on the concern that had arisen due to the ubiquitous presence of PFOS in the blood of their employees.⁹ In 2005 Sweden proposed to add PFOS to the Stockholm Convention on Persistent Organic Pollutants, as it fulfills the criteria to be persistent, bioaccumulative and toxic (PBT).¹⁰ In 2009 PFOS was finally listed in Annex B of the Stockholm Convention.³³ In 2006 the EU Directive 2006/122/EC amending directive 76/769/EEC restricted the marketing and use of perfluorooctane sulfonates.³⁴ The directive became effective in 2008 and applies to substances and preparations with concentrations equal to or higher than 0.005 % by mass. In 2010 the EU lowered the limit to 0.001 % by mass.

Semi-finished products, articles or parts thereof may not be placed on the market if the concentration of perfluorooctane sulfonates is equal to or higher than 0.1 % by mass. For textiles or other coated materials, the limit is 1 $\mu\text{g}/\text{m}^2$ of the coated material. Furthermore, the European Commission defined Environmental Quality Standards (EQS) for PFOS in 2011.¹² The EQS document states that PFOS concentrations should not exceed 0.13 ng L^{-1} in marine waters.

PFOA is not regulated in the EU or at an international level. It does not fulfill the criterion of a bioaccumulative compound according to the Stockholm Convention. Nevertheless, in 2006 the US Environmental Protection Agency agreed with eight major global PFAS producers (Arkema, Asahi, BASF Corporation (successor to Ciba), Clariant, Daikin, 3M/Dyneon, DuPont and Solvay Solexis) to launch the “PFOA Stewardship Program”. The program agreed on a reduction of global facility emissions and product content of PFOA by 95% by 2010 (measured against a year 2000 baseline) and to work towards completely eliminating emissions and product content by 2015.^{35,36} However, fluorotelomer based precursor compounds, which can be transformed to PFCAs (including PFOA) metabolically or in the environment, are currently not regulated and no voluntary commitment to reduce emissions exists.

1.8 State-of-science of PFAAs in the aquatic environment in Sweden and the Baltic Sea region prior to this thesis

Up to this thesis there have only been a handful national reports (often written in the native language) and peer-reviewed articles published focusing on PFAAs in various environmental water compartments in Sweden and the Baltic Sea catchment. Representative concentrations of a suite of PFAAs in wet deposition were only available from Northern Germany.³⁷ Other studies usually reported PFAA levels from single rain events focusing on a limited number of PFAAs (often only PFOA and PFOS).^{38,39} Only two peer-reviewed studies on WWTP influents/effluents were published from Denmark and Finland and one study on PFAAs in tap water from Stockholm, Sweden.^{40–42} There were no peer-reviewed studies on PFASs in aqueous fire-fighting foams (AFFF) and their impact on the surrounding environment in the EU.

One of the main reasons for the lack of data has been the analytical challenges in quantification of trace levels of PFAAs in various environmental waters. These challenges comprised inadequate sensitivity, precision and robustness

of methods used in the analysis as well as procedural blank contamination from diffuse sources in the lab. The latter has led to elevated method detection limits (MDLs), jeopardizing the possibility to detect a large number of PFAAs in pristine water bodies.

In a recent research project (COHIBA), concentration data in waste water treatment plant waters was produced for a suite of PFAAs in all of the countries of the Baltic Sea region, except Russia.⁴³ In addition, a Swedish national report from 2014 has shed some light on PFAA contamination in Swedish rivers.⁴⁴ However many data and knowledge gaps still remained on the input pathways, occurrence, transport behavior and fate of PFAAs in the Swedish and Baltic Sea aquatic environment.

2. Overarching aim of the thesis and specific objectives of papers I-IV

The overarching aim of this PhD thesis was to improve our understanding of PFAA input pathways, transport behavior and fate in the aquatic environment in Sweden and in the Baltic Sea catchment. To this end, four different studies were conducted, each of them targeting specific objectives as detailed below (**Paper I-IV**).

Paper I

The main objective of this study was to investigate the spreading of PFAAs from an AFFF impacted site (former military airfield) to the surrounding environment. All point sources of PFAAs within this military airfield had to be identified and the migration of the different PFAAs from these point sources through the soil column and into the ground water was studied.

Paper II

The main objective of this study was to investigate if PFAAs in waste water treatment plant (WWTP) influents predominantly originated from recent primary emissions from the technosphere or from environmental recirculation. A second objective was to assemble a mass balance of PFAAs in the WWTPs in order to evaluate the removal efficiency as well as the presence of precursor compounds in the wastewater stream.

Paper III

The primary objective of this study was to gain a holistic understanding of the major input and output pathways and inventories of PFAAs in the Baltic Sea. A second objective was to identify current knowledge gaps in our understanding of sources and fate of PFAAs in the aquatic environment.

Paper IV

The main objective of this study was to test if PFAA inputs through atmospheric deposition to the catchments of pristine rivers are reflected by riverine PFAA outputs, and thus to improve our understanding of retention processes of PFAAs in the soil column and in ground water. A second objective was to investigate seasonality of PFAA fluxes in atmospheric deposition (rain and snow) and in riverine discharges over a whole year.

3. Experimental section

3.1 Paper I

Paper I describes a case study in Tullinge, Stockholm, where fire-fighting exercises with AFFF formulations on a former military airfield have led to a severe local environmental contamination with PFAAs. The contamination was discovered during a summer school for high school students held at ITM, Stockholm University in 2011, when high PFOA and PFOS concentrations were measured in tap water from Tullinge.¹¹ The water production site was using ground water located under the former military airfield (hereafter called F18). In **Paper I** a systematic approach was used to investigate the magnitude of the contamination, including interviews with former staff of the F18. Furthermore, samples of surface water, ground water, surface soil, soil cores and fish were taken and analyzed.

Examples of some of the questions used in the interviews are:

- ◆ Where and when have AFFFs been used in fire-fighting exercises at the F18?
- ◆ What was the frequency and procedure of the exercises?
- ◆ Where on the airfield have accidents happened with subsequent use of large quantities of AFFFs?

Ground water samples were collected throughout the transect of the former military airfield from ground water wells. Before collecting the samples each ground water well was purged with at least 3 times the volume of the well. Automated pumps were used to pump up the water from 15-30 m depth.

For all surface waters including lakes and ponds the grab sampling technique was used. Grab sampling results in representative samples for the time and place of sampling. Water samples from lakes and ponds were analyzed in order to elucidate the lateral spreading of PFAAs and to identify if the lakes were either contaminated via surface runoff or ground water. Tap water samples were collected in homes surrounding the airfield.

Fish were collected using gill netting in the surrounding lakes in order to identify potential risks for sport fishermen. For details on all samples taken and sampling procedures see the experimental section in **Paper I**.

The extraction of water samples was achieved using a commonly applied solid phase extraction (SPE) method. Soil and fish samples were analysed by solid-liquid extraction (Figure 6). Briefly, dried soil and fresh fish muscle samples were homogenized and extracted using acetonitrile. Internal standards (IS) were added and used for quantification of the target compounds. All samples were analyzed using high performance liquid chromatography coupled to a tandem mass spectrometer (HPLC-MS-MS). Recovery internal standards (RIS) were used for quantification of IS recoveries in the quality control of the method.

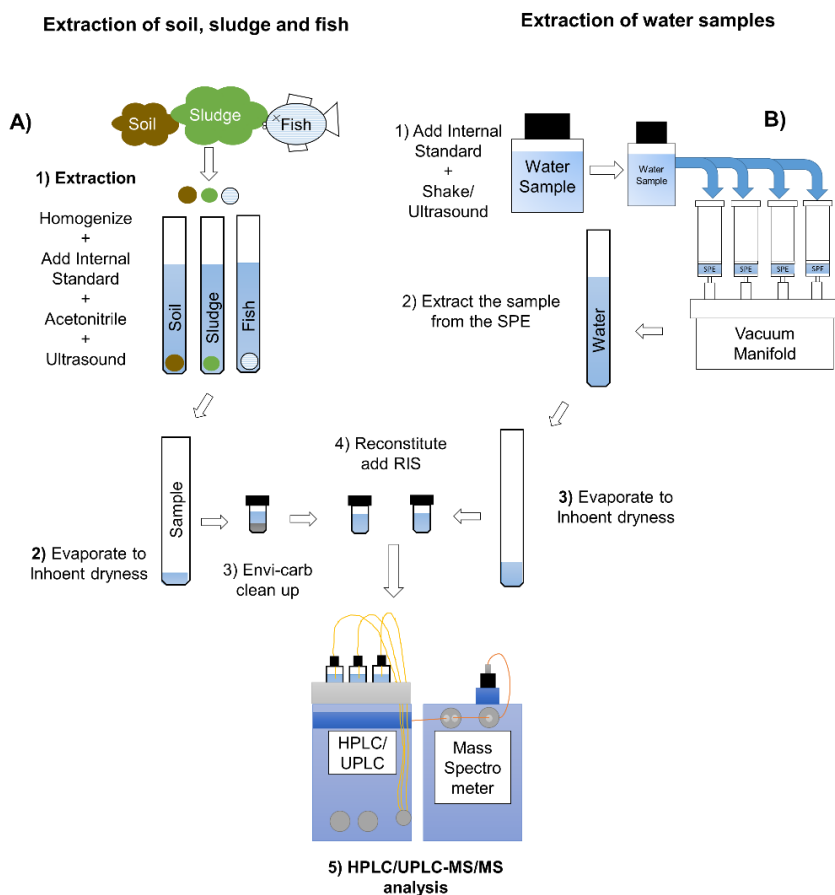


Figure 6. Illustration of the analytical method used for **A)** extraction of soil, sludge (**Paper II**) and fish muscle tissue and **B)** extraction of water samples. The same HPLC-MS-MS method was used for all sample extracts.

3.2 Paper II

Waste water treatment plants (WWTPs) are primarily designed to remove bacteria and various nutrients from the water. Current purification techniques are well suited for this purpose. On the other hand, PFAAs that are present at background concentrations in the waste water show low removal efficiencies. Therefore, it is important to monitor and understand the transport of PFAAs from the technosphere to WWTPs and further into the environment.

In **Paper II** three WWTPs in the cities Stockholm, Umeå and Bollebygd were chosen to investigate the sources of PFAAs to and fate within the WWTPs. The three cities have varying population sizes and use different source water for tap water production, i.e., surface water, river infiltration and ground water. In order to investigate the sources of PFAAs to the WWTPs, tap water from the WWTP drainage area and influent samples were analyzed and PFAA concentrations compared. In order to understand the fate of PFAAs within the WWTPs, chemical mass balances were assembled including PFAAs in influents, sludge and effluents. All samples were collected during cold (below the freezing point) or dry sampling periods (without rain) to avoid a significant contribution of surface runoff to the WWTP influents.

For tap water, primary and secondary sludge sampling daily grab samples were collected. For WWTP influents and effluents a different sampling approach was applied, i.e., time-integrated sampling over 24 h. This method results in representative daily samples despite changing water flows during the course of a day. The sampling procedures and the analyzed samples are described in detail in the experimental section of **Paper II**.

All water samples were extracted using SPE. Primary and secondary sludge samples were analyzed by an ultrasound assisted solid-liquid extraction (Figure 6). All sample extracts were analyzed using ultra performance liquid chromatography (UPLC) coupled to MS-MS.

3.3 Paper III

The Baltic Sea is one of the world's largest brackish water bodies with a surface area of 415 266 km² and a volume of 21 721 km³. The total area of the Baltic Sea catchment is 1 720 270 km².

The Baltic Sea can be divided into five basins, i.e., Bothnian Bay (BB), Bothnian Sea (BS), Baltic Proper (BP), Gulf of Finland (GoF) and Gulf of Riga

(GoR). The Baltic Sea catchment has more than 150 rivers with mouths towards the Baltic Sea. In total there are more than 85 million people living in the catchment and approximately 15 million live within 10 km of the coastline. The population density varies widely from over 500 inhabitants per km² in urbanized regions of Poland, Germany and Denmark to less than 10 inhabitants per km² in northern parts of Finland and Sweden, making it a very diverse catchment.

In **Paper III** mass balances of four PFAAs (PFHxA, PFOA, PFDA and PFOS) were assembled for the Baltic Sea. The mass balances were based on the highest quality available literature data of PFAA concentrations in various media reported after 2006. Calculations were performed on a basin level. Due to the homogeneity of the PFAA concentrations in the different basins, a simple one-box model was finally applied for the Baltic Sea. Furthermore, mass balances of the four target PFAAs were also assembled for the river Oder catchment, in order to better understand the pathways of PFAAs to the rivers discharging into the Baltic Sea. The mass balance models used in this study are shown schematically in Figure 7. To set bounds on the uncertainty, two estimates were calculated: a) High bound estimate (HBE), for which all of the data points reported as non-detected were set to the method detection limit (MDL), and b) low bound estimate (LBE), for which all of the data points below MDL were set to 0.

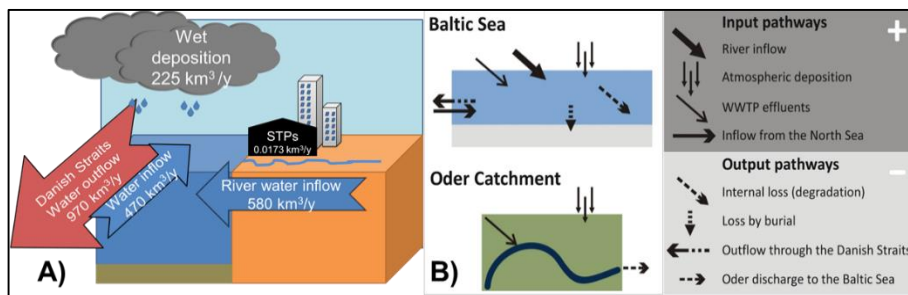


Figure 7. A) Water mass balance of the Baltic Sea. All water fluxes are presented as km³/yr. B) Input and output processes considered for the different basins of the Baltic Sea and for the river Oder catchment in the PFAA mass balances.

In order to be able to calculate basin specific chemical fluxes, the riverine water discharges had to be calculated on a basin basis. This was achieved using basin specific river runoff data from a model by the Nordic Council of Ministers.⁴⁵ Furthermore, basin specific data to calculate wet deposition were needed. These were also taken from the model by the Nordic Council for BB and BS. This model did not distinguish between BP, GoR and GoF. Basin

specific wet deposition was thus estimated by assuming that the wet deposition rate per surface area was equal for these three basins.

3.4 Paper IV

In **Paper IV** mass balances of ten PFAAs were assembled over a whole year for two pristine stream catchments within the Krycklan Catchment Study (KCS) approximately 60 km inland from the Baltic Sea in Northern Sweden. The two streams, hereafter referred to as stream 2 and stream 16 with their respective catchments C2 and C16, were chosen to represent different catchment sizes (C16 is the whole Krycklan catchment whereas C2 is a small sub-catchment) and hydrological functions. Atmospheric deposition was considered as input pathway and stream discharges as output pathway in the mass balance model.

Rain samples including particles and dry deposition were collected between May and November 2011 using a home-made atmospheric bulk deposition sampler (Figure 8). Atmospheric deposition from the winter 2011/2012 was captured in a snow lysimeter. Snowmelt was then sampled during the melting period in April and May 2012. The atmospheric samplers were placed on an open field in the KCS. Stream water of stream 2 and stream 16 was collected as grab samples at the outlets of C2 and C16, respectively. The sampling frequency was twice a month during summer and autumn 2011 and five to six times per month during the spring flood period in April and May 2012. Meteorological records and river flow data were provided by Umeå University.

All water samples were extracted using SPE and analyzed by UPLC-MS-MS as shown schematically in Figure 6B. Details of the analytical procedure and the mass balance calculations are given in **Paper IV** and the corresponding supporting information.

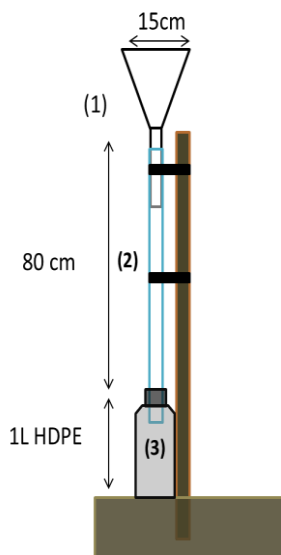


Figure 8. The atmospheric deposition sampler used in **Paper IV**. 1) Polypropylene funnel; 2) polyethylene tubing; 3) high-density polyethylene bottle wrapped in aluminium foil.

4. Results and discussion

4.1 Case study of a point source pollution with PFAAs from usage of aqueous film forming foams (Paper I)

Several publications have pointed out usage of AFFFs especially at airfields as potential point sources of PFAAs to the ground water and surrounding environment.^{46–48} However, airfields are generally large areas that may contain several point sources. In the case of the F18 in the present study interviews with former F18 staff were used to identify all known sites of contamination within the airfield. Multiple point sources were identified where AFFFs have been used during different eras (Figure 9). At these sites surface soil samples and soil cores were collected.

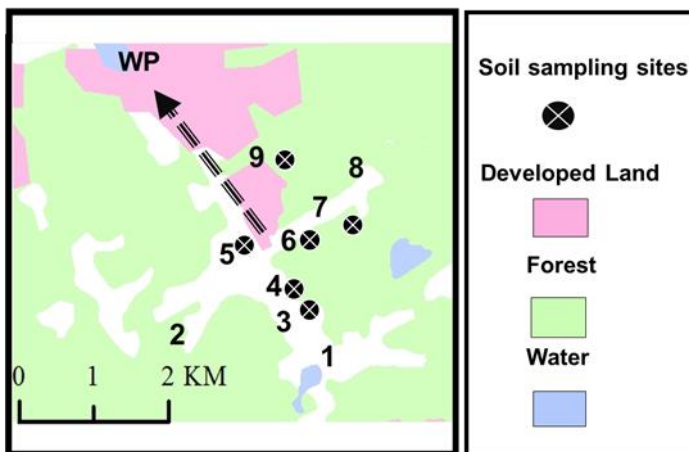


Figure 9. Map of the former air force base F18 in Tullinge. The numbers denote the sites where AFFFs have been used. The surface soil and soil core sampling points are marked with circles. The black dashed arrow illustrates the hydrological flow of the ground water and WP stands for the tap water production plant.

Soil cores down to 4 m depth were analyzed from three AFFF affected sites, the old fire station, the Napalm training ground and the main fire-fighting training facility. The depth profiles of the contamination with PFOS and PFOA are shown in Figure 10. Even though no soil samples were available from 4 m down to 20-30 m (ground water level), the depth profiles indicate that the major part of PFOS is still located in the top 2 m of the soil for the old fire station and the main fire-fighting training facility, or in the top 4 m for the Napalm training ground. The first major results of the study was thus that long-chain PFAAs used in AFFFs could be retained for many years in the soil, with only a slow vertical movement through the soil column. This suggests that the PFOS concentrations in the ground water will increase, possibly for decades to come. On the other hand, it should be possible to remediate the contaminated sites by taking care of the top 2-3 m of soil.

A second observation was that the spreading of PFAAs from the spots of contamination happened via two different pathways, through surface run-off and via ground water. Surface run-off showed to be an important pathway of PFAAs to lakes in the surroundings. PFOS was detected in muscle tissue of several fish species up to 370 ng/g wet weight, representing some of the highest concentrations ever measured.⁴⁹ On the other hand, high PFAA concentrations $>1 \mu\text{g L}^{-1}$ were also observed in the ground water (Table 1 in **Paper I**), which led to contamination of the source water in the tap water production plant (WP) shown in Figure 9.

This study provides detailed information about a severe contamination by PFAAs through application of AFFFs over a long period of time. It highlights the urgent need to find and implement soil (and water) remediation strategies at fire-fighting training sites, not only in Sweden, but also around the world, in order to reduce the risk of future PFAA leakage and exposure of ecosystems and humans.

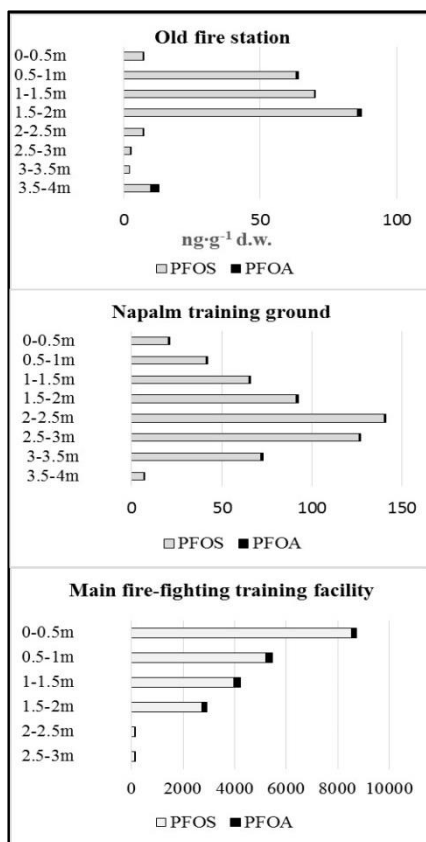


Figure 10. Concentrations of PFOS and PFOA in soil cores in ng g^{-1} dry weight (d.w.).

4.2 Sources and mass balances of PFAAs in waste water treatment plants (Paper II)

In **Paper I** high concentrations of PFAAs were observed in ground water and consequently also in the tap water produced from the ground water source. Tap water is the major water source to WWTPs. These considerations led to the main hypothesis for **Paper II**:

“Tap water may contribute PFAAs to WWTPs that are attributable to environmental recirculation rather than recent releases from the technosphere”

To test the hypothesis tap water, WWTP influents, effluents and sludge were collected in three cities in Sweden. Stockholm, the capital of Sweden, is a heavily urbanized area and therefore elevated levels of PFAAs could be expected in the tap water. In contrast, Bollebygd (semi-rural small city) and Umeå (medium size city in Northern Sweden) were chosen as less urbanized cities with no known PFAA contaminated sites.

The results showed that a suite of PFAAs were ubiquitously present in the tap water of all cities, yet at different levels. PFAA concentrations in tap water from Stockholm were in the ng L^{-1} range, whereas in Umeå and Bollebygd the PFAAs were mostly at low pg L^{-1} levels (Table 1 in **Paper II**). PFBA, a short chain PFCA, was reported for the first time in tap water from Scandinavia. Short chain PFAAs are currently used as replacement chemicals for the long chain PFAAs such as PFOA and PFOS. On the other hand, PFAAs in WWTP influents and effluents were in the ng L^{-1} range in all three cities. Short chain PFAAs were at similar concentrations in the influents and their corresponding effluents, whereas the concentrations of longer chain PFAAs were considerably lower in the effluents due to higher affinity to sludge. The mass balances were roughly closed for most PFAAs when comparing chemical mass flows in the influents with mass flows in effluents plus sludge (Figure 1 in **Paper II**). However, for PFHxA and PFOA an increase of concentrations and chemical mass flows in the effluents compared to the influents was observed. We suggest that degradation of precursors in the biological or abiotic treatment processes within the WWTPs led to these findings.

In Bollebygd and Umeå the low levels of PFAAs in the tap water did not markedly influence the concentrations found in the WWTPs. However, in Stockholm the PFAAs measured in tap water contributed significantly (up to 86 % for PFBS) to the levels in WWTP influents and thus also effluents. Using PFAA concentrations in the effluents to calculate emissions to the environ-

ment would thus lead to an overestimation of new releases from the technosphere. To estimate primary discharges from households and the technosphere, a compound-specific correction factor should thus be applied to account for the environmentally recirculated PFAAs in the tap water. The corrected population normalized primary PFAA emission rates cER_{PFAA} ($\mu\text{g d}^{-1} \text{Pe}^{-1}$) via effluent water are calculated according to

$$cER_{PFAA} = \frac{(C_{WWTP\ influent} - C_{Tap\ water})}{C_{WWTP\ influent}} * ER_{PFAA}$$

where $C_{Tap\ water}$ is the PFAA concentration in tap water (pg L^{-1}), $C_{WWTP\ influent}$ the PFAA concentration in the WWTP influent (pg L^{-1}) and ER_{PFAA} is the conventionally calculated population normalized emission rate ($\mu\text{g d}^{-1} \text{Pe}^{-1}$) based on the quantified PFAA concentration in the effluent. This concept is not only valid for PFAAs, it is valid for all mobile chemicals which are present in source waters used for tap water production and poorly removed by water purification plants.

The concept presented in **Paper II** led to the following suggestion: If elevated PFAA concentrations are observed in commonly monitored WWTP effluents, then the tap water from the drainage area of the WWTP and the influent should be analyzed separately. In case the tap water is a significant source of the contamination, then action may be required to reduce human exposure through water consumption. In case the tap water is not contaminated, there may be a point source of PFAAs in the drainage area (e.g. industry or an AFFF contaminated site) that could potentially be identified and eliminated in order to minimize the leakage of PFAAs to the aquatic environment via WWTPs.

4.3 Mass balance of PFAAs in the Baltic Sea (Paper III)

One of the challenges in **Paper III** was to calculate basin specific PFAA input fluxes originating from the technosphere surrounding the Baltic Sea. This was done by calculating country specific population normalized PFAA discharges from WWTPs and applying them to the coastal cities surrounding the Baltic Sea. Interestingly, the concentrations of PFHxA, PFOA and PFOS in WWTP effluent waters were significantly higher for the countries with a high gross domestic product (GDP) >37 000 US\$ (Sweden and Finland) in comparison to the group of countries with a lower GDP <20 500 US\$. This might be due

to differences in use and application of PFAS containing products such as (pricey) durable water repellent outdoor clothing.

The results of the PFAA mass balance calculations for the Baltic Sea are summarized in Table 1. Rivers were a major source of all investigated compounds to the Baltic Sea as was atmospheric deposition followed by the inflow from the North Sea and WWTP discharges. These results are generally consistent with previous studies from the Great Lakes by Boulanger et al. and Scott et al.^{50,51}

Table 1. Summary of the PFAA mass balances for the Baltic Sea. The ranges are delineated by the low bound estimates (LBE) and high bound estimates (HBE).

Input [kg/yr]	PFHxA	PFOA	PFDA	PFOS
Riverine discharges	16-426	401-641	54.4-311	876-924
Atmospheric deposition	60.2-62.9	365-367	141-144	239
WWTP discharges	6.84	10.6	0.72-0.99	12.6
North Sea inflow	80.8-85.5	66.5-69.4	0.00-6.18	0.00-14.3
Sum	164-582	843-1090	195-462	1130-1190
Output [kg/yr]				
Sediment burial	2.18	14.9	5.53-23.3	17.7
Danish Straits outflow	155	370	16.5-47.5	177
Transformation	0.0940	0.210	0.00770-0.292	0.0983
Sum	157	385	22.0-70.8	195
Inventory [kg]				
Baltic Sea water	3080	7270	260-1030	3460
Sediment	125	827	314-1250	986
Sum	3200	8100	574-2280	4450

A major observation was that WWTP discharges directly to the Baltic Sea made a negligible contribution to the overall inputs in the mass balances, whereas atmospheric deposition was an important pathway of PFAAs to the Baltic Sea. Previous studies have shown a good correlation between the population size in river catchments and PFAA fluxes in the rivers.⁵² It has been assumed that this correlation showed that primary releases from the technosphere via WWTPs were a major source of PFAAs to the aquatic environment.⁵²

However, the population size in a catchment is likely to also correlate with the catchment area, which is proportional to the amount of precipitation to the catchment (within a given climate zone) and thus the input fluxes of PFAAs

via atmospheric deposition. Therefore, the relative importance of different input pathways to watersheds cannot be elucidated by correlation studies. It has to be investigated for each catchment of interest individually, as catchments in different parts of the world differ markedly, not only in population size or density, but also in the degree of industrialization (e.g., see discussion on GDP above), topology and hydrology.

The observation of the significance of atmospheric deposition for PFAA inputs to the Baltic Sea revealed an important knowledge gap, i.e., how PFAAs are being released/transferred to the atmosphere. Are industrial emissions to air most important? Is degradation of volatile, airborne PFAA precursor compounds an important pathway? Or are atmospheric levels of PFAAs primarily the result of environmental circulation from surface water, e.g., via sea spray?²⁴ These are some of the research questions that are still unanswered. However, if the last hypothesis on the importance of environmental circulation was true, then at least a part of the input surplus observed in the mass balance (see the section below) would be compensated by sea spray as an output pathway, which was not considered in the present study.

The last major observation was the positive mass balance for the Baltic Sea, i.e., a surplus of chemical input fluxes compared to output fluxes (Table 1). From this surplus and from the chemical inventory in the Baltic Sea water doubling times for the different PFAAs could be calculated. The estimated doubling times for PFOA and PFOS were 12-16 yr and 4 yr, respectively. These were broadly consistent with the doubling times observed in bio-monitoring data for Baltic Sea herring.⁵³ Furthermore, a recent study on PFAA concentrations in soil collected worldwide showed that some PFAAs were ubiquitously present.⁵⁴ An estimation of the total amount of PFOS in soil in the Baltic Sea catchment, based on the concentrations measured in this worldwide study,⁵⁴ showed that the soil could be a larger reservoir of PFOS than the Baltic Sea itself. This finding is in line with the conclusion from Paper I, that PFOS is strongly retained in the soil.

4.4 How do atmospheric inputs of PFAAs relate to stream discharges in two remote watersheds? (Paper IV)

One of the major conclusions from **Paper III** was that atmospheric deposition and riverine discharges were the main pathways for PFAAs to the Baltic Sea. In **Paper IV** we wanted to investigate whether riverine PFAA fluxes in a pristine region of the Baltic Sea watershed represented recent atmospheric inputs or if the concentrations and patterns in the streams are influenced by historic inputs and/or environmental attenuation of the PFAAs in the soil and deep ground water zone.

PFCAs and PFSAAs were detected in both rain and snowmelt samples, with distinct differences in concentrations and patterns as shown in Figure 2 in **Paper IV**. While PFHxA and PFOA dominated in the rain samples, both relatively to the odd chain PFCAs and absolutely compared to snowmelt samples, PFHpA and PFNA were the dominant PFAAs in the snowmelt. Average concentrations of these four PFCAs were in the hundreds pg L^{-1} .

The dominance of PFHxA and PFOA in rain could be due to season-specific transformation of airborne precursor compounds. Concentrations of PFSAs were considerably lower compared to PFCAs. This is likely due to the phase-out of the manufacturing of PFOS and its precursors by the 3M Company in 2002, while the production and use of PFCAs and their fluorotelomer-based precursors is still continuing.

The concentrations and patterns of the PFAAs in the samples from stream 2 and 16 are shown in Figure 11 for sequential samples taken over a year. A significant difference between the two stream systems is observed when comparing PFAA concentrations between spring flood and the rest of the year. For stream 2 there are no noteworthy seasonal trends for any of the investigated PFAAs, whereas stream 16 showed considerably lower levels of PFHxA, PFOA, and PFHxS during the rest of the year compared to spring flood (Figure 11B). The low concentrations in stream 16 during the rest of the year indicate that the upstream inflow from stream 2 and similar catchments was diluted by water inflow from other (uncontaminated) sources. This confirmed the results of an earlier study estimating that 79%-85% of the water in stream 16 during baseline flow consists of old groundwater (presumably several decades old).

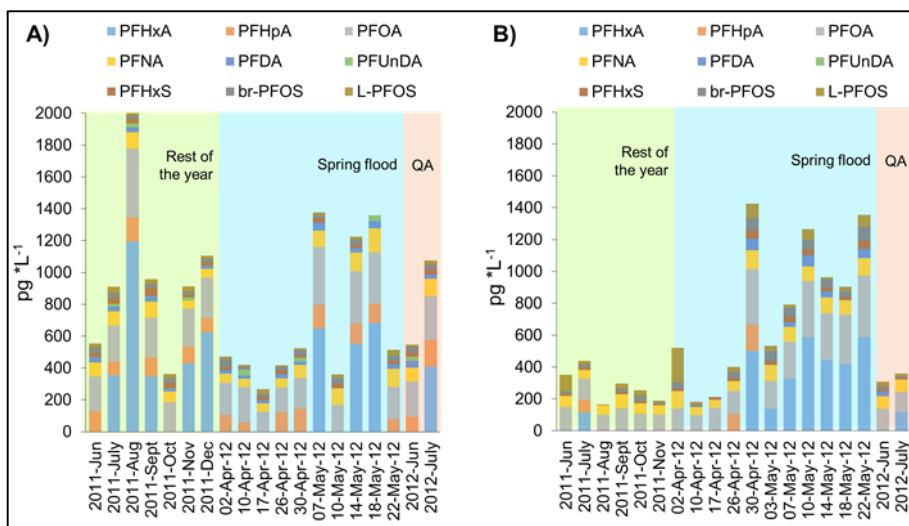


Figure 11. LBE concentrations (pg L^{-1}) and patterns of PFAAs in A) stream 2 samples and B) stream 16 samples. The results are shown sequentially according to the time point of sampling. Results for samples from June and July 2012 are shown to demonstrate the comparability between years (compared to June and July 2011). However, these results were not used in the mass balance calculations.

The chemical fluxes in atmospheric deposition and in stream 2 and 16 were used as inputs and outputs, respectively, in the mass balance model. The PFAA mass balances over the whole year are similar in C2 and C16 as shown in Figure 12. Marked differences in the output/input ratios (Figures 12A1 and 12B1) are apparent for PFHxA and PFHpA (higher value for C2) as well as for br-PFOS and L-PFOS (lower value for C2). This can be explained by a combination of the expected recent temporal trends of emissions and therewith atmospheric inputs (increasing for PFHxA, PFHpA and their precursors due to the shift in production from long-chain PFCAs to short-chain homologs; decreasing for PFOS and its precursors due to the production phase-out by the 3M Company in 2002) and the average age of the water in the streams (older water in C16).

The main observation in Figure 12 is that atmospheric inputs were considerably larger than riverine outputs for all PFAAs except PFHxS in both catchments. As PFAAs are not expected to degrade in the environment, nor to volatilize, the positive mass balances suggest that the PFAA inventories in the soil or the deep ground water of the watersheds are increasing. This is consistent with observations in **Paper I** and **Paper III** indicating that a considerable fraction of PFOS entering the Baltic Sea catchment is "stored" in the soil.

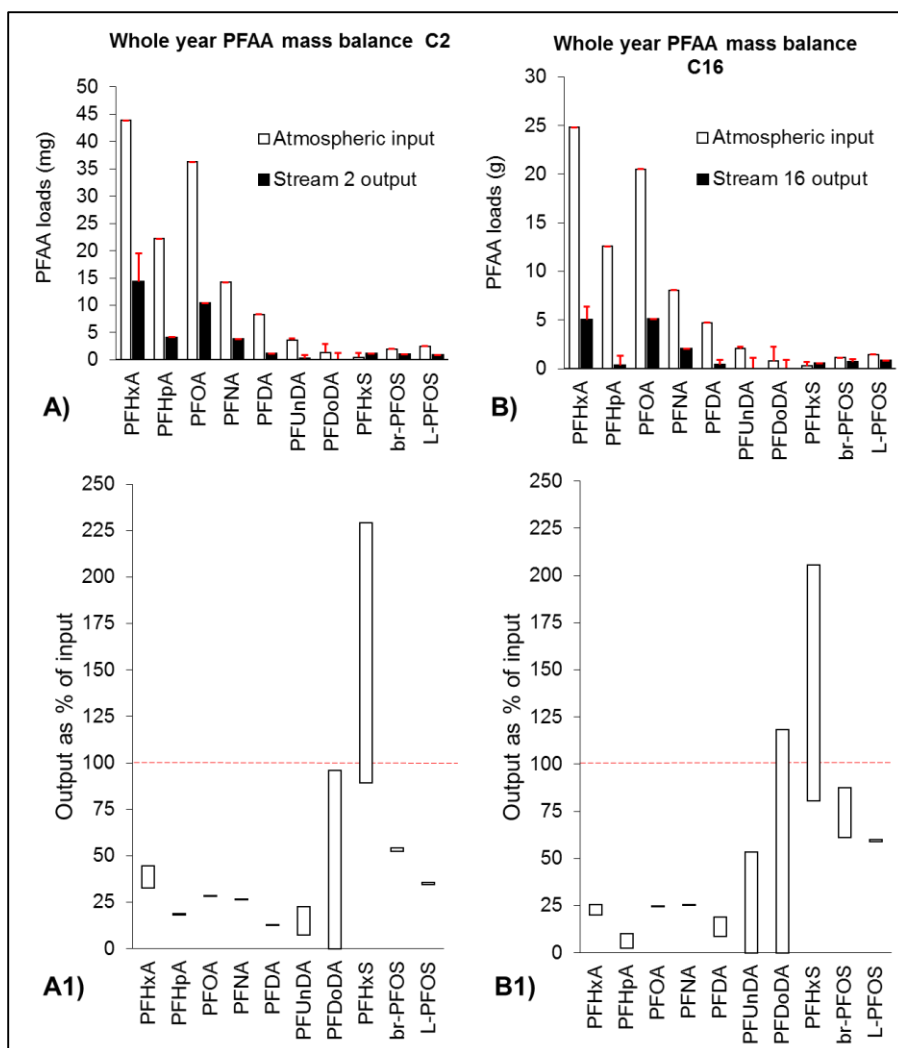


Figure 12. Total PFAA atmospheric inputs (white bars) and stream discharges (black bars) over the whole year are compared for A) C2 and B) C16. The LBE values are shown with solid bars and the HBE values with error bars. The output expressed as a percentage of the input is shown for A1) C2 and B1) C16. The ranges depict LBE_{output}/HBE_{input} to HBE_{output}/LBE_{input} . A closed mass balance would correspond to 100% (horizontal dotted line).

5. Conclusions

This doctoral thesis combined trace analytical measurement techniques with mass balance modelling in order to increase our holistic understanding of the transport and fate of PFAAs in the aquatic environment. PFAAs were found to be omnipresent in the Nordic aquatic environment, even in remote and pristine regions.

In **Paper I** it was shown in a case study that the historical use of AFFFs has led to a severe contamination of soil, surface water, ground water and consequently also drinking water. This awareness has initiated a program by the Swedish Chemicals Agency and the Swedish National Food Agency aiming at mapping all former AFFF training sites and their potential hydrological connections to drinking water resources, leading to the identification of a number of such cases in Sweden. Hopefully, this approach will be copied by other countries. Despite the fact that PFOS-containing AFFFs are not used in Sweden any more for several years, the problem of PFOS leaking from highly contaminated soils into ground water aquifers will occupy us for many years or decades to come. This is corroborated by findings in **Paper III and IV**. Remediation strategies for contaminated soils are thus a high priority research issue.

The extraordinary persistency together with the widespread distribution and high mobility of especially short chain PFAAs lead to an environmental recirculation of PFAAs. This phenomenon is explored in detail in **Paper II** for WWTPs. But also in the context of the presence of PFAAs in atmospheric deposition samples in **Paper III** the question of environmental recirculation as a potential pathway for PFAAs to the atmosphere was discussed. Environmental recirculation needs to be investigated and understood better in order not to overestimate current (new) emissions of PFAAs.

PFAA precursor compounds have not been investigated within this doctoral thesis. Nevertheless, indirect evidence in both **Paper II and IV** suggested that precursor degradation is an important contributor to current PFHxA and PFOA emissions to the environment. The relative importance of a multitude of precursors for environmental levels of PFAAs is a current research topic, but still far from being well understood.

A major conclusion from **Paper III** is that atmospheric deposition is likely the primary pathway for PFAAs to the European Nordic environment, whereas emissions via WWTPs play a minor role. However, this may look different in other parts of the world. Furthermore, it remains to be investigated whether or not PFAA levels measured in atmospheric deposition are influenced by environmental recirculation. From our current understanding discussed in **Paper III** we can expect that the levels of long chain PFAAs in the Baltic Sea are increasing. This is in line with the conclusion discussed above that a considerable fraction of historic emissions of long chain PFAAs is assumed to be stored in soil and slowly leaking into ground water and surface water (**Paper I and IV**). Hence, the concentration peak in the aquatic environment may well lie ahead of us for several PFAAs.

In 2011 the European Commission proposed a European quality standard (EQS) for PFOS in marine waters. According to the EQS, PFOS levels in marine waters should not exceed 0.13 ng L^{-1} . Current PFOS levels in the Baltic Sea clearly exceed the EQS and are expected to increase for an unknown period of time in the future (**Paper III**). This poses a challenge for industry, scientists, engineers and regulators alike.

6. Outlook

Monitoring of PFAAs in tap water and ground water both in Sweden and worldwide has been focusing primarily on PFOA and PFOS. These two PFAAs are important to monitor given their large historical production volumes as well as from a regulatory point of view. However, industrial production and use patterns of PFASs have been changing over the last 15 years. Future research and monitoring should thus always include a suite of homologs for both PFCAs and PFSAs. This is important in order to fully understand the different physical-chemical properties of the PFAAs and the risk from exposure to the mixture of PFAAs present in the environment, including drinking water and food.

Many studies have been focusing on emissions of PFAAs via WWTPs. We have shown that this may not be a primary research need for Northern Europe. However, monitoring of novel PFAS replacement chemicals in WWTPs should be included in upcoming studies in order to understand the implications of recent changes in the PFAS industry. Furthermore, elucidation of the pathways of PFAAs to the atmosphere, including the role of precursors and of environmental recirculation should be given a high research priority.

This thesis provides comprehensive methods for assembling PFAA mass balances in the aquatic environment. In view of the constantly increasing amount of available monitoring data and the temporal changes in production and emissions of PFAAs, this work should be continued, updated and extended to further PFAAs and their precursors. This will help to even better understand the environmental behavior and fate of PFAAs as well as illuminate future temporal trends in emissions and levels in the environment.

A major observation in three of the presented papers is that long chain PFAAs can be strongly retained in soil. Once emitted to the terrestrial environment (e.g., through atmospheric deposition, application of WWTP sludge in agriculture or use of AFFFs) these compounds can leak over decades into ground water and surface water. The magnitude and potential impact of this “ticking time bomb” have not been investigated so far and need urgent attention.

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