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Evaluation of PFAS removal from nanofiltration membrane concentrate using foam fractionation

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Abstract

Per- and polyfluorinated substances (PFASs) have become an urgent topic in the water treatment industry in recent years as a consequence of new scientific discoveries of the correlation between the ingestion of some PFASs and their toxicity in humans and other organisms. PFASs are synthetic compounds present in a variety of products. Due to their desirable physical and chemical properties, PFASs are found in everything from clothes and furniture to aqueous fire-fighting foams. These compounds have also been identified in food and drinking water. The flourine-carbon bond present in these chemicals are exceptionally strong. Hence PFASs are persistent in nature when leaked to the environment. Additionally, the mobility properties of PFASs in the soil leads to contamination of surface and groundwater, necessitating actions from drinking water treatment plants (DWTP).

Nanofiltration plants have shown to successfully reduce the PFASs content in contaminated waters. The accumulation of PFASs in the concentrate is a potent source of these compounds and requires treatment before leaving the DWTP. Foam fractionation (FF) is an aeration technique that utilizes the hydrophobic properties of the PFASs compounds, in which PFASs adsorbs to the interfaces of introduced rising air-bubbles. The foam forming at the surface is then extracted, reducing the contamination.

In this study, the efficacy of the FF system on a concentrate from a two-stage nanofiltration membrane was evaluated. Also, the ability of surfactants to enhance the PFAS reduction was explored. The study was conducted in two parts. The first part was executed in a laboratory scale environment where five surfactants were added to a batchwise FF system. A minimum dose was determined and four experimental runs were then executed for each surfactant: Zero surfactant, 1x minimum dose, 2x minimum dose and 5x minimum dose. The results were evaluated and the surfactant showing the greatest improvement of PFASs removal, in this study a cationic surfactant, was chosen for further investigations in the second part. A continuous pilot FF system was used in the second part, the inner diameter of the colon was 54 mm, the height of the water column was held at 1 m prior to the aeration, the contact time (CT) was 10 minutes and the air-flow rate was set to be 4 L/min in all runs. Four experimental runs were conducted with different doses of the cationic surfactant: Zero surfactant, 1x minimum dose, 2x minimum dose and 3x minimum dose. Each experiment was repeated three times. A total of 12 runs were performed.

The results showed a removal efficiency of > 99 % of long-chained PFASs in all conducted experimental runs. Without the addition of surfactant, the average removal efficiency of $\sum$ short-chained PFASs was 61 % whereas maximum removal (77 %) was obtained with the highest surfactant dose applied. The mean reduction of $\sum$PFASs was 90 % in the zero surfactant run and 94 % in the highest dose experiment. The main findings from the study were that: 1) FF is an efficient method for the removal of long-chained PFASs from concentrate 2) Surfactants can be added to increase the removal of short-chained PFASs, 3) Higher dosing of the surfactant positively correlated with the removal efficiency of $\sum$short-chained PFASs in the FF system, however the relationship was not linear.

Keywords: PFAS, Aeration foam fractionation, Nanofiltration membrane, DWTP, Surfactant

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Referat

Per- and polyfluorerade ämnen (PFAS) är ett högaktuellt forskningsområde inom dricksvattenproduktion. På senare år har ny forskning påvisat korrelationen mellan intag av vissa PFAS-ämnen och hälsoproblem hos både människor och djur. PFAS är syntetiskt framställda kemikalier som förekommer i flertalet av våra vardagliga produkter på grund av dess fördelaktiga fysiska- och kemiska egenskaper. PFAS används i allt från smink och möbler till brandskum men har också påträffats i dricksvatten och mat. Kol-fluor bindningen som förekommer i alla PFAS-ämnen tillhör den organiska kemins starkaste bindningar. Följaktligen bryts PFAS-ämnen ned extremt långsamt när de hamnar i naturen. PFAS förmåga att mobilisera sig i jorden leder till kontaminering av yt- och grundvatten vilket tvingar dricksvattenverk att vidta åtgärder.

Nanofiltration har visat sig vara en kraftfull metod för att rena vatten från PFAS. I koncentratet, det vill säga det vatten som inte renas genom membranen, ackumuleras PFAS vilket förutsätter en separat reningsprocess innan vattnet kan släppas ut i naturen. Skumfraktionering är en luftbaserad teknik som utnyttjar hydrofobiciteten i PFAS. PFAS-ämnen adsorberas till ytan hos de injicerade luftbubblorna och transporteras till vattenytan där det bildar ett skum. Uppsamling av skummet reduceras således kontamineringen.

I den här studien bedömdes effektiviteten av skumfraktionering på koncentratet från ett två-stegs nanofiltrationsmembran. Därutöver undersöktes effekterna av att tillföra surfaktanter till systemet för att optimera reduceringen. Studien genomfördes i två delar. Den första delen ufördes i en mindre skala där 5 olika surfaktanter adderades till en satsvis-skumfraktioneringsprocess. Initialt bestämdes en minimum dosering för alla surfaktanter. Totalt genomfördes 4 experiment: Ingen surfaktant, 1x minimum dosen, 2x minimum dosen, 5x minimum dosen. Den surfaktant som påvisade bäst effekt på reduceringen av PFAS, i detta fall en katjonisk surfaktant, användes sedan.

I den andra delen av arbetet användes en kontinuerlig skumfraktioneringsprocess. Den inre diametern på kolonnen var 54 mm, vattenkolumnen hölls konstant på 1 m innan luftningen, kontakttiden var 10 min och lufthastigheten var satt till 4 L/min. Totalt genomfördes 4 experiment: Ingen surfaktant, 1x minimum dosen, 2x minimum dosen, 3x minimum dosen. Varje experiment upprepades tre gånger.

Resultatet visade att > 99 % av ∑långkedjiga PFAS-ämnen reducerades i alla genomförda experiment. Den genomsnittliga reduktionen av ∑kortkedjiga PFAS-ämnen var 63 % i experimenten utan surfaktant, medan i experimenten med den högsta doseringen var reduktionen 77 %. Den genomsnittliga reduktionen av $\sum_{11}$ PFAS var 94 % för den högsta doseringen medans den var 90 % i experimentet utan surfaktant. Studien visade att:
1) Skumfraktionering är en effektiv metod för att rena koncentrat från långkedjiga-PFAS 2) Surfaktanter kan fördelaktigen användas för att optimera reningen av kortkedjiga-PFAS ämnen. 3) Högre dosering av surfaktanter korrelerade med högre reduktion av ∑kortkedjiga PFAS i skumfraktioneringsprocessen, ökningen var dock inte linjär.

Nyckelord: PFAS, Skumfraktionering, Nanofiltration, Vattenverk, Surfaktant

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Preface

This thesis was written as the final part of the master program Environmental and Water Engineering at Uppsala University and the Swedish University of Agricultural Sciences (SLU). The thesis hold 30 credits and is the conclusive part of my education. The study has been conducted in close contact with my supervisor Philip McCleaf from Uppsala Vatten and Avfall AB and my subject reviewer Lutz Ahrens from the Department of Aquatic Sciences and Assessments at SLU.

I would like to take this moment and thank Philip and Lutz for their commitment and enthusiasm regarding this project. Without their knowledge and valuable inputs, this work would never been done. Thank you for your willingness to share your expertise and your genuine interest of the subject. I have learned so much from you.

I am also very greatful for the hospitality at Uppsala Vatten and Avfall AB which provided me with all the necessary equipment, water analysis and access to Bäcklösa water treatment plant where the experiments were executed. Also, a huge thank you to the staff at Uppsala Vatten and Avfall AB which made the breaks fun and relaxing.

William Stefansson
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Populärvetenskaplig sammanfattning

Per- och polyflourinerade ämnen (PFASs) har blivit allt mer omtalade på senare år till följd av att ny forskning påvisat kopplingen mellan några av dessa konstgjorda ämnen med negativa hälsoeffekter för människor och djur. PFAS förekommer inte naturligt i naturen utan har framställts av människan för dess attraktiva egenskaper. PFAS används flitigt av industrier och förekommer i flertalet av våra vardagliga produkter så som smink, stekpannor och brandskum men även i mat och dricksvatten. Det stora problemet med PFAS-ämnen är dess stabilitet. När PFAS når naturen bryts de ned oerhört långsamt, och restprodukterna blir istället andra likvärdigt stabila ämnen. Utifrån detta har begreppet ”evighetsämnen” myntats och givits till PFAS. Effekterna blir att PFAS som kommer ut i miljön blir kvar.

PFAS-ämnen som hamnar i marken stannar inte på ytan utan följer med regnvattenströmmar ned genom jorden och når tillslut grundvattnet. I Uppsala har man haft stora problem med höga halter av PFAS i vissa delar av stadens grundvattenmagasin. Detta har inneburit att åtgärder har behövt vidtas för att sänka halterna till säkra nivåer. Livsmedelsverket som är ansvariga för vilka nivåer som är godkända att släppa ut i dricksvattnet har nyligen lämnat in nya lagförslag på striktare regleringar som förväntas bli aktuella 2026. Till följd av framtida krav på högre rening har Uppsala Vatten och avfall AB börjat utreda möjligheterna av en framtida reningsprocess.

Alternativet som utretts har varit att implementera ett nanofiltrationsmembran, vilket är ett typ av filter som förhindrar PFAS-ämnena att passera. När vattnet transporteras genom membranet fastnar de oönskade ämnen på utsidan av filtret och ackumuleras i ett vatten som kallas koncentrat. Vattnet som går igenom membranet blir renat. Utmaningen ligger i att behandla koncentratet vars PFAS halter är för höga för att få släppas ut i naturen.

Skumfraktionering är en metod för att separera PFAS från vatten. Detta görs genom att luftbubblor pumpas in från botten i en behållare varvid PFAS-ämnen fastnar på det stigande bubblorna. Skummet som bildas på toppen sugs sedan upp och det renade vattnet leds vidare. I den här rapporten undersöktes det hur effektiv skumfraktionerings processen var på att separera PFAS från koncentratet från ett nanofiltrationsmembran. En annan del av arbetet var att utreda effekterna av att addera olika surfaktanter (kemiska ämnen som underlättar skumbildning) för att öka effektiviteten i processen.

Arbetet utfördes i två delar. Första delen av studien gick ut på att testa olika surfaktanter i en mindre skumfraktioneringsuppställning. Detta för att få en känsla för vilka doseringar som var effektiva men också för att selektera fram den surfaktant som visade sig ha störst positiv effekt på reduceringen av PFAS. I del två så användes den utprövade doseringen från del ett samt den surfaktant som presterade bäst i en större pilot-uppställning. Fyra experiment genomfördes. Det första experimentet var skumfraktionering utan tillsats av surfaktant medans de tre övriga innehöll olika doseringar.

Resultatet visade att skumfraktionering var en effektiv metod för att rena koncentratet på PFAS-ämnen. Speciellt effektiv var metoden att rena koncentratet från en viss typ av PFAS-ämnen, långkedjiga sådana. Bortförande graden låg strax över 99 % för denna typ. Kortkedjiga PFAS-ämnen reducerades till 61 % i processen utan användning av surfaktant. När en positivt laddad surfaktant användes ökade reduktionen till 77 % i det experimentet med högst dosering. Slutsatsen blev att skumfraktionering är en effektiv metod för att rena koncentratet från

långkedjiga PFAS-ämnen. För att öka bortförande graden av kortkedjiga PFAS-ämnen kan surfaktanter adderas till skumfraktioneringsprocessen.

Abbreviations

- AFFF – Aqueous film-forming foam
- CT – Contact time
- DWTP – Drinking water treatment plant
- EFSA – European Environment Agency
- EID – Experimental ID
- EtFOSA – N-ethyl perfluorooctane sulfonamide
- EtFOSAA – N-ethylperfluorooctanesulfonamido acid
- EU – European Union
- FF – Foam fractionation
- FOSA – Perfluorooctanesulfonamide 1
- FOSAA – Perfluorooctane sulfonamidoacetic acid
- GAC – Granular activated carbon
- HCL – Hydrochloric acid
- HPFHpA7 – 7H-perflouroheptanic acid
- LAS – Linear alkylenebenzene sulfonic acid
- LOR – Limit of reporting
- MeFOSA – N-methyl perfluorooctane sulfonamide
- MeFOSAA – N-methylperfluorooctanesulfonamido acid
- MeFOSE – N-methyl perfluorooctane sulfonamidoethanol
- MEUF – Micellar enhanced ultrafiltration
- NF – Nanofiltration
- PFAS – Per- and polyfluorinated substance
- PFBA – Perfluoro+A1:D32-n-butanoic acid
- PFBS – Perfluorobutanesulfonic acid

- PFDA – Perfluoro-n-decanoic acid
- PFDoDA – Perfluoro-n-dodecanoic acid
- PFDoDS – Perfluorodecane sulfonic acid
- PFDS – Perfluorodecanesulfonic acid
- PFHpA – Perfluoro-n-heptanoic acid
- PFHpS – Perfluoroheptanesulfonic acid
- PFHxA – Perfluoro-n-hexanoic acid
- PFHxS – Perfluorohexanesulfonic acid
- PFNA – Perfluorononanoic acid
- PFNS – Perfluorononane sulfonic acid
- PFOA – Perfluorooctanoic acid
- PFOS – Perfluorooctanesulfonic acid
- PFPeA – Perfluoro-n-pentanoic acid
- PFPeS – Perfluoropentane sulfonic acid
- PFTeDA – Perfluoro-n-tetradecanoic acid
- PFTriDA – Perfluoro-n-tridecanoic acid
- PFUnDA – Perfluoro-n-undecanoic acid
- PF37DMOA – Perfluoro-3,7-dimethyloctanic acid
- SFA – Swedish Food Agency
- WWTP – Waste Water Treatment Plant
- 4:2 FTSA – Fluorotelomer sulfonic acid
- 6:2 FTSA – Fluorotelomer sulfonate
- 8:2 FTSA – Fluorotelomer sulfonate

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1 Introduction

Per- and polyfluoroalkyl substances (PFASs) are an emerging subject in our society due to the recent discoveries of their environmental and human health effects (EPA 2022). PFASs have been around since the 1940s and are frequently used in industries and consumer products globally due to their useful physical and chemical properties (EPA 2022). The carbon-flourine bond that occurs in all PFAS compounds is one of the strongest chemical bonds found in organic chemistry, hence their ability to remain stable during extreme conditions such as under profound heat exposure (ECHA 2022). The unique properties of PFASs makes them suitable for a variety of products such as furniture, clothes, aqueous fire fighting-foam (AFFF), food packaging and frying pans (Franke *et al.* 2019). They have also been identified in food and drinking water (EPA 2022). The stability of PFASs does not just make them desirable for industrial applications, these characteristics also make the carbon-fluorinated substances persistent in nature (ECHA 2022). PFASs have enough mobility to percolate and contaminate groundwater (Linderoth *et al.* 2016). Three of the most researched PFASs are Perfluorooctanoic acid (PFOA), Perfluorooctanesulfonic acid (PFOS) and Perfluorohexanesulfonic acid (PFHxS). All these compounds have been linked to bioaccumulation and toxicity (Domingo 2012).

In Uppsala, Sweden, high concentrations of PFASs are present in some parts of the drinking water distribution net, due to the use of AFFF at a military airport in the northern parts of Uppsala. Uppsala Water and Waste AB modified 10 existing granular activated carbon (GAC) filters in April of 2015 at Bäcklösa drinking water treatment plant (DWTP) to reduce the amounts and to satisfy the PFAS effluent requirements. The Swedish National Food Agency (Livsmedelsverket), the central authority responsible for supervising the drinking water regulations, has recently published a legislative proposal regarding the allowed concentrations of PFASs in the drinking water. This follows a recent report conducted by the European Food Safety Authority (EFSA), which expressed health concerns associated with the ingestion of some PFASs (Livsmedelsverket 2022). The current allowed amount of PFAS effluent, 90 ng/L for PFAS 11, will be lowered to 4 ng/L for PFAS 4. 10 more compounds will also be included in a new category, PFAS 21, with a limit of 100 ng/L. The legislation is expected to be implemented in 2026 (Livsmedelsverket 2022). Table 1 explain each PFAS category.

Uppsala Water & Waste AB is interested in using nanofiltration (NF) for the future removal of PFASs. Franke *et*.al (2019) showed that NF could remove on average 99 % of PFASs in the groundwater of Uppsala. A major concern regarding NF is the produced concentrate during operation. At least 10 % of the treated volume becomes highly concentrated concentrate (Franke et. al 2021), also known as reject. In the same study, the authors emphasized the importance of treating the concentrate in a full-scale NF installation.

Commonly, concentrates from NFs are led into rivers, watercourses or to a wastewater treatment plant (WWTP) (Franke *et al.* 2019). Conventional treatment methods at WWTPs have shown to be ineffective in their removal of PFAS (Schultz *et al.* 2006). Thus a method to reduce the concentration of the concentrate is of great interest. The current environmental quality norm in Sweden is 90 ng/L of PFAS 11 in groundwater and surface water (Kemi 2020), however new investigations regarding PFASs conducted by SGI in 2022-2024 could result in substantially lowered values and include more PFAS compounds, as been observed in the newly proposed drinking water regulations (Livsmedelsverket 2022).

Foam fractionation is a process showed to lower PFASs in leachate (Kjellgren 2020; Robey *et al.* 2020), AFFF solution (Meng *et al.* 2018) and in contaminated groundwater (Dai et.al, 2000).

This thesis will investigate the efficacy of the FF system for PFAS removal in the concentrate of a two-staged nanofiltration process. The report will also cover the use of surfactants to potentially enhance the reduction of PFAS in FF.

1.1 Aim and research questions

The aim of the thesis was to investigate if FF could be efficiently used to remove PFASs in the concentrate from a nanofiltration membrane pilot plant. The other objective was to inquire into the potential of using surfactants to enhance the process. The following three research questions were addressed:

- Is foam fractionation an efficient method to remove PFASs from the nanofiltration membrane concentrate?
- Could surfactants be used to enhance the removal of PFASs in the foam fractionation process?
- Is the reduction of PFASs in the foam fractionation process affected by different concentrations of surfactants?

1.2 Hypothesis

The hypothesis is that the FF system will efficiently reduce the PFASs in the concentrate. Additionally, it is hypothesized that the use of surfactants in the FF process will enhance the removal efficiency of PFASs. Finally, its hypothesized that there will be a correlation between the addition of the surfactant and the removal efficiency of PFASs in the FF system.

2 Theory

2.1 PFAS

2.1.1 Introduction to PFASs

PFASs are fluorinated aliphatic substances where one or more carbon atom inside the chain have replaced its hydrogen atoms with flourine. PFASs is the acronym for the two subsets of fluorinated aliphatic compounds, polyfluoroalkyl- and perfluoroalkyl substances (KEMI 2015). Perfluoroalkyl substances have their carbon chains fully saturated with flourine atoms, except the carbon involved in the functional group. Polyfluoroalkyl substances are not fully saturated, they still contain some hydrogen bonds along the fluorinated aliphatic chain (Buck *et al.* 2011). Due to the occurrence of hydrogen bonds, polyfluorinated substances are less stable and can be broken down into perfluorinated compounds (KEMI 2015). All PFASs have at least one perfluoroalkyl moiety, $-C_nF_{2n}$, inside their molecule structure (Buck *et al.* 2011).
The differences between polyfluorinated and perfluorinated compounds are shown in figures 1 and 2. PFAS contains a hydrophobic tail and a polar head, hence the compounds are surfactants. Fluorocarbon-tailed surfactants lowers the surface tension more efficiently than their hydrocarbon substitute (Rosen & Kunjappu 2012).

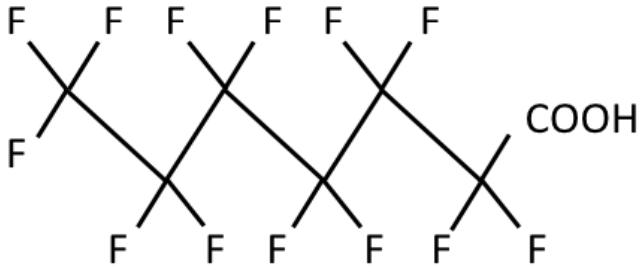


Figure 1: Example of a perflourinated compound, adapted from Buck et al. 2011

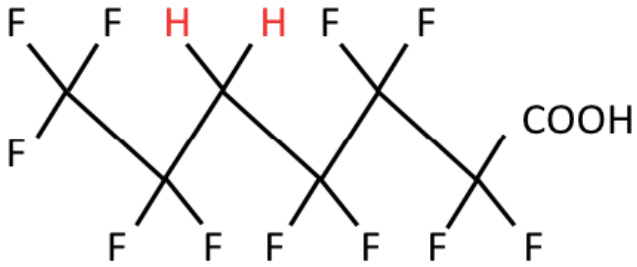


Figure 2: Example of a polyfluorinated compound, adapted from Buck et al. 2011

2.1.2 The manufacturing process of PFASs

PFASs are produced mainly through two manufacturing processes, electrochemical flourination and telomerization (Buck *et al.* 2011). During electrochemical fluorination, a natural organic compound is placed in a hydrogen-flourine solution. The substances are generated through electrolysis of the carbon compound in the mixture, replacing the hydrogens with flourine atoms (Buck *et al.* 2011). Telomerization is a step-wise process where a perfluoroalkyl iodide first reacts with tetrafluoroethylene to form longer perfluorinated molecules. Depending on the desired product, the produced compounds can be used in further reactions (Buck *et al.* 2011).

2.1.3 Classification of PFASs

There are over 4700 different kinds of PFASs on the global market (Franke *et al.* 2017). Some compounds have more similar properties than others. Below, are four common ways to divide PFASs according to different properties.

- Length of the carbon-chain
- Functional-group
- Branched or linear
- Precursors

PFASs are usually categorized into short- or long chained compounds. The classification depends on both the number of carbons within the aliphatic chain and the functional group. PFCAs (perfluoroalkyl carboxylic acids) and PFASs (perfluoroalkyl sulfonic acids) are both linked to the terminology of long and short chained PFASs (Franke *et al.* 2017). For PFCAs, 7 or more carbons are included in the aliphatic chain in the group classified as long-chained. For PFSAs are compounds with 6 carbons or more in the aliphatic chain classified as long-chained PFSAs. The functional group of PFCAs is the carboxylic acid (-COOH), whereas PFSAs contains the sulfonic acid ($-SO_3H$).

Depending on the manufacturing process of PFASs, both branched and linear chains may be produced. Isomers of PFASs have different chemical properties which are important to consider in the treatment process (Franke *et al.* 2017). Precursors are defined as the PFASs that degrades into long-chained PFCAs and PFSAs (Franke *et al.* 2017). A common precursor is fluorotelomer sulfonate (6:2 FTSA) (Livsmedelsverket 2022).

2.1.4 Regulations of PFASs in drinking water, groundwater and surface water

The European Union (EU), implemented limits for PFASs in the drinking water directive in 2020 (ECHA 2020). The new rules were a minimum directive, obligating all member states to achieve the set limits, while also retaining the option to introduce stricter legislation. The European Food Safety Authority (EFSA) provided new guidelines in 2020 for the amount of PFASs that could be safely ingested by humans. As a consequence of the report, the Swedish Food Agency (SFA), proposed new legislation for lowering the limit values of PFASs in the Swedish drinking water. The new regulation is expected to be implemented the 1st of January 2026 (Livsmedelsverket 2022). The proposed limits are:

- **PFAS 4**: 4 ng/L
- **PFAS 21**: 100 ng/L

Today, PFAS 11 are not allowed to exceed 90 ng/L in the drinking water in Sweden (Livsmedelsverket 2022). The environmental quality norm of PFAS 11 in groundwater is 90 ng/L in Sweden, PFOS is limited to 45 ng/L. Surface water used in drinking water production has the limit of 90 ng/L (Kemi 2020).

PFAS 4 includes the following compounds: PFOA, PFNA, PFOS, PFHxS. These substances were directly targeted in the EFSA report, where human toxicity was shown, when above certain concentrations (EFSA 2020). PFAS 21 includes all the 20 substances that needs to be regulated according to the EU-directive, as well as 6:2 FTS, which have been included for a

long time in the PFASs removal list controlled by the SFA (Livsmedelsverket 2022). Table 1 shows all 21 compounds included in PFAS 21, PFAS 11 and PFAS 4 are marked.

Table 1: All compounds included in PFAS 21. PFAS 4 and PFAS 11 are marked with x.

PFCAs		PFAS 4	PFAS 11
PFBA	Perfluoro-n-butanoic acid		x
PFPeA	Perfluoro-n-pentanoic acid		x
PFHxA	Perfluoro-n-hexanoic acid		x
PFHpA	Perfluoro-n-heptanoic acid		x
PFOA	Perfluoro-n-octanoic acid	x	x
PFNA	Perfluoro-n-nonanoic acid	x	x
PFDA	Perfluoro-n-decanoic acid		x
PFUnDA	Perfluoro-n-undecanoic acid		
PFDoDA	Perfluoro-n-dodecanoic acid		
PFTrDA	Perfluoro-n-tridecanoic acid		
PFSAs			
PFBS	Perfluorobutanesulfonic acid		x
PFPS	Perfluoropentane sulfonic acid		
PFHxS	Perfluorohexanesulfonic acid	x	x
PFHpS	Perfluoroheptanesulfonic acid		
PFOS	Perfluorooctanesulfonic acid	x	x
PFNS	Perfluorononanesulfonic acid		
PFDS	Perfluorodecanesulfonic acid		
PFUnDS	Perfluoroundecanesulfonic acid		
PFDoDS	Perfluorododecanesulfonic acid		
PFTrDS	Perfluorotridecanesulfonic acid		
Precursors			
6:2 FTSA	Fluorotelomer sulfonate		x

2.1.5 PFASs impacts on humans and the environment

PFASs are extremely stable compounds that do not easily degrade in nature. The carbon-flourine bond present in all of these compounds is one of the strongest bonds found in organic chemistry (ECHA 2022). As many persistent chemicals, PFASs ends up in nature which leads to problematic accumulation (ECHA 2022).

The mobility properties of PFASs in the soil causes contaminations of surface water and groundwater (KEMI 2015). The main concerns regarding PFASs is that they have shown to bioaccumulate in living organism with toxic health implications. Some PFASs have been associated with increased risks of cancer and recent research suggests the correlation between decreased vaccine efficacy in young children and ingestion of PFASs (ECHA 2022; EFSA 2020). The most researched PFASs (PFOS, PFOA and PFHxS) have all been linked to toxicity and bioaccumulation (Domingo 2012). The most substantial contribution of PFASs pollution comes from industrial manufacturing. Humans are mostly exposed to PFASs through food and drinking water (ECHA 2020). The largest contributing point source of PFASs in Sweden is the use of AFFFs at military facilities across the country. These areas contains high concentrations of PFAS in their soils which contaminates the surface water and groundwater during rain events (Linderoth *et al.* 2016).

2.2 Surfactants

2.2.1 Introduction to surfactants

Surfactants, or surface-active agents, are multifaceted compounds which properties are favorable in a variety of products. They are used in everything from pharmaceuticals and motor oils to detergents. In recent years, surfactants have also been used in novelty technologies as biotechnology and microelectronics (Rosen & Kunjappu 2012).

Surfactants belongs to the group of amphiphiles which are molecules with both hydrophobic and hydrophilic properties. Surfactants consists of mainly two parts, one polar head and one non-polar tail. The head is usually hydrophilic and the tail hydrophobic (Renoncourt 2005). The most common hydrophobic tail is made up of hydrocarbons, but could also consist of a siloxane chain or fluorocarbons (Rosen & Kunjappu 2012). The classification of surfactants are usually made due to the charge of the head, which can be anionic (negative charge), non-ionic (no charge), cationic (positive charge) or zwitterionic (contains both a positive and a negative charge) (Renoncourt 2005). Figure 3 shows a simplified image of the structure of a surfactant.

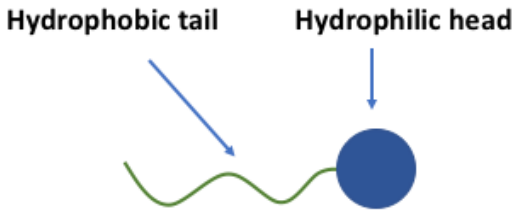


Figure 3: Simplified structure of a surfactant

2.2.2 Surfactants and their function

The mechanism behind surface active compounds is that they adsorbs to surfaces and interfaces when present at low concentrations, lowering the tension of each stretched film. The interface is the dividing line between two unmixable liquids, and the surface is obtained between a gas and a liquid (Rosen & Kunjappu 2012). The interfacial (or surface) energy is defined as the minimum work required to obtain and sustain an interface per unit area. The interfacial (or surface) tension is the amount of work needed to stretch, or to create, the interface (or surface) per unit area. Generally, low concentrations of surfactants lowers the interfacial (or surface) energy, hence reducing the amount of work needed to stretch the interface (or surface). In other words, surfactants facilitate the stretching of interfaces and surfaces (Rosen & Kunjappu 2012). Water molecules at the surface, have less adjacent molecules for bonding due to their exposure to air. This phenomenon increases the difference in energy states between the molecules at the surface and in the solution. The surface tension reduces the surface area thus lowering the dissimilarity in energy between the molecules in the solution and on the surface (Nakama 2017).

Inside the solution, the hydrophobic tail of the surfactant breaks the hydrogen-bonds between the water molecules, thus increase the free energy of the system. To lower the energy, some surfactants are expelled to the surface where they orient in a single layer (Rosen & Kunjappu

2012). At the surface are the tails pointing outwards due to their hydrophobicity. Figure 4 shows the orientation of surfactants at the surface with hydrophobic tails and hydrophobic heads.

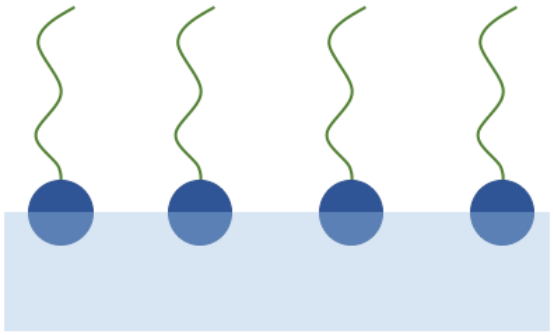


Figure 4: Shows the orientation of surfactants at the water-air interface with hydrophilic heads and a hydrophobic tails.

Surfactants migrate back into the solution, forming micelles, when saturation occurs at the surface. Micelles are self-aggregating structures, where usually the lipophilic tails are enclosed by its hydrophilic head to form stabile structures inside the solution (Renoncourt 2005). The critical micelle concentration (CMC) is the concentration needed for the formation of the micelles. The CMC is controlled by factors such as temperature, electrolyte concentrations, chemical properties of the surfactant and pH (Renoncourt 2005; Nakama 2017).

The solubility of surfactants is greatly influenced by the length of the hydrophobic group. A long hydrophobic tail increase the chance of the compound being expelled to the surface, due to higher hydrophobicity. At the surface, the surfactants merge together as a consequence of higher affinity towards each other. The merging of surfactant will increase the likelihood of the formation of micelles and it will also enhance the sensitivity of ionic surfactants for precipitation with counter ions (Rosen & Kunjappu 2012).

A branched hydrophobic group increases the solubility of the surfactant. It could also impact the biodegradability negatively (Rosen & Kunjappu 2012).

2.2.3 Why are surfactants used in products?

The main function of surfactants is to lower the surface- or interfacial tension. By doing so, a variety of applications are available. As earlier mentioned, surfactants are used in many different products. In cosmetics, surfactants are used for stabilizing solutions, for keeping immiscible liquids evenly mixed (such as oil and water) and for increasing the absorption in the skin and hair. The function of the surfactant depends on its concentration (Nakama 2017). When using detergents, lowering of the surface tension increases the wettability of the solution, hence dirt are easily removed (Britannica 2022).

2.2.4 The role of surfactants in foam fractionation

Huang et al. (2019) showed that the use of a nonionic-anionic surfactant mix (Triton-X100/SDS) could be used to enhance the removal of a FF system of low doses of Cadmium from micellar enhanced ultrafiltration (MEUF) in waste water-treatment plants. The report also concluded that, high additions of Triton-X100 had a negative impact on the removal due to the

decreased interaction between SDS and the divalent ions in the presence of Triton-X100. The authors theorized the mechanisms behind the increased removal rates as, enhanced foam properties due to the addition of surfactant.

Meng et al. (2018) showed that the use of a co-existing surfactant improved the removal rate of PFOS in the aeration foam-collection process of an AFFF solution (Meng et al. 2018). In the report, an alkyl polyglucoside (non-ionic hydrocarbon) surfactant was used. The surfactant showed to be efficient in enhancing the removal of high concentrations of PFOS.

2.3 Foam fractionation

2.3.1 Introduction to Foam fractionation

FF is a well-established particle separation technique that has been used in different industries since it was developed in the 1940s (Buckley *et al.* 2021). In recent years, the interest for the use of FF in the water treatment industry has surged due to its potential in removing surface active-contaminants, its low capital and operating costs, its simplicity and its low energy usage (Buckley *et al.* 2021; Wong *et al.* 2001).

FF is a physiochemical process where pressurized air is introduced into a container of liquid (Buckley *et al.* 2021). The rising bubbles furnishes an abundance of air-water interfaces where surface-active compounds and hydrophobic molecules adsorbs. The rising bubbles creates a foam, given that the bubbles are stable, at the surface which can be extracted to separate the adsorbed particles from the aqueous solution (Lemlich 1968). FF can be operated either continuously, semi-batchwise or batchwise (Buckley *et al.* 2021).

In continuous operation, the container of water is constantly feed with untreated liquid. It is of great importance to keep the surface height constant during continuous operation to secure steady-state with respect to inflow, outflow, foam formation and foam uptake. The concentration of the feed should also be constant (Buckley *et al.* 2021). The point of the feed intake determines the type of which continuous operation that takes place. Stripping mode refers to a setup where the intake is above the air-water interface, whereas enriching mode has the feed entering below the water surface (Figure 5). The harvested foam can be reinserted for increased removal (Figure 6).

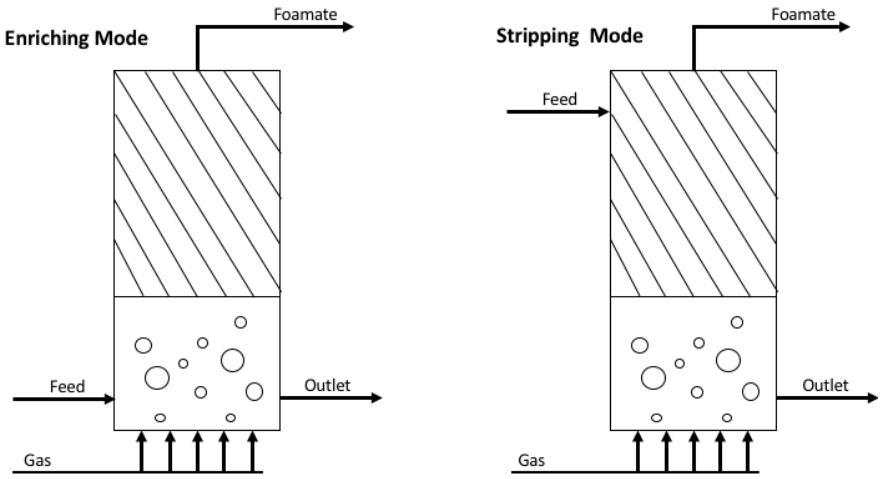


Figure 5: Two different continuous modes of foam fractionation operation, stripping mode and enriching mode. Adapted from Buckley et.al 2021.

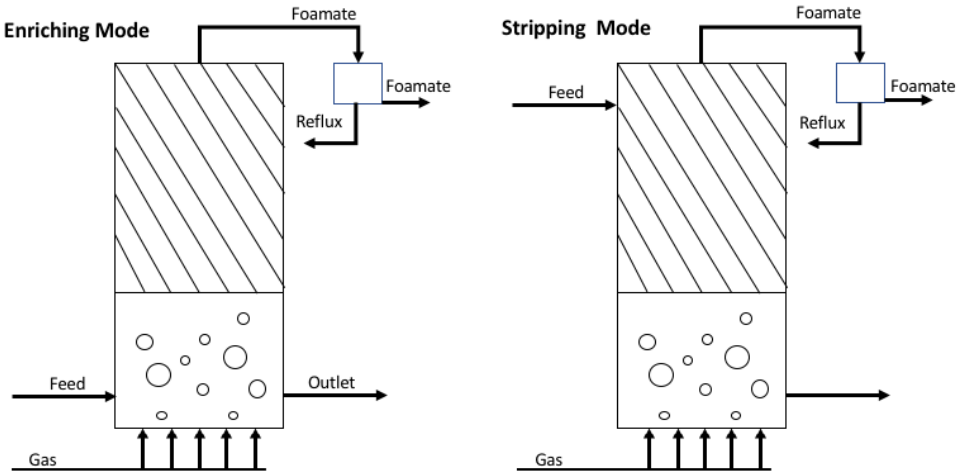


Figure 6: Two different continuous modes of foam fractionation with reflux. Enriching mode and stripping mode. Adapted from Buckley et.al 2021.

Enrichment is the terminology used for relating the ratio between the concentration in the collected foam to the feed. Recovery is used to describe the ratio between outflow and feed. It describes how much of the targeted compound that was removed in the process. The foam fractionation process can be optimized by changing factors such as the temperature, pH, poor-size of air-diffusing membrane, feed flow rate, and gas flow rate (Merz *et al.* 2011).

2.3.2 Foam stability

The formation of foam occurs if the surface energy of the adsorbed material is low enough to stabilize the film of the bubble. Foam formation and its stability is governed by mainly three mechanisms; gas diffusion, bubble coalescence and the drainage of the thin film between adjacent bubbles (Buckley 2021). Gas diffusion occurs due to the difference in pressure between adjacent bubbles of different size. Smaller bubbles have higher internal

pressure than larger bubbles, hence the air diffuses through the point of contact until the small bubble evanesce. Simultaneously, the larger bubble increases in size. The results of gas diffusion and bubble coalescence are less air-liquid interfaces and losses of liquid with adsorbents from the foam due to the gravitational forces (Buckley 2021).

The Young-Laplace equation is the common formula to describe the relationship between inner pressure and the exterior pressure as a consequence of surface tension for a spherical bubble (Matsumoto & Tanaka 2008).

$$P_{vap} = P_{liq} + \frac{2\gamma}{R} \qquad (1)$$

P_{vap} is the inner pressure, P_{liq} is the outer pressure, γ is the surface tension and R is the radius. The theory states that the stability of a bubble increases with lowered internal pressure. By decreasing the surface tension, when adding surfactants, the inner pressure of the bubble could be reduced and the general stability of the bubble would then be increased (Meng *et al.* 2018) .

There are other phenomena involved in foam stability. The Marangoni effect describes the surfactants role in the stability by opposing any local stretches of the bubbles (Lemlich 1968). The diffusion of surfactants inside the film of the bubble isn't immediate, which entails that the surface tension increases locally due to more hydrogen-bonds in the stretched area (less surfactants). The increase in local surface tension opposes the forces to stretch the bubble film (Lemlich 1968).

Another factor of importance for foam stability is the electric repulsion force between surfactants of different surfaces. If the repulsion between charged surfaces in two parallel bubble films is high enough, the force will oppose coalescence (potential rupture) (Lemlich 1968).

A third mechanism that is involved in foam stability is the Gibbs effect (Lemlich 1968). . The Gibbs effect is similar to Marangoni and describes the inability of the molecules to diffuse completely as a response to a local stretch. The Gibbs effect states that the local increase in surface tension are not completely temporary. This phenomena is present regardless of the molecules diffusion rate in the bubble film (Lemlich 1968).

2.3.3 Conducted studies on PFAS removal with foam fractionation

Meng et al. (2018) used aeration foam-collection to efficiently remove PFOS from an AFFFs solution. The column used had a diameter of 0.05 m and the treated volume was 0.6 L. The pore diameter of the diffusing membrane was 10 μm and the aeration flow rate was 0.075 L/min. The concentration of PFOS were 0.093 mmol/L. The report showed that the recovery of PFOS was 96 % after two hours of aeration.

Kjellgren (2020) showed that aeration foam-collection could efficiently be used to remove PFASs from leachate water. The water column used had a diameter of 0.057 m and the treated volume was 2.5 L. The concentration of ΣPFASs in the leachate were approximately 5500 ng/L. Both continuous and batch experiments were conducted. The continuous experiments showed an average removal of 86 % which were 8% higher than the batchwise tests. Also, the use of

surfactants (a detergent called YES) were shown to improve the removal compared to the reference without additives. Different air flows were tested which implied that a higher flow rate of 4 L/min and 6 L/min were superior to 2 L/min for the batchwise experiments. The continuous tests only used an aeration flow rate of 2 L/min. The report also concluded that additives like NaCl (0.16 and 0.31% of leachate) and FeCl (0.09% of leachate) improved the recovery of ΣPFASs. A contact time of 20 minutes were also shown to be superior over 10 and 5 min in terms of ΣPFASs removal. A conclusion from the study were that the reduction of ΣPFASs in the aeration foam collection process is strongly dependent on the chain length of the PFASs compounds, where longer chained compounds were more easily removed. The reduction was also dependent on the functional group. Shorter chained PFCAs had the lowest removal rates.

Krögerström (2021) used a continuous aeration foam fractionation process to remove PFASs from leachate water. The column used, had a diameter of 0.186 m, the aerated flow rate was 10 L/min and the treated volume was 46 L. The report concluded that PFSAs were more easily reduced than PFCAs with an average removal rate of 59 % compared to 48%. The recovery for precursors were 78%. The study focused on the impacts of contact time and the fraction of foam harvested. The results implied that a contact time of 30 minutes with a harvested foam fraction of 5% provided the best outcome in terms of ΣPFASs removal. Important conclusions from the report were that longer chained PFASs had a higher reduction than shorter compounds and that the recovery was impacted by the functional group. The report also stated that aeration foam fractionation had very low removal of some shorter PFASs compounds.

2.4 Nanofiltration

2.4.1 Introduction to nanofiltration

Nanofiltration (NF) is a pressurized separation technique that utilizes semipermeable membranes to remove unwanted dissolved substances in the raw water (Bergman 2007). NF can also remove particular matter, macromolecules, multivalent ions and also smaller organic compounds to some extent (Bruggen *et al.* 2003). High loads of larger particles can lead to rapid fouling, hence NF is often used in the later stages of the water treatment process. NF membranes can not be backwashed as a consequence of the membrane not being porous (Bergman 2007). Hence the membranes needs chemical treatment for regeneration.

One common NF configuration used in commercial application is the spiral-wound NF. Spiral-wound membranes generally consist of two sheets of membranes, each attached on a backing-material, separated by a medium, which facilitates the transportation of the permeate. The double sheet is rolled into the shape of a spiral. Three of four sides of the layered sheets are glude together, and the remained opening is directed to the permeate channel located in the center of the spiral. A plastic layer is added to each “envelope” to separate membranes of different envelopes. Water that does not pass the membranes are collected as concentrate. (Bergman 2007)

The main removal mechanism behind pressurized membranes is the size-exclusion of compounds and particles greater than the size of the pores (Van deer Bruggen, B., 2003). The poor size of the membrane is in the range of 1-10 nm, which is in between ultrafiltration and reverse osmosis in terms of its potential in rejecting ionic or molecular compounds (Ismail & Matsuura 2022).

2.4.2 Nanofiltration and PFASs removal

Nanofiltration and its ability to remove PFASs from water are well documented (M. Rahman 2014; Franke et.al 2019; Franke et.al 2021). A nanofiltration pilot plant at Bäcklösa Uppsala Sweden showed PFASs removals of >98 % (Franke et.al 2021). Nanofiltration have shown to remove PFASs particles smaller than the pores of its membrane, indicating the presence of other active removal processes than only size-exclusion (Franke. et al. 2019).

2.4.3 Nanofiltration set-up

A spiral-wound nanofiltration pilot was used for the creation of concentrate used in the thesis. The pilot was a two-stage NF system. The first stage consisted of 6 spiral-wound membranes (NF90-400; Dow Filmtech Membranes) and the second stage contained three. The flow-rate of the feedwater was 8 m^3 $hr^{-1}$and the recirculation was 6 m^3 hr^{-1}. The feedwater was pretreated before entering the membranes through a 5 um prefilter containing 7 elements (*GE Infrastructure Water and Process Technology Purtrex 5− 30 filter).* Pretreatment was executed to remove any solid particles present in the water.

3. Method and Materials

3.1 Targeted PFASs

Table 2 displays the targeted PFASs, PFAS 11. The list was retrieved from SFA (Livsmedelsverket 2022).

Table 2: List of targeted PFASs, their acronym,full name and perfluorocarbon chain length

PFCAs		Perfluorocarbon chain length
PFBA	Perfluoro-n-butanoic acid	C3
PFPeA	Perfluoro-n-pentanoic acid	C4
PFHxA	Perfluoro-n-hexanoic acid	C5
PFHpA	Perfluoro-n-heptanoic acid	C6
PFOA	Perfluoro-n-octanoic acid	C7
PFNA	Perfluoro-n-nonanoic acid	C8
PFDA	Perfluoro-n-decanoic acid	C9
PFSAs		
PFBS	Perfluorobutanesulfonic acid	C4
PFHxS	Perfluorohexanesulfonic acid	C6
PFOS	Perfluorooctanesulfonic acid	C8
Precursors		
6:2 FTSA	Fluorotelomer sulfonate	C6

3.2 Surfactants

Table 2 displays the surfactants used in the laboratory work, their surfactant classification and their molecular formula. Information regarding the molecular formula was retrieved from the distributor. If not given, the CAS number was used.

Table 3: Surfactants used in the Laboratory work, their classification and molecular formula

Name	Classification	Molecular formula
Montaline C 40	Cationic	$C_{10}H_{21}O_3N_3 - R$ (R=12-18)
Marlinat 282/24	Anionic	Not given
Simulsol SL 10	Non-ionic	$C_6H_{11}O_6 - R$ (R=10-12)
Linear alkylbenzene sulfonate	Anionic	$C_{18}H_{30}O_3S$
YES (Detergent)	Mix of Anionic and Zwitterionic	Anionic: Not given Zwitterionic: $(CH_2)10 - 12, C_4H_{11}NO)$

Simulsol SL 10 is a non inonic high foaming alcyl polyglucoside surfactant derived from glucose and fatty alcohols, with CAS number 110615-47-9. Montaline C 40 is a polyvalent

cationic surfactant with good foaming abilities. It is a quartenised coconut oil and the INCI name is cocamidopropyl betainamide mea chloride. Its CAS number is 164288-56-6. Marlinat 242/28 is an anionic surfactant. The INCI name is Sodium Laureth sulfate and the CAS number is 68891-38-3. Linear alkylbenzenesulfonic acid (LAS) is an anionic surfactant. Linear alkylbenzene sulfonates was first introduced on the market in the 1960s as a substitute for non-biodegradable surfactants. Linear alkylbenzene sulfonates are characterized as the most important anionic surfactant in textile cleaning due to its low cost and great performance (St. Laurent *et al.* 2007). The CAS number of LAS is 68584-22-5. YES is a common detergent used in Sweden. Its chemical composition is a mixture of ethoxylated alcohols C9-14, sulphated sodium salts, and lauryl dimethylamine.

The biodegradability, bioaccumulation and toxicity profile of each surfactant are summarized in Table 4. Information was retrieved from respective safety sheet.

Table 4: Surfactants used in the laboratory work, their biodegradability, bioaccumulation potential and toxicity profile for aquatic life

Name	Classification	Biodegradability	Bioaccumulation Potential	Toxicity
Montaline C 40	Cationic	Readily biodegradable	Low	Toxic to aquatic life
Marlinat 242/28	Anionic	Readily biodegradable	Low	Toxic to aquatic life
Simulsol SL 10	Non-ionic (Alkyl glucoside)	Readily biodegradable	Low	Not classified as toxic
LAS	Anionic	Not given	Low	Low aquatic toxicity
YES	Mix of Anionic and Zwitterionic	Biodegradable	Low	Toxic to aquatic life

3.3 Nanofiltration concentrate

The laboratory- and pilot work used a two stage nanofiltration concentrate which was stored in a 600 liter PE (polyethylene) container. The concentrate was extracted with a hose connected to the tank bottom. A large mechanical stirrer was attached for mixing and was turned-on for at least 1 hour before retrieving the concentrate. Several samples were taken from the container during the experiment period to detect any significant changes in the chemistry of the water.

The concentrate was transported in a 10 L plastic container for the lab-scale experiments and in a 10 L carboy of glass for the pilot setup. Both containers were put on a magnetic stirrer for 15 min in preparation for every experimental run.

A lot of the harvested water were consumed during the lab-scale and the anticipation of higher demand for the pilot-setup resulted in a refill of the tanks before the pilot experiments were conducted. The two stage nanofiltration concentrate therefor differed slightly between the two set-ups.

3.4 Laboratory-scale

Prior to investigate the effects of surfactants on the FF process in the pilot-scale, initial experiments were conducted in a laboratory-scale environment. The objective was to determine if the reduction of PFASs in the FF process could be enhanced by the addition of surfactants, and if so, identify the surfactant with the greatest contribution in terms of increased removal efficiency. Five surfactants were selected, Table (3), and a total of 20 experimental runs were conducted, four runs for each surfactant (Table 5, section 3.7.1).

The lab-scale experiments were divided into two parts. The first part was to determine the minimum dose of the surfactants. In the second part, four experiments were conducted for each surfactant; zero surfactant (only concentrate), 1x the minimum dose, 2x the minimum dose and 5x the minimum dose. The minimum dose was used to simplify the comparison between the effects of different surfactants on the foam, also to give indications of the concentrations needed for PFAS removal. The criteria for the minimum dose were:

- *A significant change in the foam composition compared to the reference of no addition of the surfactant*
- *The elevation of the highest bubbles in the foam must be in the range of the 290-300 mL in the glass column, which was approximately 20-30 ml above the reference (≈2 cm)*

Every surfactant formed a unique foam in terms of bubble size, foam height and stability. Also, PFASs are surfactants, hence a foam appears on the surface during FF operation without any addition of surfactants. Two samples were harvested for each concentration, one for the foam and one for the remaining liquid in the column. Early testing in the laboratory-scale indicated that a strong stock solution was required to observe any visual effects on the foam, hence a stronger stock solution for all surfactants were used during the procedure compared to the expected concentrations prior to the testing. 1 mL of the initial stock solution would give a surfactant/PFAS mole ratio of 1/1 when mixed with the concentrate. Part one showed that effects of the foam was observed at surfactant/PFAS mole ratios > 1000 (Table 5).

3.4.1 Experimental set-up

Figure 7 shows the batchwise experimental set-up for the foam fractionation system used in the Laboratory-scale. A 1000 mL glass column was used with an inner diameter of 5.2 cm and length 55 cm. A sintered glass filter (Saveen and Werner) was mounted in the bottom of the column for dispersion of incoming air. Air was introduced from the bottom of the column and the flow was adjusted with a rotameter. The flow of the air-pump (JBL ProSilent a100**)** was approximately 100 L/h for all experiments. Foam was entering a plastic collector [1] through hose [2] by activation from the vacuum pump (GAST, DOA-P504-BN). Samples of the collapsed foam, was taken from the collector and weighed. After aeration, the hose in the bottom of vent [5] was removed and a sample flask was placed underneath to capture the treated liquid remaining in the column. The weight was measured.

All samples were harvested in 250 mL plastic bottles. Both collected samples were diluted with Milli-Q ultrapure water (Milli-Q™, IQ 7000) to reach approximate 250 mL. Their weight was measured before and after dilution on an analytical scale (Mettler Toledo, PB602-S/FACT). The column was filled with a 250 mL mixture of two-stage NF concentrate and a surfactant. The surfactants used in the laboratory-scale were Montaline C 40 , Marlinat 242/28, Simulsol

SL 10, Linear alkylbenzensulphonic acid (LAS) and YES which is a commonly used detergent in Sweden. Each surfactant had 4 experimental runs. The doses used were: *no surfactant* (reference)*, 1x minimum dose, 2x minimum* dose and *5x minimum dose.* Appendix A.1 displays information of all harvested samples.

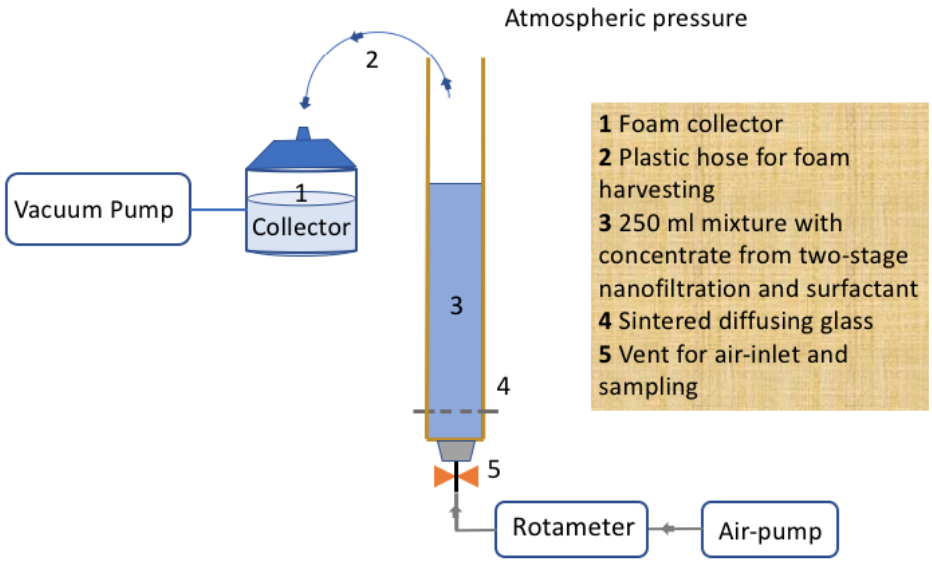


Figure 7: Foam fractionation setup for the laboratory experiments

3.4.2 Execution

A 1000 ml stock solution was made with each surfactant. The concentration of surfactant in the stock solution was approximately 1.1 mM, which was approximately 10^6 higher than the PFASs molar concentration in the NF concentrate. The calculated amount was placed in a 1000 mL volumetric flask of glass filled with Milli-Q ultrapure water (Milli-Q™, IQ 7000). The mixture was placed on a magnetic stirrer for 10 min. Appendix A.7.1 displays the calculations of the added amount of surfactants in each stock solution.

The column was filled with 250 mL of stirred two-staged NF concentrate and the air-pump was activated. The solution was aerated for one minute, with an approximate air flow-rate of 100 L/h. 0.1 mL of stock solution was added progressively until the appearance and the height of the foam satisfied the predefined characteristics of the minimal dose. When the approximate dosage was determined the set-up was cleaned and the dose was added directly in the next step. If the appearance of the foam, still satisfied the criterion of the minimal dosage, the amount added was noted. If not, the set-up was cleaned and the procedure was repeated with a slightly higher or lower added volumes. The addition of stock solution was adjusted until a minimal dosage was determined. The end product of the first part of the Laboratory-scale was an approximate minimum dose, thus the 1x minimum dose, 2x minimum dose and 5x minimum dose was settled.

The determined dosage of the stock solution was added to the column, the aeration and the vacuum-pump was turned on. The hose connected to the vacuum [2] was placed at the 300 mL mark of the column for 1 minute. If the elevation of the foam failed to reach 300 mL, the hose was slightly lowered to reach the foam, which was the case for the no surfactant experiments. The vacuum hose was slowly lowered to the 250 mL mark where it as kept for 1

minute. The final step was to lower the hose slowly until the surface level of the solution reached approximately the 200 mL mark. At that point, both the vacuum and the air-pump was turned off. The air-hose connected to the vent in the bottom of the column [5] was removed and a 250 mL plastic flask was placed underneath to collect the treated solution. The weight of the sample was noted. The collected foam was poured into a 250 mL plastic flask. Both samples were diluted with Milli-Q ultrapure water to reach an approximate volume of 250 mL. Their weight was noted. Appendix A.7.4 shows the collected volumes, the added volumes during dilutions and the calculation of the dilution factors.

3.4.3 Cleaning of equipment

The column was rinsed two times with a continuous flow of tap water. Both rinses were held under a tap until the small bubbles along the side of the column (possible traces of surfactants) were observed to leave. This procedure took about 15 seconds from the time that the column was fully filled. If such bubbles were not detected, this step was ignored. The column was filled with 400 mL of Milli-Q ultrapure water and manually shaken for about 10 seconds. The water was emptied through the bottom opening of the column.

All water did not leave the column, a small layer a water beneath the sintered glass remained after rinsing. The column was therefore turned upside down, and aerated from top to bottom, for 1-2 minutes before every new experiment.

3.5 Pilot scale

Details of each experimental run conducted in the pilot scale are displayed in Table 6, in chapter 3.7.2. The table includes aeration flow-rate, contact time, surface height, surfactant/PFAS mole ratio, dosing and type of experiment.

3.5.1 Experimental set-up

Figure 8 shows the continuous foam fractionation system used in the pilot-scale. A 1500 mm acrylic plastic column was used with an inner diameter of 54 mm. Compressed air (oil-free) was introduced through the bottom of the column and the flow-rate was controlled by a rotameter. The air-flow rate, contact time and height of water column was kept constant for all experiments at 4 L/min, 10 minutes and 1 m. The air was dispersed by an air diffusing membrane (Xylem Silver Series type II aeration membrane) inserted in the bottom of the column [7]. The two-stage NF concentrate mixture with surfactant [2] was pumped into the column via a peristaltic pump (Watson Marlow) into vent [15]. Foam was entering a plastic collector [3] through a plastic hose [5] by activation of a vacuum pump (GAST, DOA-P504-BN). Samples of the collapsed foam, the foamate, was taken from the collector [3]. Samples of treated water was harvested from the exit hose [9]. A 250 mL plastic sample flask was filled with untreated water directly taken from the column through vent [16] prior to aeration. A bubble trap [6] was connected to the exit hose [9] to secure a laminar flow out of the system without entrainment of bubbles.

Three runs was executed for each concentration as shown in Table 6. The tests conducted were: *Zero surfactant, 1x minimum dose, 2x minimum dose and 5x minimum dose*. All runs were

executed for 21 minutes. Sampling of treated water were done at time-steps 5,10 and 20 minutes. Each sampling took approximately 1 min, hence the run was 21 min in total. The foam collector [3] was put on an analytical scale (Mettler Toledo, PB602-S/FACT) before and after the experiment. The mass was noted. All PFASs samplings were harvested in 250 mL plastic sampling flasks. General chemistry samplings were harvested in 500 mL plastic sampling flasks. The general chemistry samples were collected from the two-staged NF concentrate and from the treated solution during the first run of every concentration.

The tap water used for rinsing and the total gathered effluent in container [Exit water] were a sampled with 250 mL plastic flasks. Conductivity, pH and temperature measurements were conducted for the two-staged NF concentrate used prior to mixing, and on the exit water after the experiments was finished. See Appendices A.1, A.2 and

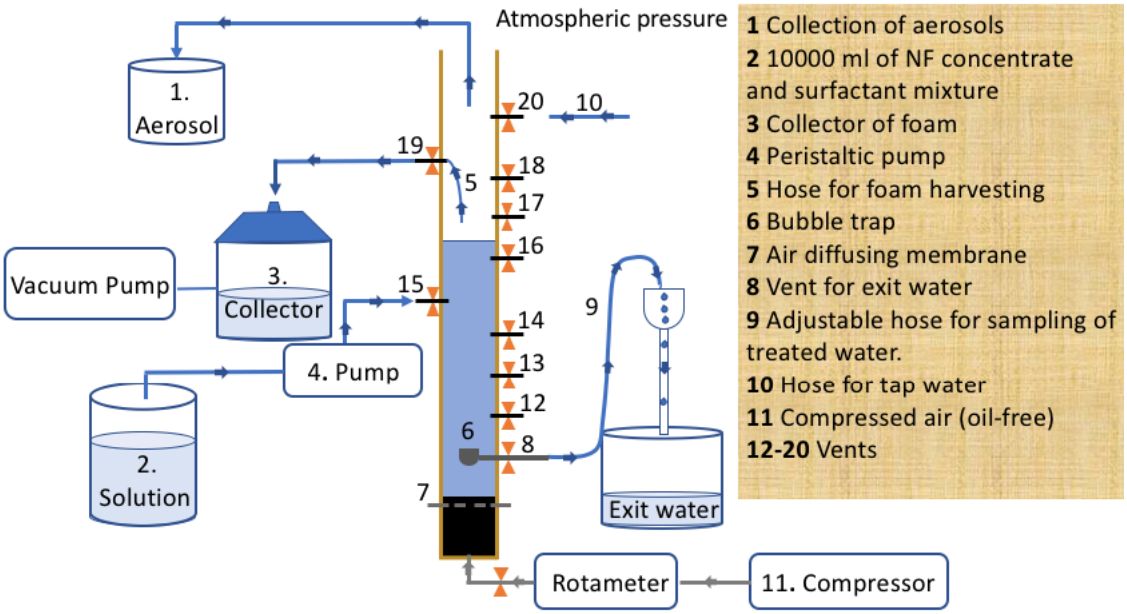


Figure 8: Experimental setup of the Pilot scale

3.5.2 Execution

A 1000 ml stock solution was made the surfactant. The surfactant molar concentration was approximately 10^6 higher than the PFASs molar concentration in the NF concentrate. The accurate amount of surfactant was placed in a 1000 mL volumetric flask of glass filled with Milli-Q ultrapure water (Milli-Q™, IQ 7000). The mixture was placed on a magnetic stirrer for 10 min. A new stock solution was made each day. The concentration of the stock solution was the same in the laboratory-scale and the pilot-scale. The elevation of the exit hose and the working rate of the peristaltic pump was determined beforehand. The aim was to have a water column of approximately 1 meter and a contact time of 10 min in each experimental run.

A 10 L carboy of glass was filled with well mixed NF concentrate. The temperature, conductivity and pH of the concentrate was noted (Appendix A.3). The volume of stock solution needed to reach the desired concentration in the carboy was extracted prior to the addition of the stock solution, thus the volume was exactly 10 L in each experiment.

A small volume was extracted with a plastic pipette. The same volume was added with the surfactant solution to reach 10 L and the desired concentration. The mixture was put on a magnetic stirrer for 15 min. The solution was pumped into the column using the peristaltic pump [4]. A 250 mL sample was taken from vent [9] of untreated water prior to the aeration. The surface was lowered to the desired elevation of 1 meter before the exit hose was opened and the pumping rate was adjusted to the pertinent flow to secure the contact time. The system was kept constant for 3 min to reach stabilization.

After 3 min, compressed air (oil free) [11] was introduced into the column and the vacuum pump was quickly turned on. The surface in the system rose initially from 100 cm to approximately 125 cm, due to the volume of the inserted bubbles. The hose of the vacuum was adjusted accordingly to capture the foam during the initial fluctuation. After 1 min, the hose was fixated at 120 cm. This procedure was repeated for all conducted experimental runs.

250 mL plastic bottles samples of treated water was collected from hose [9] at time steps 5,10 and 20 minutes. Foam was harvested continuously. The air-flow was turned off after the sampling was done at the 5 minute mark. The captured amount of foam, inside the collector [3], was quickly poured into a 1000 mL glass beaker. This procedure was done to minimize the risk of captured foam entering the vacuum-system. Subsequently, the air-flow was turned back on and the experiment continued. The same procedure was repeated after the sampling conducted at the 10 minute mark in the 2x minimum dose and the 3x minimum dose experiments, due to the potential risk of higher foam production with larger dosing.

The foamate was poured into a 1000 mL glass beaker after each run. The mass of the glass beaker before and after the experiment was measured with an analytical scale (Mettler Toledo, PB602-S/FACT). The mass of the foamate was noted. The foamate and the exit water was sampled in 250 mL plastic bottles. pH, conductivity and temperature measurements were conducted for the exit water (Appendix A.4).

3.5.3 Cleaning of equipment

Vent [12] was opened to empty the column after each experimental run. A separate plastic hose, connected to the peristaltic pump, was placed through vent [13] to remove all remaining solution. The column was rinsed with tap water. The top vent [20] was connected to a water tap hose, thus the system was cleaned from top to bottom. The column was rinsed 3 times in total. Vent [12] was kept opened during the first 2 min of the first rinse to facilitate a circulated rinsing effect in the bottom of the column. Vent [12] was then turned slightly so that the column could be filled (pass the highest point of foam), yet maintain the circulation. Lastly, vent [12] was completely opened to empty the column.

Air was let into the system during the second rinse, at 2 L/min, to increase the turbulence and potentially the efficacy of the rinse. The surface level was elevated to the height of the first rinse, and the system was kept constant for 1 min. Vent [12] was slightly opened during this

procedure, so that the column could be filled, yet maintain some rinsing circulation. Vent [12] was completely opened to empty the column.

The column was filled to the same height as previously during the third and last rinse. All vents used during the experiments, were opened for a few seconds, to wash out potential contaminants. The vacuum pump was turned on to rinse its connected hose. Vent [12] was completely opened to remove the majority of the liquid in the column. The last volume in the bottom was extracted by inserting an external plastic hose through vent [13] and connect it to a peristaltic pump. All external equipment was rinsed with tap water three times. Each object was filled with 1/3 of its volume and shaken. The hose used between the solution [2] and the column was rinsed with tap water.

3.5.4 Aerosol experiment

Two runs (EID 54, EID 55) were conducted to capture potential aerosols from the column during FF. Both experiments were executed without surfactants. The vacuum-pump was switched off during the runs. A lid was attached to the top of the column with a connected hose from a water trap. The water trap consisted of Milli-Q water and hydrochloric acid (HCl). The pH was 4.1 since PFAS is more soluble at lower pH.

Three plastic 250 mL flasks were filled with approximate 100-150 mL of solution. The mouth of the hose was placed underneath the surface. The air flow-rate was constant at 4 L/min. Three samples were collected from each run. The first sample was from 0-5 min, the second from 5-10 min and the third from 10-20 min. After sampling, the weight of the samples was measured, all flasks were diluted with Milli-Q water to reach 250 mL and weighed again.

3.6 Calculations

3.6.1 General part

The concentration of each PFASs in the concentrate were given in $\mu g/L$ and was converted into *mol/L* according to equation (1), where *M* is the specific molar mass. The molar concentration of each compound were added to receive the total molar concentration of ∑ PFASs.

$$\frac{\frac{\mu g}{L * 10^6}}{M} = \frac{\text{mol}}{\text{L}} \qquad (1)$$

Treated volume (m^3) inside the cylindrical column was calculated with equation 2. V is the treated volume, r (*m*) is the radius of the cylinder and h (*m*) is the height of the surface. The height of the water surface was kept at 1 m for all experiments and the radius of the column was 0.027 m thus the treated volume in the column were 0.00229 m^3 = 2,29 L.

$$V = 2r\pi * h \qquad (2)$$

The flow rate of out of the column were calculated with equation 3, Q is the flow-rate *(m^3/s),* V is the volume *(m^3)* of the effluent and t is the time *(s).*

$$Q = \frac{V}{t} \qquad (3)$$

Contact time of the treated water was calculated using equation 4. CT is the contact time *(min),* Q is the flow rate *(m^3/s)* and V is the volume *(m^3).* The contact time was set to be 10 min for all tests, the treated volume was 2.29 L, hence an inflow rate of $0.381*10^{\wedge-6}$ m^3/s = 0,381 mL/s was required from the peristaltic pump.

$$CT = \frac{Q}{V} \qquad (4)$$

3.6.2 Analytical part

The molar concentrations inside the diluted samples were calculated using the dilution factor (Df) seen in equation 5. All diluted samples were harvested in the laboratory experiments due to the small volumes generated in the tests. See Appendix A.7.4 for detailed calculations.

$$Df = \frac{Volume\ of\ diluted}{Volume\ of\ sample} \qquad (5)$$

Recovery of PFASs was calculated by using equation 6. C_{in} is the concentration of untreated water [ng/L] and C_{out} is the concentration of the effluent [ng/L].

$$Recovery\ [\%] = \frac{C_{in} - C_{out}}{C_{in}} * 100\ [\%] \qquad (6)$$

Standard deviations were calculated for the recoveries of all experiments repeated three times, for the concentrate concentration and for the no surfactant tests in the laboratory work. X is the value of the sample, $\bar{x}$ is the mean value and n is the number of samples included. These values are seen as error bars in the figures.

$$\sigma = \sqrt{\sum \frac{x - \bar{x}}{n}} \qquad (7)$$

Foam enrichment was quantified with equation 8. C_{foam} is the concentration of the harvested foam and C_{in} is the initial concentration.

$$E_{foam} = \frac{C_{foam}}{C_{in}} \qquad (8)$$

The difference in reduction between the no surfactant experiments and use of surfactants was calculated with equation 9. R_D is the reduction difference, R[%] is the reduction in percentage for the experiment containing surfactants, R_0[%] is the reduction in percentage for the experiment with zero addition of surfactant.

$$R_D = R[\%] - R_0[\%] \qquad (9)$$

The ratio of reduction with surfactants, to the reduction without surfactant, is expressed as the reduction ratio, R_R. R is the reduction in percentage for the experiments containing surfactants and R_0 is the reduction in percentage for the experiments conducted without surfactants.

$$R_R = \frac{R[\%]}{R_0[\%]} \qquad (10)$$

The mass balance of ∑PFASs was determined with equation 11. m_{ff} is the mass of ∑PFASs in the final foam, m_{fcm} is the mass of ∑PFASs in the harvested final column water and m_{C_0} is the mass of ∑PFASs at time zero.

$$mass\ balance = \frac{m_{ff} + m_{fcw}}{m_{C_0}} \qquad (11)$$

3.7 Conducted experiments

3.7.1 Laboratory work

Table 5 showcase the 20 batch experiments conducted in the laboratory work, four runs for each surfactant. 250 ml of two staged NF concentrate was mixed with zero surfactant (only concentrate), 1x the minimum dose, 2x the minimum dose and 5x the minimum dose. The zero surfactant experiment was the first conducted experimental run for each surfactant. Two samples were harvested for each experiment, one water (W), and one for the collected foamate (F). Information of all harvested samples are displayed in Appendix A.1. The molar concentration of YES was uncertain, hence the mass added to the stock solution was fixed at 0.5 g which was close to the amounts applied for LAS and Simulsol S 10.

Table 5:All conducted experimental runs in the laboratory work, each experimental ID, Air flow-rate used, Experiment type, Dose and their Surfactant/PFAS mole ratio

Surfactant	EID	Air flow rate (L/min)	Experiment type	Dose (ml)	Surfactant/PFAS mole ratio
Montaline C 40	1	1	Zero surfactant	0	0
Montaline C 40	2	1	1x minimum dose	0.3	1515
Montaline C 40	3	1	2x minimum dose	0.6	3029
Montaline C 40	4	1	5x minimum dose	1.5	7573
Marlinat 242/28	5	1	Zero surfactant	0	0
Marlinat 242/28	6	1	1x minimum dose	0.25	1262
Marlinat 242/28	7	1	2x minimum dose	0.5	2524
Marlinat 242/28	8	1	5x minimum dose	1.25	6311
Simulsol S 10	9	1	Zero surfactant	0	0
Simulsol S 10	10	1	1x minimum dose	0.6	3029
Simulsol S 10	11	1	2x minimum dose	1.2	6058
Simulsol S 10	12	1	5x minimum dose	3	15146
LAS	13	1	Zero surfactant	0	0
LAS	14	1	1x minimum dose	0.6	3029
LAS	15	1	2x minimum dose	1.2	6058
LAS	16	1	5x minimum dose	3	15146
Yes	17	1	Zero surfactant	0	0
Yes	18	1	1x minimum dose	0.3	-
Yes	19	1	2x minimum dose	0.6	-
Yes	20	1	5x minimum dose	1.5	-

3.7.2 Pilot work

Table 6 shows the 12 continuous runs conducted in the pilot-scale, four runs for each surfactant. 10 L NF concentrate was mixed with: zero surfactant (only concentrate), 1x the minimum dose, 2x the minimum dose and 3x the minimum dose. Each experiment was repeated three times. The CT was 10 min, the flow rate was 4 L/min and the height of the water surface was kept at 1 meter prior to aeration in all experiments. Montaline C 40 was the surfactant of choice from the pilot-scale, detailed information regarding the selection process are explained in section 4.1.7.

Three of four experiments were identical, in terms of surfactant/PFAS mole ratio, between the pilot-scale and the laboratory-scale. The difference between the two set-ups was the highest dose experiment, 3x minimum dose was conducted instead of 5x minimum dose in the pilot-scale due to the risk of excessive foaming in the larger column. Six samples were collected during every run, one from the concentrate, one from the column prior to operation, three from the treated water at time-steps 5,10 and 20 minutes and finally one from the foamate post the experiment. Detailed information of all harvested samples during the pilot-scale are displayed in Appendix A.1.

Two aerosol experiments were conducted to examine the feasibility of PFASs capture from aerosols in the air. A water trap was constructed, containing distilled water and HCL. The pH was 4.1 in the trap. Table 7 displays additional information regarding the aerosol experiment

Table 6: All conducted experimental runs in the pilot work, each experimental ID, CT, Experiment, Air flow-rate, Surface height, Experiment type, Dose and their Surfactant/PFAS mole ratio

Surfactant	EID	CT (min)	Air flow rate (L/min)	Surface height (m)	Experiment type	Dose (ml)	Surfactant/PFASs mole ratio
Montaline C 40	21	10	4	1	Zero surfactant	0	0
Montaline C 40	22	10	4	1	Zero surfactant	0	0
Montaline C 40	23	10	4	1	Zero surfactant	0	0
Montaline C 40	31	10	4	1	1x minimum dose	12	1425
Montaline C 40	32	10	4	1	1x minimum dose	12	1425
Montaline C 40	33	10	4	1	1x minimum dose	12	1425
Montaline C 40	41	10	4	1	2x minimum dose	24	2850
Montaline C 40	42	10	4	1	2x minimum dose	24	2850
Montaline C 40	43	10	4	1	2x minimum dose	24	2850
Montaline C 40	51	10	4	1	3x minimum dose	36	4275

Montaline C 40	52	10	4	1	3x minimum dose	36	4275
Montaline C 40	53	10	4	1	3x minimum dose	36	4275

Table 7: All runs executed for the aerosol experiments

Surfactant	EID	CT (min)	Air flow rate (L/min)	Surface height (m)	Experiment type	Dose (ml)	pH
-	54	10	4	1	Aerosol	0	4.1
-	55	10	4	1	Aerosol	0	4.1

3.8 Sampling analysis

The PFASs analysis was performed by ALS Scandinavian, Stockholm. The measurements were conducted with Liquid Chromatography – Tandem Mass Spectrometry (LC-MS-MS) according to US EPA 537 and CSN P Cen/TS 15968**.** Table 8 displays all PFAS included in the analysis, the detected compounds and their limits of reporting (LOR). LOR is the lowest concentration of detection with the specific method. Each PFASs full name are listed in Appendix A.2 . All samples were homogenized before analysis. General chemistry analysis was performed by Uppsala Water and Waste AB's SS-EN ISO/IEC 17025 accredited laboratory in Sweden.

Table 8: All analysed PFASs, each limit of reporting value (LOR), detected compounds in the analysis, classification and perfluorocarbon chain length. PFCAs are marked in green, PFSAs are marked in red and precursors are marked in yellow.

Acronym	LOR	Detected	PFCA	PFSA	Precursor	Perfluorocarbon chain length
PFBA	0.0020	x	x			C3
PFPeA	0.00030	x	x			C4
PFHxA	0.00030	x	x			C5
PFHpA	0.00030		x			C6
PFOA	0.00030	x	x			C7
PFNA	0.00030		x			C8
PFDA	0.00030		x			C9
PFBS	0.00030	x		x		C4
PFHxS	0.00030	x		x		C6
PFOS	0.00030	x		x		C8
6:2 FTS	0.00030				x	C6
PFUnDA	0.00030		x			C10
PFDoDA	0.00030		x			C11
PFTriDA	0.00030		x			C12
PFTeDA	0.00030		x			C12

PFPeS	0.00030	x		x		C5
PFHpS	0.00030			x		C7
PFNS	0.00030			x		C9
PFDS	0.00030			x		C10
PFDoDS	0.00030			x		C12
4:2 FTS	0.00030				x	C4
8:2 FTS	0.00030				x	C8
FOSA	0.00030				x	C8
MeFOSA	0.0020				x	C8
EtFOSA	0.0020				x	C8
MeFOSE	0.0020				x	C8
EtFOSE	0.0020				x	C8
FOSAA	0.0010				x	C8
MeFOSAA	0.0010				x	C8
EtFOSAA	0.0010				x	C8
HPFHpA	0.0010					C7
PF37DMOA	0.0010					C7

4 Results

7 of 11 targeted PFASs were detected above the LOR-value in the NF concentrate used in both the laboratory- and the pilot-scale. The undetected compounds PFNA, PFDA, PFHpA and 6:2 FTSA were excluded in the analysis. Of the 7 identified targeted PFASs were three long-chained PFASs (PFOA (C7), PFHxS (C6) and PFOS (C8)), the remaining four compounds were short-chained PFASs (PFBA (C3), PFPeA (C4), PFHxA (C5) and PFBS (C4)).

4.1 Laboratory work

4.1.1 Targeted PFASs concentration in NF concentrate

$\sum_{11}$PFASs in the NF concentrate was 300 ng/L (Table 9). The most abundant compound was PFHxS with > 50 % of the total concentration of PFASs, and lowest concentrations were observed for PFPeA and PFOA (Figure 9). ∑long-chained PFASs were 220 ng/L (82 % of $\sum_{11}$PFASs) and ∑short-chained PFAS was 85 ng/L (28 % of $\sum_{11}$PFASs). The raw data is found in appendix A.8.2.

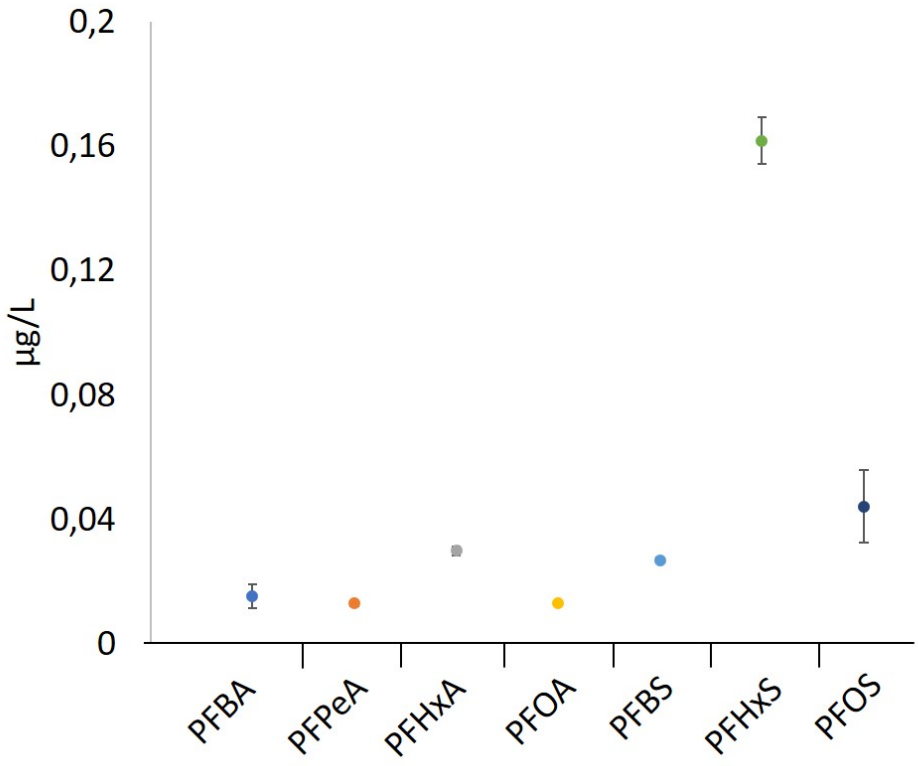


Figure 9: Average concentration for individual PFASs and their standard deviations detected in the concentrate.

Table 9: Average concentration of PFASs in the NF concentrate

PFASs	Nanofiltration concentrate (ng/L)	Short chained	Long-chained
PFBA (C3)	15	x	
PFPeA (C4)	13	x	
PFHxA (5)	30	x	
PFOA (C7)	13		x
PFBS (C4)	27	x	
PFHxS (C6)	160		x
PFOS (C8)	44		x
PFAS 11	**300**		
PFAS 4	**220**		
Short-chained	**85**		
Long-chained	**220**		

4.1.2 Zero surfactant experimental runs

Four experiments were conducted for each surfactant as previously mentioned. The zero surfactant experiment, conducted for each surfactant, was used as the reference when calculating the reduction efficiency of each surfactant in the FF process. PFBA (C3) and PFPeA (C4) had a significant deviation in reduction for the conducted zero surfactant experimental runs (Figure 10). The large deviation observed for these compounds between the zero surfactant runs was taken into account when evaluating the results.

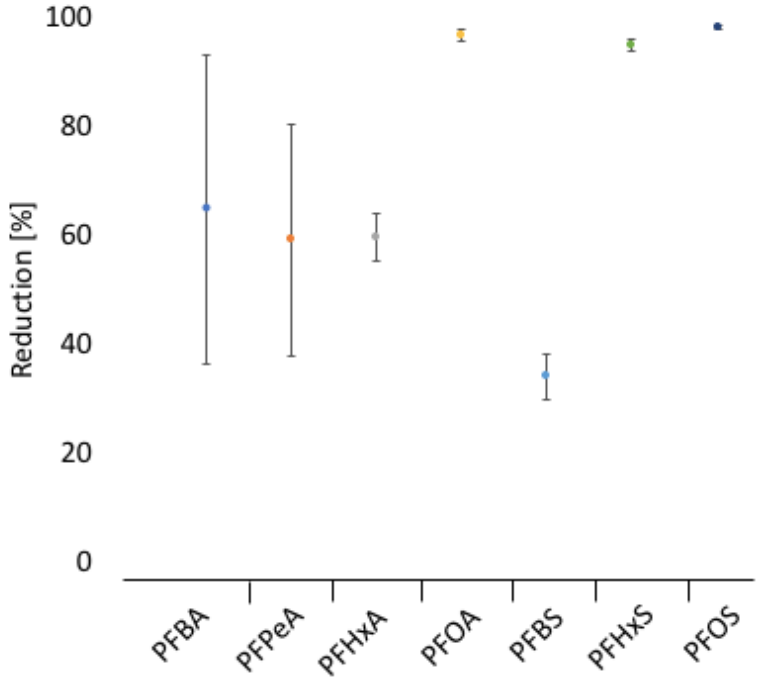


Figure 10: Average reduction and standard deviations for individual PFASs in the experimental runs with no addition of surfactants.

4.1.2 Montaline C 40

The reduction of the short-chained PFASs; PFHxA (C5), PFBS (C4) and PFPeA (C4) were higher in the experimental runs containing the surfactant compared to the zero surfactant run (Figure 11a, Figure 11b). The reduction of PFBS (C4) increased by 61 %, PFHxA (C5) was improved with 42% and the reduction of PFPeA (C4) was increased with 48 % in the highest dose experiment (EID 4), compared to the reference with no dose of surfactant (EID 1). These differences in reduction between the two experimental runs corresponded to an increase of 120% (PFPeA (C4)), 81 % (PFHxA (C5)) and 218 % (PFBS (C4)) in the highest dose experiment, 5x minimum dose, compared to the zero surfactant run (Figure 11c). The reduction of PFBA (C3) was not improved when adding Montaline C 40. The mass balance was close to 90 % in the zero surfactant experiment, and approximately 60 % for experimental runs containing surfactant (Figure 11d).

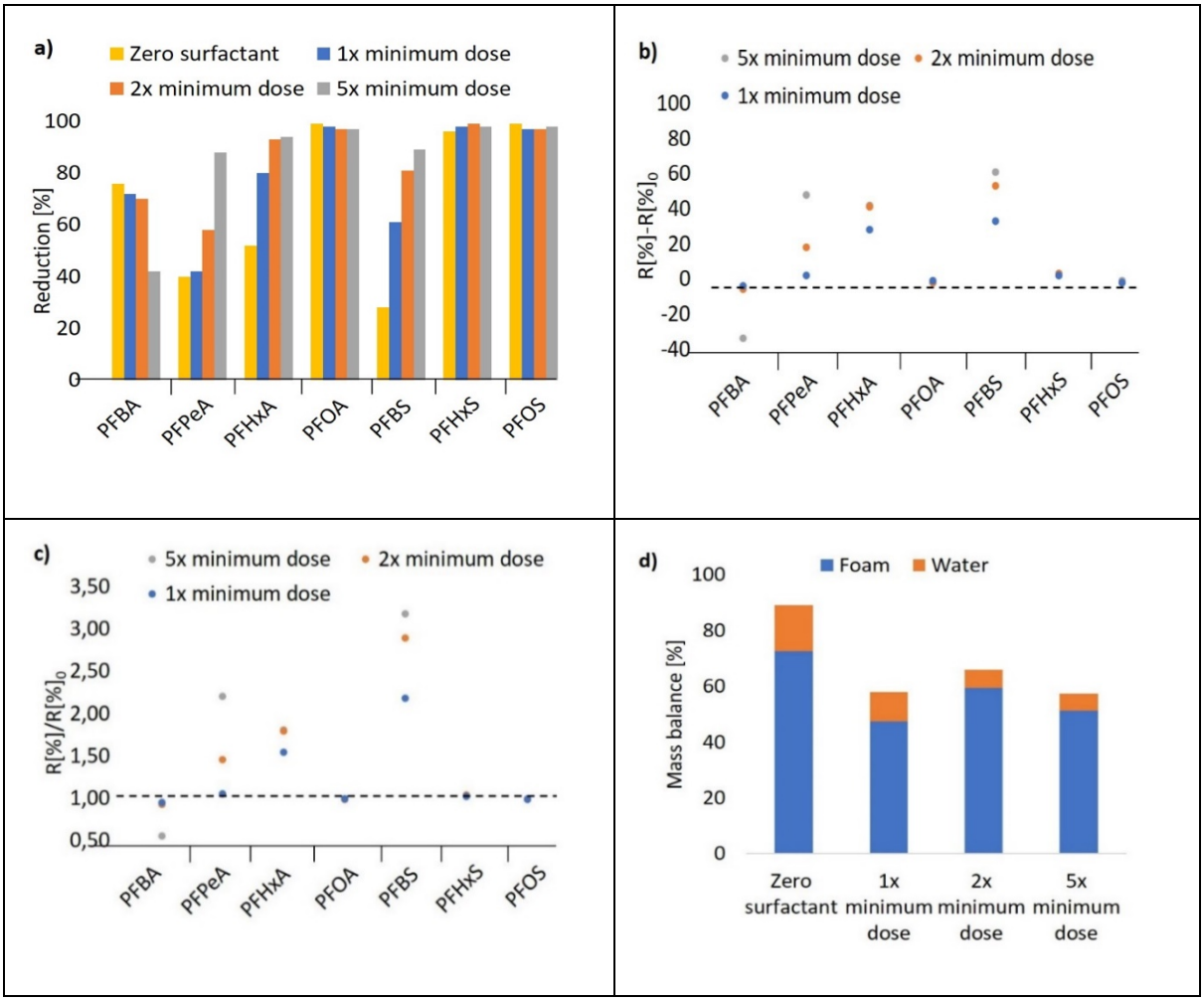


Figure 11: a). Reduction of $\sum_{11}$PFASs with different doses of Montaline C 40 b). Difference in reduction between experimental runs containing surfactant and the reference of no surfactant. c). Change in reduction of PFASs expressed as a factor between the runs containing Montaline C 40 and the reference with zero addition d). Mass balance for each experiment.

4.1.3 Marlinat 282/42

The reduction of the short-chained PFASs: PFBA (C3), PFPeA (C4), PFHpA (C6) and PFBS (C4) were enhanced in the FF process when applying Marlinat 282/42 (Figure 12a). The highest reduction of these compounds were obtained in the 5x minimum dose experiment (EID 8), whereas the lowest reduction efficacy was obtained in the zero surfactant run (EID 5). The removal efficiency of PFPeA (C4) was greatly improved with the addition of Marlinat 282/42 (Figure 12 b), especially in the highest dose experiment (EID 8). The reduction of PFBA (C3), PFPeA (C4), PFHxA (C5) and PFBS (C4) was improved with 9 %, 42 %, 7 % and 19 % respectively in EID 8 compared to EID 5 (Figure 12). These values corresponded to an improved reduction of 30 % (PFBA (C3)), 117 % (PFPeA (C4)), 12 % (PFHxA (C5)) and 61 % (PFBS (C4)). The mass balance calculations showed that 70-95 % of the PFASs was collected in the executed runs, the highest value was obtained for 1x minimum dose (EID 6) and the lowest value was observed in EID 8 (Figure 12 d).

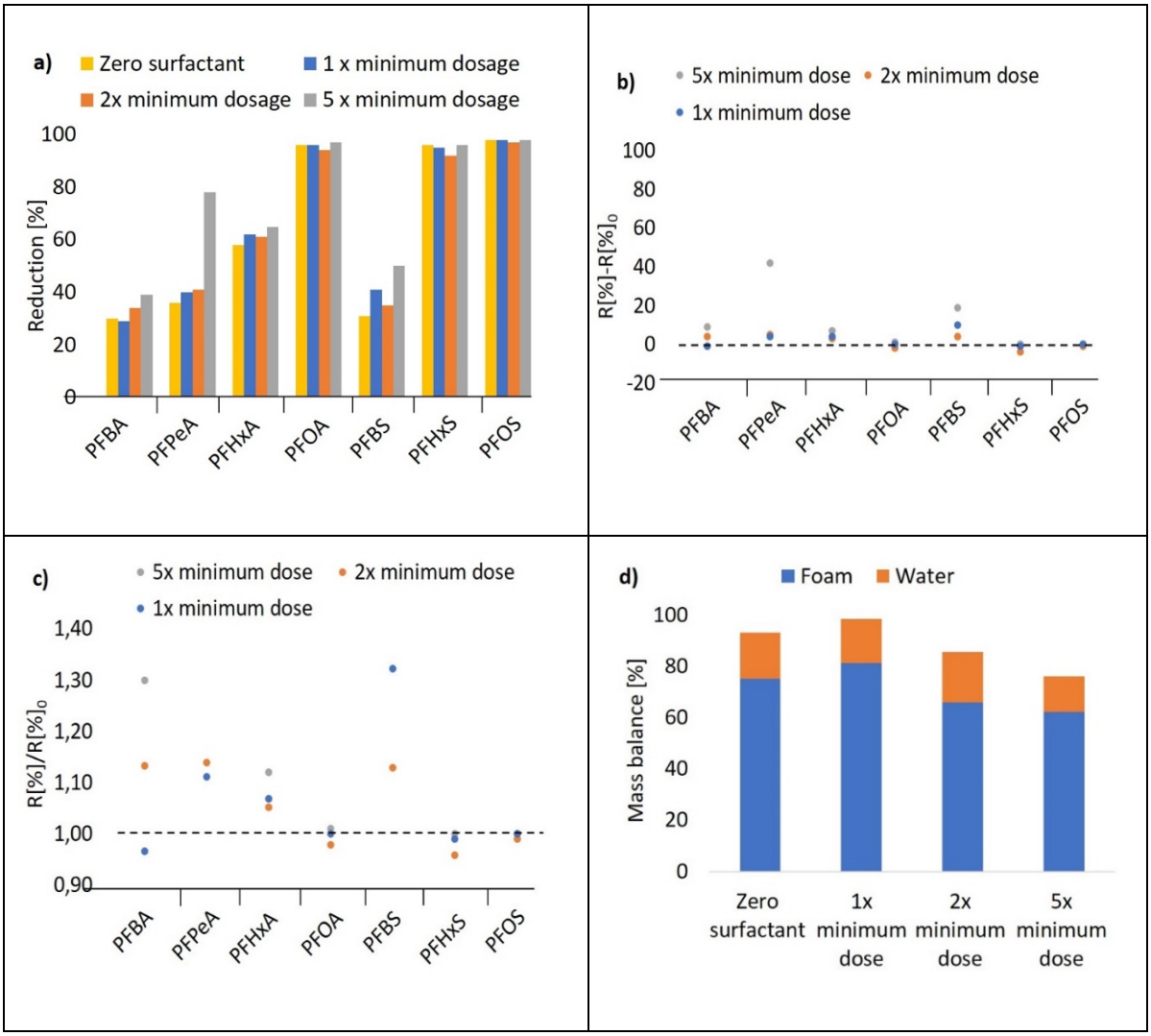


Figure 12 : a). Reduction of $\sum_{11}$PFASs with different doses of Marlinat 242/28 b). Difference in reduction between experimental runs containing surfactant and the reference of no surfactant. c). Change in reduction of PFASs expressed as a factor between the runs containing Marlinat 242/28 and the reference with zero addition d). Mass balance for each experiment.

4.1.4 Simulsol S 10

The removal efficiency of PFBA (C3) and PFPeA (C4) in the zero surfactant experiment (EID 9) (Figure 13a) was relatively high compared to EID 1 and EID 5. No improvement in the removal of these compounds was obtained when adding Simulsol S 10 (Figure 13b), however the reduction of PFHxA (C5) and PFBS (C4) were enhanced. The highest reductions of PFHxS (C6) and PFBS (C4) were obtained in the highest dose experiment, 5x minimum dose (EID 12), and the lowest removal was obtained in EID 9. PFHxA (C5) was improved with 11 % in EID 12, which was a 17 % increase in removal compared to EID 9 . The concentration of PFBS (C4) was decreased with 54 % in EID 12, which was a 17 % increase in reduction compared to EID 9. A removal increase of 17 % in EID 12 compared to EID 9, corresponded to an increased reduction of 46 % (Figure 13c).

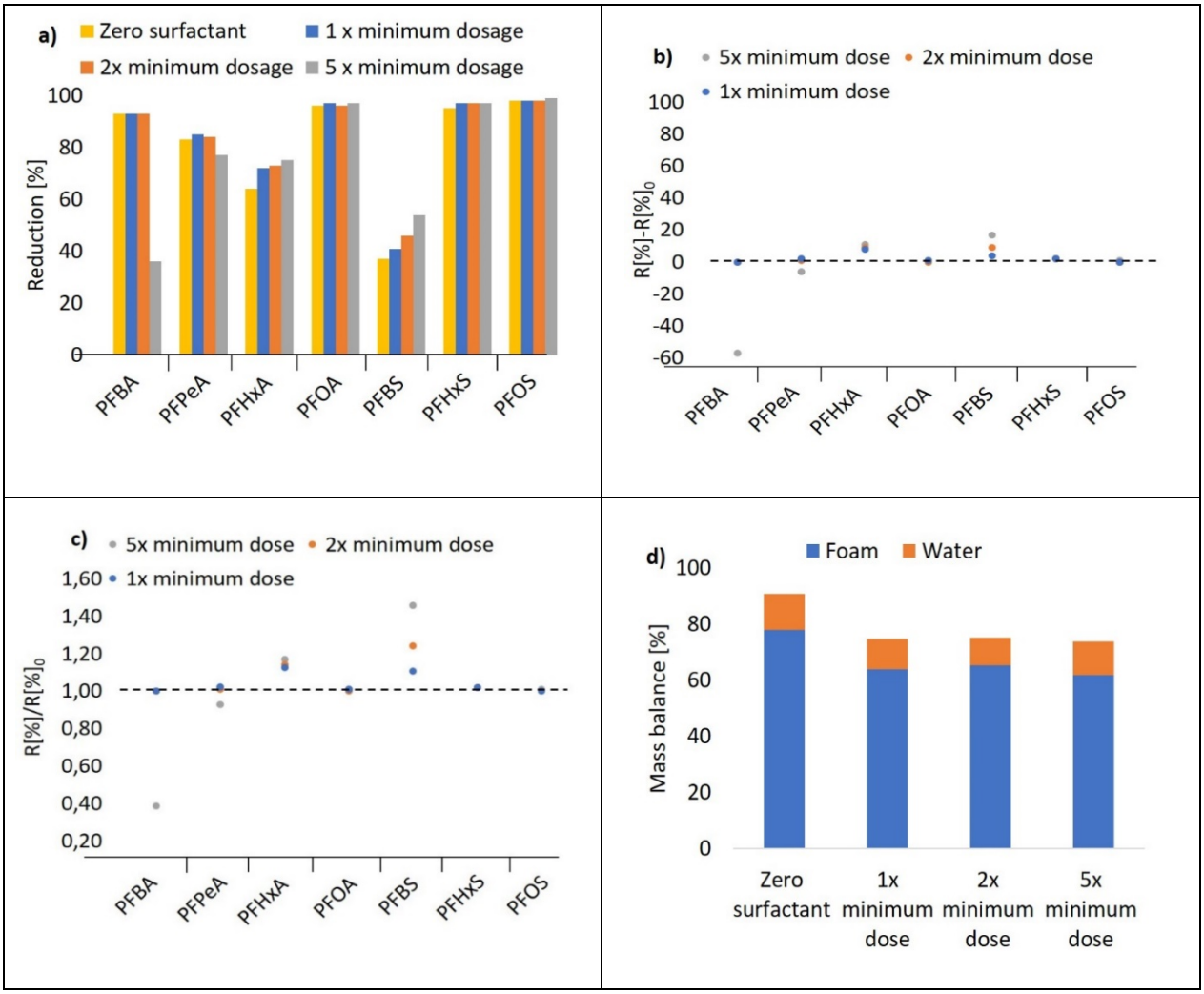


Figure 13 : a). Reduction of $\sum_{11}$PFASs with different doses of Simulsol S 10 b). Difference in reduction between experimental runs containing surfactant and the reference of no surfactant. c). Change in reduction of PFASs expressed as a factor between the runs containing Simulsol S 10 and the reference with zero addition d). Mass balance for each experiment.

4.1.5 LAS

The use of linear alkylenebenzene sulfonic acid (LAS) showed no consistent improvement in reduction of PFBA (C3), PFBS (C4) and PFHxA (C5) (Figure 14a, Figure 14b). The removal efficiency of the 2x minimum dose experiment (EID 15) was consequently lower than the 1x

minimum dose run (EID 14) and 5x minimum dose run (EID 17). The reduction of PFBA (C3), PFHxA (C5) and PFBS (C4) peaked in EID 17 and had its lowest values in EID 15. The application of LAS in the FF process lowered the reduction of some short- and long-chained PFASs (Figure 14c). The mass balance calculations showed that between 70-90 % of the PFASs was collected in the executed runs, the highest value was obtained for EID 15 and the lowest value was observed in EID 17 (Figure 14d).

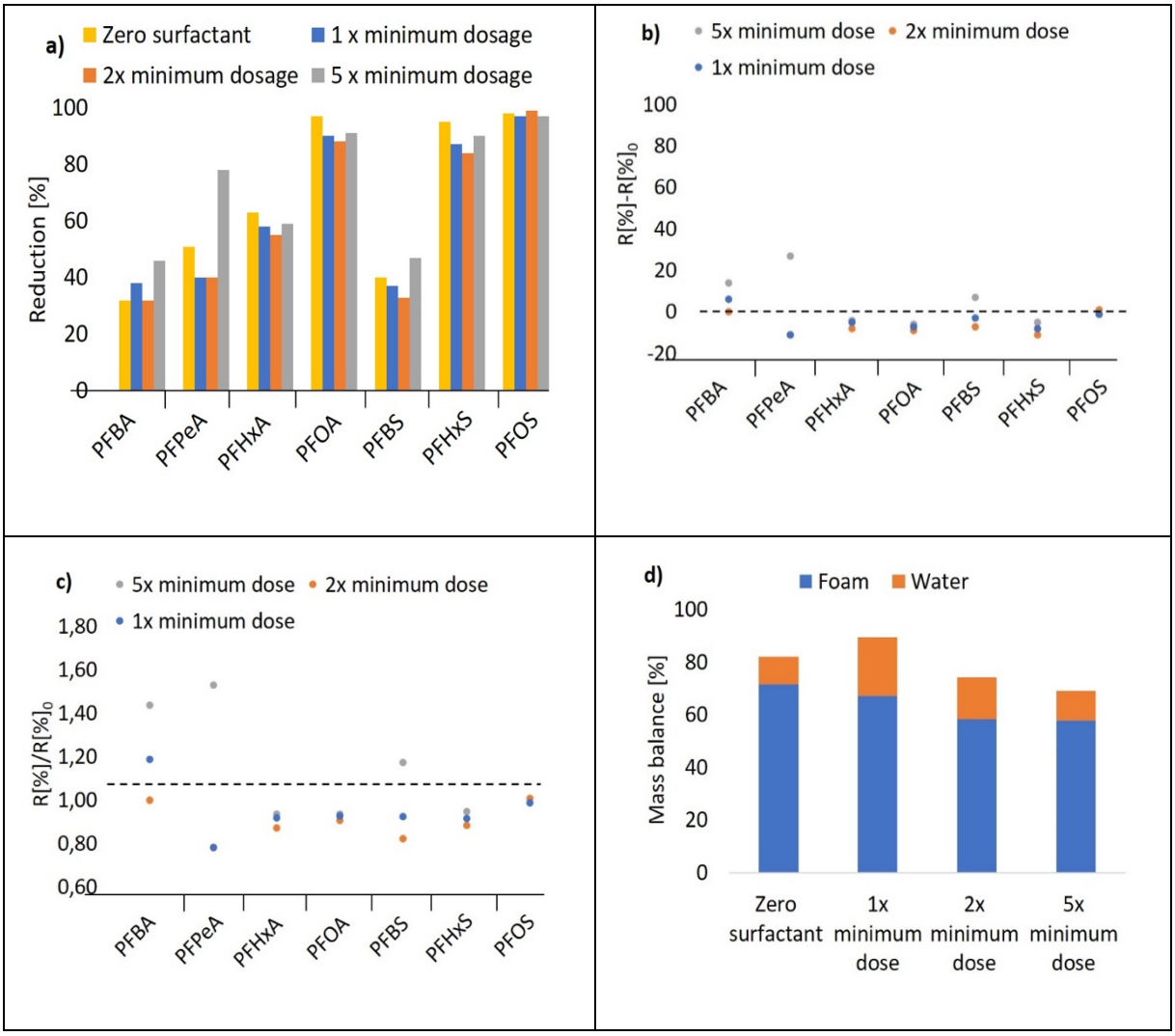


Figure 14 : a). Reduction of $\sum_{11}$PFASs with different doses of LAS b). Difference in reduction between experimental runs containing surfactant and the reference of no surfactant. c). Change in reduction of PFASs expressed as a factor between the runs containing LAS and the reference with zero addition d). Mass balance for each experiment.

4.1.6 YES

No clear improvement in the reduction of short-chained PFASs was observed when adding YES to the FF process (Figure 15a, Figure 15b). All experiments conducted showed the same high removal efficiency. The high reductions obtained for the zero surfactant experiment (EID 17) of PFBA and PFPeA compared to EID 1,5,9,13 indicates that something was strange with the data. The increase in removal compared to EID 17 was not greater than 10 % in any

experimental run (Figure 15b). The similar reductions between EID 17 with the 1x minimum dose run (EID 18), the 2x minimum dose run (EID 19) and the 5x minimum dose experiment (EID 20) also points to errors in the data or that no improvement was obtained. The mass balance of the conducted runs displays that the highest value was observed in EID 17 and the lowest value was obtained in EID 19.

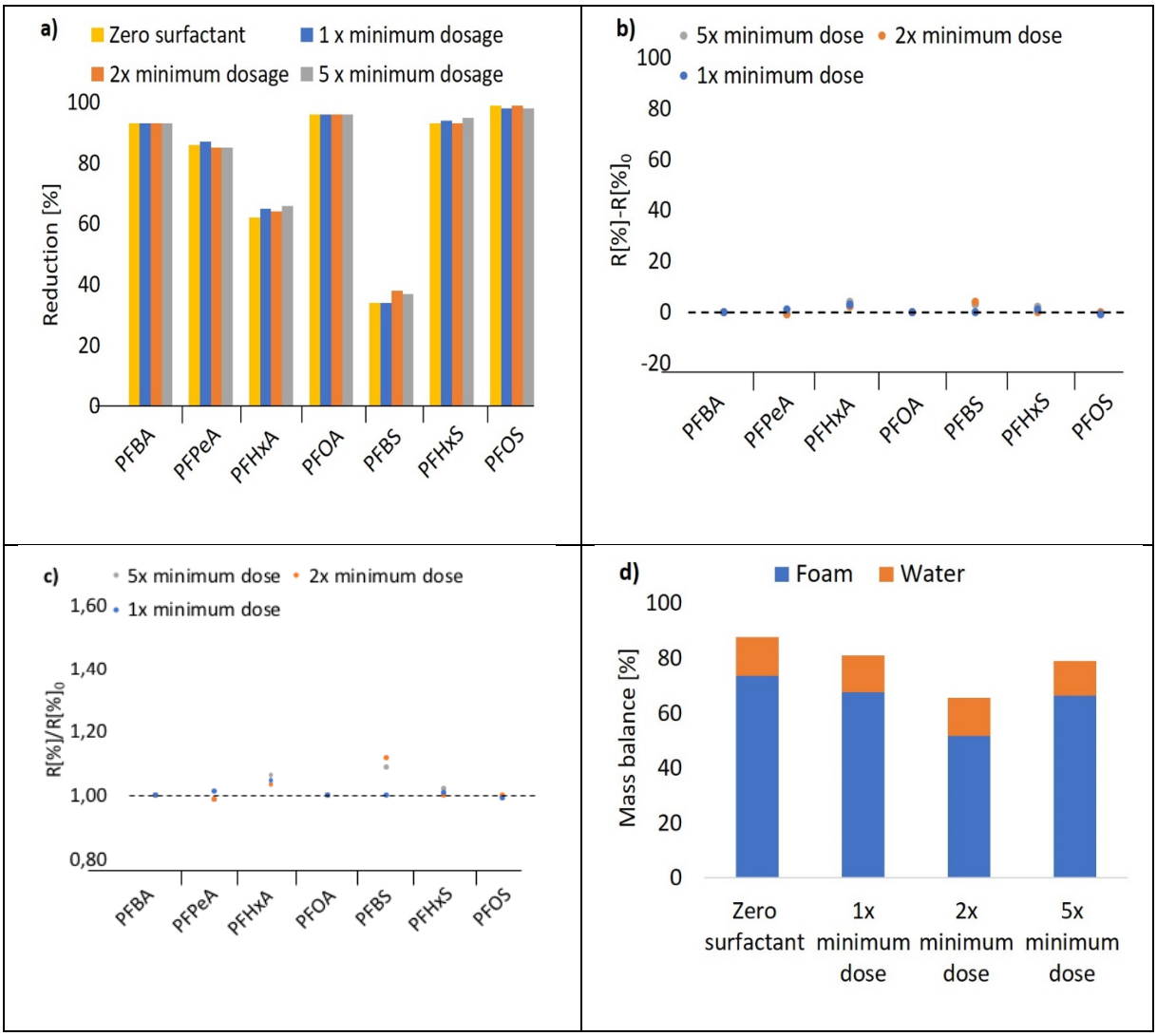


Figure 15 : a). Reduction of ∑$_{11}$PFASs with different doses of YES b). Difference in reduction between experimental runs containing surfactant and the reference of no surfactant. c). Change in reduction of PFASs expressed as a factor between the runs containing YES and the reference with zero addition d). Mass balance for each experiment

4.1.7 Surfactant of choice for further investigation

Only one surfactant from the laboratory-scale was used in the pilot-scale, due to the time limitation of the thesis. The aim was to select the surfactant with the highest potential of enhancing the removal of ∑short-chained PFASs in the continuous FF pilot set-up. The surfactants impact on the reduction of long-chained PFASs was excluded in the assessment as

a consequence of the exceptionally high removals of these compounds obtained in all experiments conducted.

Figures 11 a-c), 12 a-c), 13 a-c), 14 a-c) and 15 a-c) were compared. The experimental run with the highest removal efficiency of short-chained PFASs for each surfactant are displayed in Table 10. The dose used and the corresponding Surfactant/PFAS mole ratio are also shown. A low surfactant to PFASs mole ratio was desired. Table 11 shows the impact of the surfactants in the FF process on long-chained PFASs. These numbers were close to zero.

Montaline C 40 had the highest reduction of PFPeA (C4), PFHxA (C5) and PFBS (C4), all over > 80% compared to the zero surfactant (EID 1). These results were observed for the experimental run with the highest concentration of 5x the minimum dose EID 4. EID 4 was also the experimental run in the laboratory-scale with the greatest removal increase of a single PFASs, 218% improvement of PFBS compared to the reference. Montaline C 40 also had relatively low PFAS/Surfactant mole ratio. The cationic surfactant Montaline C 40 was the chosen compound to be used in the pilot work.

Table 10: Each row displays the most efficient experiment for each surfactant in the laboratory-scale in terms of removing ∑short-chained PFASs. The difference in reduction compared to the reference of zero surfactant are displayed. The parenthesis shows the improved reduction as a factor expressed in %.

Surfactant	Dose	Surfactant/PFAS mole ratio	PFBA	PFPeA	PFHxA	PFHpA	PFBS
Montaline C 40	5x minimum	7573	0	48 (120%)	43 (81%)	11 (13%)	61 (218%)
Marlinat 282/24	5x minimum	6311	9 (30%)	42 (117%)	7 (12%)	0	19 (68%)
Simulsol S 10	5x minimum	15146	0	2 (2%)	11 (17%)	11 (46%)	17 (46%)
LAS	5x minimum	15146	14 (44%)	27 (53%)	0	1 (1%)	7 (18%)
YES	5x minimum	Unknown	0	1 (1%)	4 (6%)	4 (5%)	4 (9%)

Table 11: Difference in reduction in % compared to the reference of zero surfactant for the experimental run with the highest removal efficiency for each surfactant. The parenthesis displays the change in %.

Surfactant	Dose	PFASs/Surfactant mole ratio	PFHxS	PFOS	PFOA
Montaline C 40	5x minimum	7573	2 (2 %)	-2 (-2%)	-2 (-2 %)
Marlinat 282/24	5x minimum	6311	0	0	1 (1%)
Simulsol S 10	5x minimum	15146	2	1 (1%)	0 (0 %)
LAS	5x minimum	15146	-5(-5%)	-1(-1%)	-6 (-6%)

YES	5x minimum	Unknown	2 (2%)	1 (1%)	0 (0%)

4.2 Pilot

4.2.1 Targeted PFASs concentration in NF concentrate

Figure 16 shows the average concentration and standard deviations for $\sum_{11}$PFASs in the NF concentrate collected tank water samples taken prior to each of the 12 conducted runs. The average sum of the detected 7 compounds was 350 ng/L. The most abundant PFASs in the two-staged nanofiltration concentrate was PFHxS (C6) with a mean concentration of 180 ng/L which was 51 % of ∑PFASs. PFOS (C8) were detected at a mean concentration of 63 ng/L, which was 18 % of $\sum_{11}$PFASs. These two compounds were the ones with the largest standard deviations. PFPeA (C4) had the lowest concentration of 12 ng/L. PFAS 4 was 260 ng/L and the short-chained PFASs was 86 ng/L. Table 12 displays the concentration of each PFASs in the concentrate.

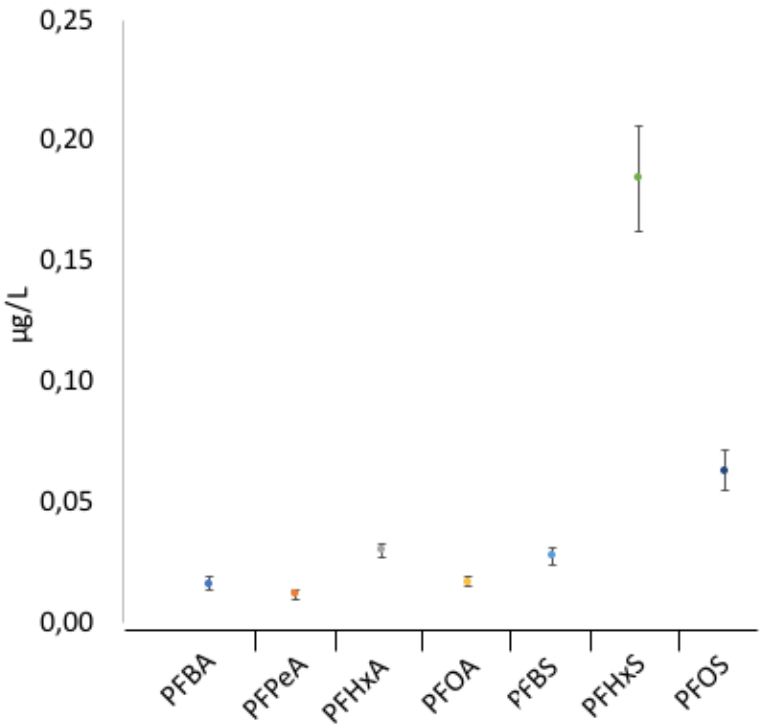


Figure 16: Average concentration for individual PFASs and their standard deviations detected in the NF concentrate.

Table 12: Average PFASs concentrations in the NF concentrate used in the pilot-scale

PFASs	Concentrate (ng/L)	Short-chained	Long-chained

PFBA (C3)	16	x	
PFPeA (C4)	12	x	
PFHxA (C5)	30	x	
PFOA (C7)	17		x
PFBS (C4)	28	x	
PFHxS (C6)	180		x
PFOS (C8)	63		x
PFAS 11	***350***		
PFAS 4	***260***		
Short-chained	***86***		
Long-chained	***260***		
PFCA	***75***		
PFSA	***280***		

4.2.2 Reductions efficiencies at different time steps

Figure 17 shows that runs 21-23 (EID 21-23), the zero surfactant runs, had the lowest removal efficiencies of the conducted experimental runs. The chart also displays a small correlation between improvement in reduction with an increase in time step. The removal efficiency of $\sum_{11}$PFASs were consistent in the repeated runs containing the surfactant (Table 7). $\sum_{11}$PFASs was more efficiently removed at the 10 and 20 min harvested samples compared to the 5 min in runs 21-23 (Figure 17).

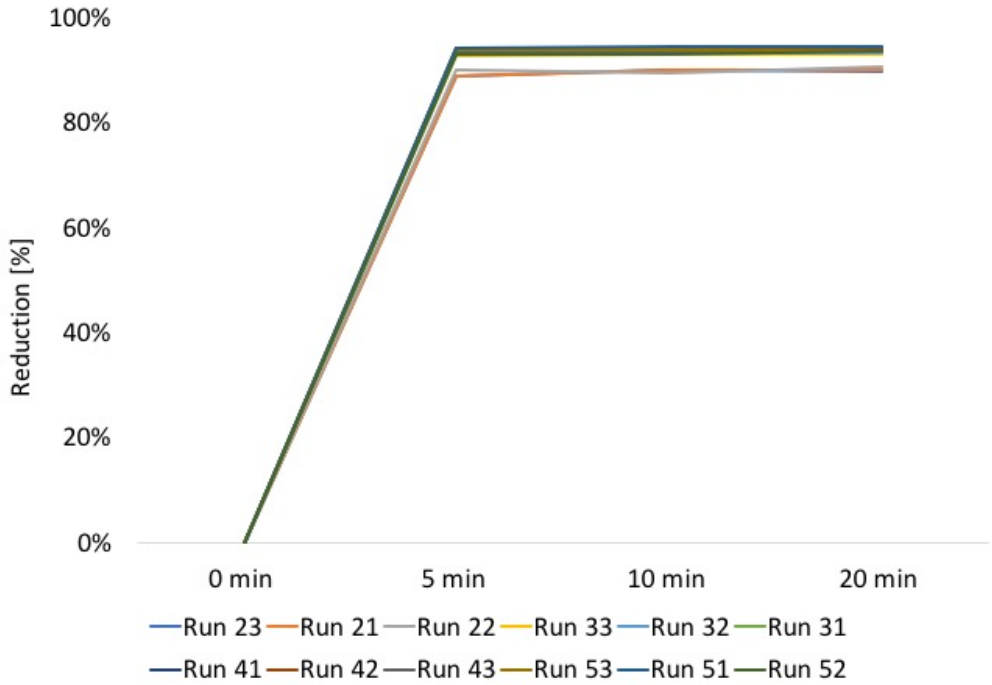


Figure 17: Reduction of $\sum_{11}$PFASs for all executed experimental runs at different time steps. Run 21-23 (Zero surfactant), run 31-33(1x minimum dose), run 41-43 (2x minimum dose) and 51-53 (3x minimum dose).

Table 13: Mean reduction of $\sum_{11}$PFASs at different time steps for each experimental dose

Time	Zero surfactant	1x minimum dose	2x minimum dose	3x minimum dose
5 min	89 %	93 %	94 %	94 %
10 min	90 %	93%	94 %	94 %
20 min	90 %	93 %	94 %	94%

The reduction of ∑short-chained PFASs were slightly impacted by the time of sampling according to figure 18. An increase in removal efficiency between sampling time steps of 5 and 20 min was observed in runs 21-23 (zero surfactant) and 33-35 (1x minimum dose). The reduction also increased with a higher concentration of surfactant in the FF process. The removal efficiency of ∑short-chained PFASs in runs 51-53 (3x the minimum dose) was significantly higher than runs 21-23 (zero surfactant). Run 53 (3x the minimum dose) showcased the highest reductions of ∑short-chained PFASs, whereas run 21 and 23 obtained the lowest values.

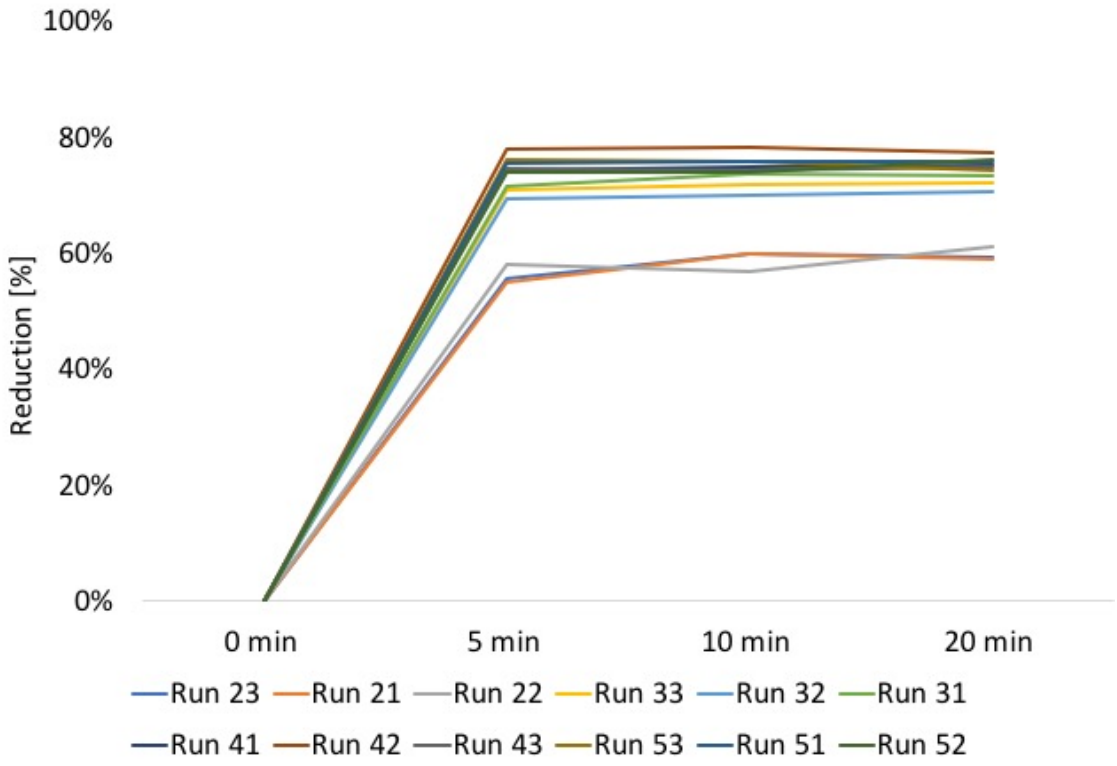


Figure18: Average reduction of ∑short-chained PFASs at different time steps for each experimental run. Run 21-23 (Zero surfactant), run 31-33(1x minimum dose), run 41-43 (2x minimum dose) and run 51-53 (3x minimum dose)

The long-chained PFASs were removed equally in all conducted experimental runs (Figure 19). The removal efficiency was > 99 % in all runs and the reduction of ∑long-chained PFASs remained constant after 5 minutes.

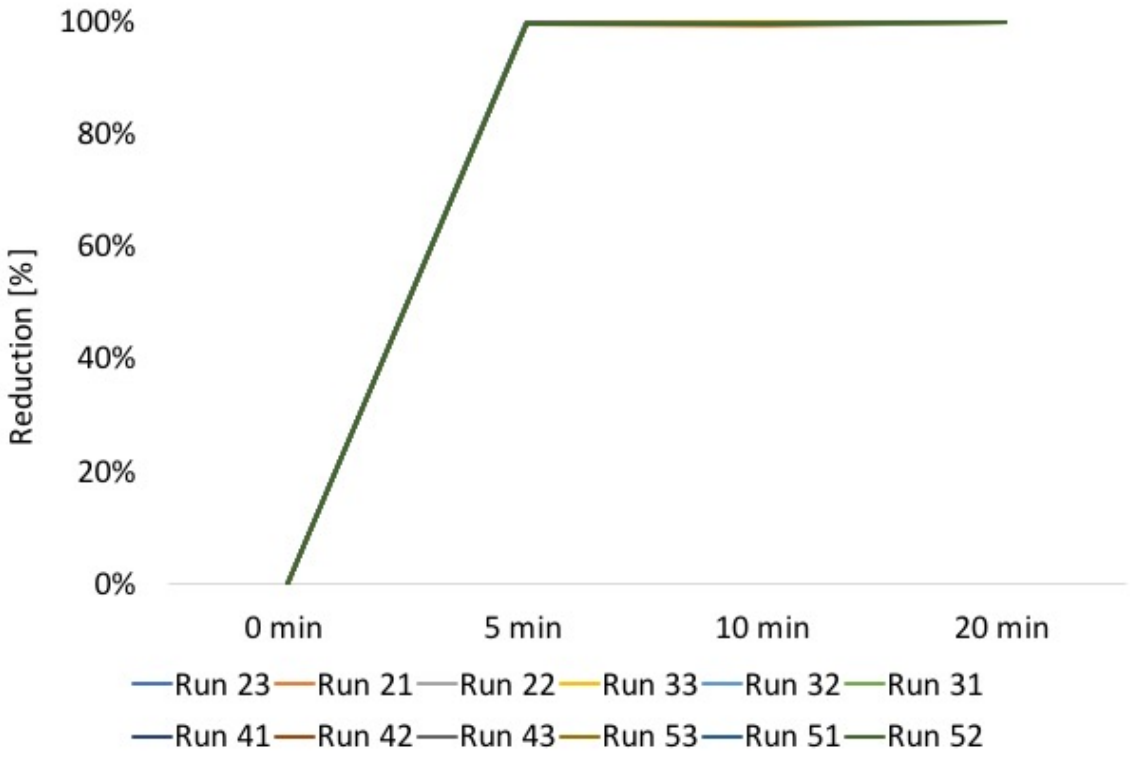


Figure 19: Average reduction of ∑long-chained PFASs at different time steps for each experimental run. Runs 21-23 (Zero surfactant), 31-33 (1x minimum dose), 41,43 (2x minimum dose) and 51-53 (3x minimum dose).

4.2.3 Overview of results

The final PFASs reduction calculations were based on the mean values retrieved from the 20 min samples. The reason being that some short-chained PFASs were more efficiently removed at time steps 10 and 20 min according to figure 20. The 20 min sample seemed as the better choice due to the systems contact time of 10 min.

The final results of the pilot-scale showed that ∑long-chained PFASs were reduced > 99% in all conducted experimental runs (Figure 20). The reduction of PFBS (C4), PFPeA (C4) and PFHxA (C5) were all enhanced with increasing doses of surfactant. The removal of PFBA (C3) was inefficient in the FF process, only ≈ 15 % was reduced in the conducted experiments. Also, the reduction was not improved when adding the surfactant. $\sum_4$PFASs was < 1 ng/L in the treated water in all executed experiments. Table 14 displays the average concentrations of PFASs in the effluent waters.

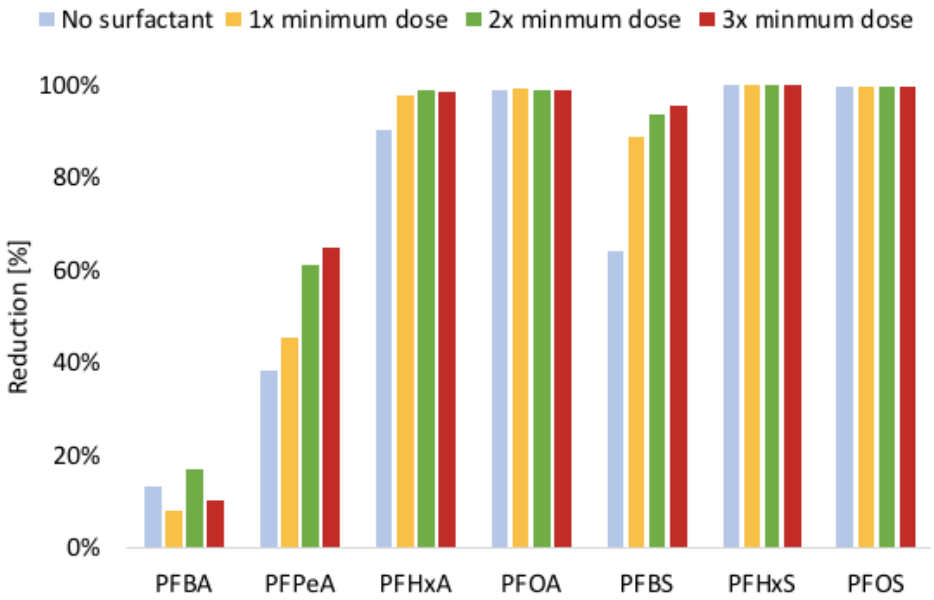


Figure 20: Average reduction for individual PFASs in the experimental runs with different doses of surfactant.

Table 14: Average PFASs concentrations in NF concentrate and the effluent water. The chart displays the average concentration of individual PFASs, $\sum_{11}$PFASs, $\sum_{4}$PFASs, ∑short-chained PFASs, ∑long-chained PFASs, ∑PFCAs and ∑FSAs in each experiment.

PFASs	**Concentrate (*ng/L*)**	**Zero surfactant (*ng/L*)**	**1x minimum (*ng/L*)**	**2x minimum (*ng/L*)**	**3x minimum (*ng/L*)**
PFBA (C3)	16	14	15	14	15
PFPeA (C4)	12	7.1	6.3	4.5	4.0
PFHxA (C5)	30	2.8	0.7	0.4	0.4
PFOA (C7)	17	0.2	0.2	0.2	0.2
PFBS (C4)	28	10	3.3	1.7	1.0
PFHxS (C6)	180	0.2	0.2	0.2	0.2
PFOS (C8)	63	0.2	0.2	0.2	0.2
PFAS 11	350	35	26	21	21
PFAS 4	260	0.6	0.6	0.6	0.6
Short-chained	86	34	25	21	20
Long-chained	260	0.6	0.6	0.6	0.6
PFCA	75	24	22	19	20
PFSA	280	10	3.7	2.1	1.4

The average reduction of $\sum_{11}$PFASs was 90 % in the zero surfactant experiment (Table 15). The highest removal efficiencies (94 %) were observed in the 2x minimum dose and the 3x minimum dose experiments. ∑long-chained PFASs were reduced > 99 % in all conducted experiments. The highest reduction of ∑short-chained PFASs was seen in the 3x minimum dose experiment (77 %), whereas the lowest reductions was observed in the zero surfactant runs (61 %). PFSAs were efficiently reduced in all experiments, however the removal efficiency of PFBS (C4), the short-chained PFSA, , was significantly improved when using the surfactant. PFCAs were removed up to 73 % with the highest dose of the surfactant.

Table 15: The average removal efficiency of PFASs at time step 20 min

Time	Zero surfactant	1x minimum dose	2x minimum dose	3x minimum dose
∑ PFASs (%)	90	93	94	94
Short-chained (%)	61	71	76	77
Long-chained (%)	> 99	> 99	> 99	> 99
PFCA (%)	68	71	75	73
PFSA (%)	96	98	99	99

The average reduction of each individual PFASs in the zero surfactant runs were subtracted from the experimental runs containing surfactants in figure 21. The difference in removal efficiencies and their standard deviations are plotted in the chart. The results showed that the removal efficiency of PFASs improved for PFPeA (C4), PFHxA (C5) and PFBS (C4) when using the surfactant in the FF process. ∑long-chained PFASs (PFOA (C7), PFHxS (C6) and PFOS (C8)) were reduced > 99% in all experiments, thus any potential improvement was not distinguishable. No increase in reduction of PFBA (C3) was observed when adding the surfactant.

T-tests were executed to determine if the differences in removal efficiencies were statistically significant between the different experiments (Figure 21). The results showed that the reduction of PFBS (C4), PFHxA (C5) and PFPeA (C4) were significant, when the surfactant was applied in the FF process. The reduction of PFBS (C4), PFHxA (C5) and PFPeA C(4) were increased with higher doses of surfactant (Table 16-17). The 2x minimum dose and the 3x minimum dose experiments were superior in reducing PFBS (C4), PFHxA (C5) and PFPeA (C4) compared to the lower dose of 1x minimum dose (Table 17). The removal of PFBS (C4) was enhanced most efficiently in the highest dose experiment (Table 18). There was no statistical significant difference between the 2x minimum dose and 3x minimum dose experiments in their removal of PFPeA (C4) and PFHxA (C5).

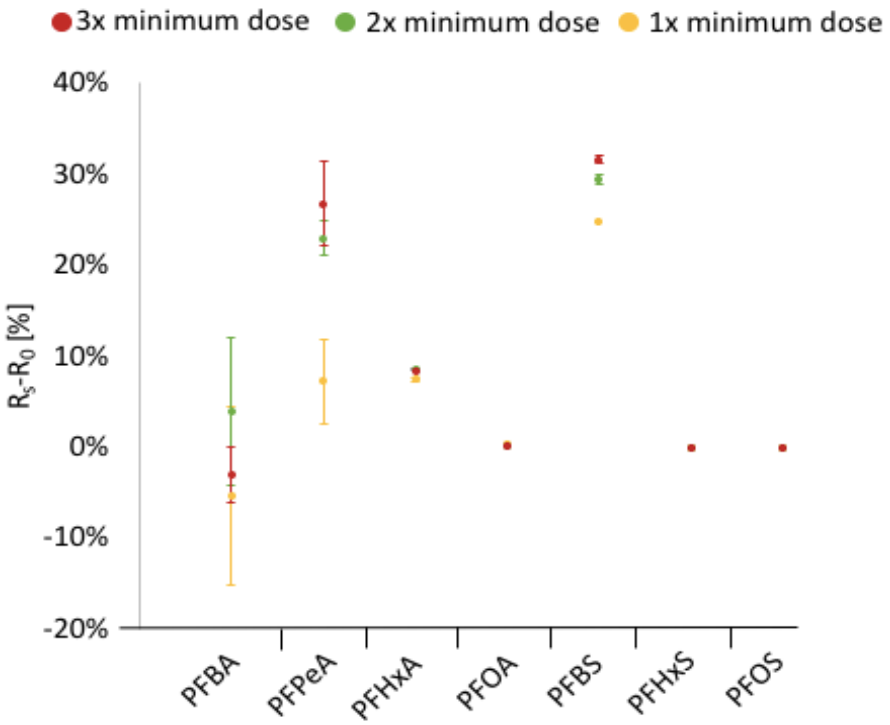


Figure 21: Reduction of the experimental runs with surfactant compared to the reference of zero surfactant

Table 16: T-test between the reduction of individual PFASs in the zero surfactant with 1x- and 2x the minimum dose runs. Values that indicates statistical significance (< 0.05) are highlighted in red.

	1x minimum dose	*2x minimum dose*	*3x minimum dose*
PFBA	0.29	0.65	0.65
PFPeA	0.15	0.002	0.0037
PFHxA	0.0067	0.070	0.0070
PFOA	0.058	0.73	0.48
PFBS	0.029	0.022	0.020
PFHxS	0.59	0.59	0.34
PFOS	0.60	0.87	1.00

Table 17: T-test between the reduction of individual PFASs in the 1x minimum dose run with 2x- and 3x the minimum dose runs. Values that indicates statistical significance (< 0.05) are highlighted in red.

	2x minimum dose	*3x minimum dose*
PFBA	0.37	0.78
PFPeA	0.028	0.014
PFHxA	0.020	0.024
PFOA	0.061	0.22
PFBS	0.019	0.0074
PFHxS	0.37	0.23
PFOS	0.58	0.60

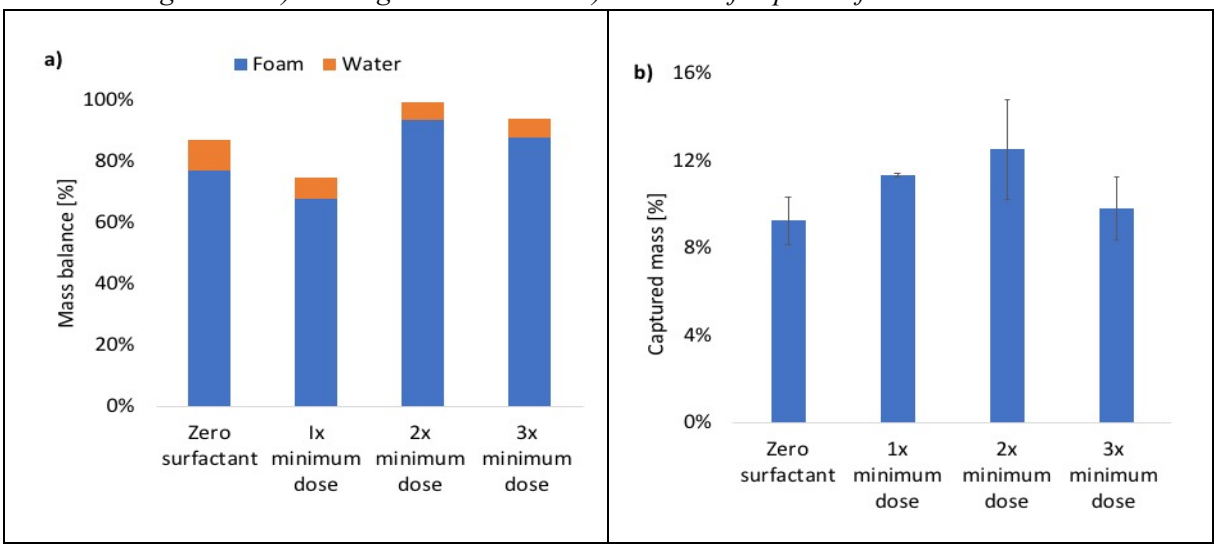
Table 18: T-test between the reduction of individual PFASs in the 2x minimum dose run with the 3x the minimum dose run. Values that indicates statistical significance (< 0.05) are highlighted in red.

	3x minimum dose
PFBA	0.35
PFPeA	0.36
PFHxA	0.29
PFOA	0.62
PFBS	0.0094
PFHxS	0.76
PFOS	0.92

4.2.4 Mass balance and collection of foam

The mass balance showed that ≥ 87 % of the initial PFASs were found in the foam or the treated water. The exception was the 1x minimum dose experiment where only 75 % of the PFASs was detected (Figure 22a). The 2x minimum dose experiment showcased a mass balance of 99 %. Figure 22 b) displays the amount of foam captured in each experiment. The average amount of collected foam was between 9 and 13 % of the treated concentrate.

Figure 22: a). Average mass balance b). Amount of captured foam relative to the amoun



5. Discussion

5.1 Laboratory-scale

All conducted experimental runs showed efficient removal of $\sum_{11}$PFASs in the FF process. ∑long-chained PFASs were removed ≥ 90 % in 22 of 25 conducted runs. High removal efficiencies were obtained for all conducted experiments, even in the zero surfactant runs. The removal efficiency of ∑short-chained PFASs was different depending on the type of surfactant and the dose applied, all surfactants, except YES indicated improvement in removal for some of these compounds. Montaline C 40, a cationic surfactant, increased the reduction of ∑short-chained PFASs most efficiently. The results showed that the reduction of PFPeA (C4), PFHxA (C5) and PFBS (C4) increased with higher dosing (Figure 11a). The highest removal of $\sum_{11}$PFASs for Montaline C 40 was observed in the experiment with the highest added dose of surfactant.

An important aspect of the laboratory-scale was that each experimental run was only conducted once. That provides low level of certainty in the results. However, similar trends for the increased removal efficiency of ∑short-chained PFASs, when using Montaline C 40 in th FF

process, were observed in both the laboratory- and the pilot-scale (Figure 11a, Figure 20). The reduction of the short-chained compounds PFPeA (C4), PFHxA (C5) and PFBS (C4) increased as the dose of the surfactant rose for both set-ups. Also, PFBA (C3), the shortest PFCA, was not improved in either of the experiments conducted in the laboratory- or the pilot-scale. The similarity of trends observed in these results implies that the laboratory-scale could be used as a screening method for early indications of the surfactants potential effects on the FF process. However, repeated experiments would be needed to confirm this finding. Besides from Montaline C 40 (cationic), both Marlinat 242/28 (anionic) and Simulsol S 10 (non-ionic) showed increased removal efficiencies of some short-chained PFASs (Figure 12a, Figure 13a) when applied in the FF process. Repeating the laboratory-scale experiments would have been valuable to confirm that Montaline C 40, the cationic surfactant, was indeed the best choice of surfactant.

The use of YES in the FF process displayed high removals for the majority of the targeted PFASs, but its reference, the zero surfactant run, was equally efficient, which implied that YES did not enhance the removal of PFASs. Similarly, the experimental runs conducted for LAS showed no correlation between the dose applied and improved removal. The amount of YES used in its stock solution was not based on its molar concentration, due to the unknown composition of the liquid. 0.5 gram was put in its stock solution which was similar of the mass used for Simulsol SL 10 and LAS. Hence, YES could have potentially performed better if the molar concentration was known.

A major error in the laboratory work was the substantial difference in reduction of PFBA (C3) and PFPeA (C4) observed between the conducted zero surfactant runs. The removal efficiencies obtained in the zero surfactant runs for each surfactant was critical for the removal % calculations. The reduction of PFBA (C3) and PFPeA (C4) deviated between 30-92 % and 50-81% respectively which are substantial. An explanation of the errors could be that the concentrate was transported between multiple different containers before it was poured into the colon used in the FF process. The solution was initially collected from the main tank (600 L) into a plastic container (10 L), then poured into a glass beaker (5 L) before it ended up in the 250 ml volumetric flask of glass. This procedure made it difficult to secure that each container was sufficiently mixed before the concentrate ended up in the colon. Other reasons could be, analysis errors or electrostatic forces interfering with the compounds.

Another aspect of the laboratory-scale was the batchwise FF process affect on the amount of PFBA (C3) and PFPeA (C4) harvested. In the batchwise operation, 250 ml of concentrate was poured into the colon, 50 ml was collected with the vacuum hose during a time period of approximately 3 minutes. Consequently, a significant fraction of the harvested volume was liquid and not foam, which could explain the relatively higher reduction seen in the laboratory-scale of PFBA (C3) and PFPeA (C4) compared to the pilot-scale (Figure 11a-15a, Figure 20). The weaker hydrophobic properties of PFBA (C3) and PFPeA (C4), due to shorter aliphatic carbon-chains, makes them less likely to be expelled to the surface, hence a larger fraction could potentially be collected when also water is harvested.

5.2 Pilot work

The results showed that the continuous FF process, on average, reduced >99 % of ∑long-chained PFASs in all experimental runs conducted. Also, the use of a cationic surfactant, Montaline C 40, enhanced the total reduction of ∑short-chained PFASs from 61 % in the zero surfactant experiment to 77 % in the 3x minimum dose experiment. The T-test showed a statistical significant correlation between the dosing of the cationic surfactant and the increased removal of the short-chained compounds: PFPeA (C4), PFHxA (C5) and PFBS (C4) . However, the correlation was not linear, hence an arbitrary increase of the cationic surfactant above the 3x minimum dose would not directly correlate with an increase in reduction of ∑short-chained PFASs. The mean removal efficiency of $\sum_{11}$ PFASs was 90 % in the zero surfactant experiment and 94 % in both the 2x minimum dose and the 3x minimum dose experiments (Table 15).

The removal of PFBS (C4) increased with 50 % in the 3x minimum dose run compared to the zero surfactant run, from 64 % to 96 %. The reduction of PFPeA (C4) improved with 63 % in the 3x minimum dose run compared to the zero surfactant experiment, from 41 % to 67 % reduction. The removal of PFHxA (C5) increased from 91 % in the zero surfactant runs to 99 % in the 2x minimum dose and 3x minimum dose experiments. The only targeted compound, which reduction was not enhanced by the surfactant was PFBA (C3), the compound with the shortest perfluoroalkyl chain-length. PFBA (C3) was reduced with only 13 % in the zero surfactant experiment, and no statistical improvement was observed in any of the other conducted experiments. The mean reduction of $\sum_4$ PFASs was < 0.6 ng/L in all experiments, thus meeting the requirements of the new legislation of < 4 ng/L for $\sum_4$ PFASs.

Only 7 compounds from $\sum_{11}$PFASs was detected in the NF concentrate. Three of the 7 PFASs were categorized as PFSAs (PFBS (C4) , PFHxS (C6) and PFOS (C8)) and four were PFCAs (PFBA (3), PFPeA (C4), PFHxA (C5), PFOA (C7)). The mean removal of PFSAs and PFCAs were 96 % and 68 % respectively in the zero surfactant experiment. These results indicates that PFSAs were more efficiently removed in the FF process compared to PFCAs, however two of the three PFSAs were categorized as long-chained PFASs (PFHxS (C6) and PFOS(C8)), whereas only one of the PFCAs had the same classification (PFOA (C7)).

Another finding was that the removal efficiency of PFASs increased with the number of carbons included in the perfluoroalkyl carbon chain. That trend was observed for both the PFCAs and PFSAs in all experiments.

PFCAs: PFOA (C7) > PFHxA (C5) > PFHPA (C4) > PFBA (C3).

PFSAs: PFOS (C8) = PFHxS (C6) > PFBS (C4).

Earlier conducted studies of the FF process and its use in removing PFASs from leachate water concluded that the reduction of PFASs was dependent on the perfluoroalkyl chain-length and the functional group attached. These results were findings stated in both Kjellgren (2020) and Krögerstrom (2021). These reports showed that longer perfluoroalkyl chain-lengths correlated with increased removals, and that the reduction of PFSAs was more efficient than PFCAs in the

FF process. These findings were confirmed in this thesis. Kjellgren (2020) used a continuous FF process to investigate the efficacy of PFAS removal in leachate and the results showed that the reduction ranged from 71-91 % with a mean reduction of 86 % for the different experiments conducted. These results can be compared to the findings of this thesis which showed that the removal efficiency of the concentrate was even more efficient in the FF process, with reductions between 90-94 %. Also, the concentration of PFASs in the NF concentrate was 350 ng/L, substantially lower than the average of 5500 ng/L found in the leachate (Kjellgren 2020). Meng et.al (2019) showed that the use of a co-existing surfactant could enhance the PFOS (C8) removal in the FF process. Meng et.al (2019) used a nonionic surfactant to enhance the removal of PFOS (C8) in an AFFF-solution. This thesis confirms the benefits of using surfactants in the FF process to enhance the removal of ∑short-chained PFASs.

The experiments conducted in the pilot-scale were executed at different dates. The last experiment, the 3x minimum dose, was done approximately a month after the zero surfactant, 1x minimum dose, and 2x minimum dose runs. The water chemistry of the tank was sampled prior to each experiment, the results are displayed in Appendix A.3. The obtained values indicated that the water chemistry remained constant during the elapsed time period. Measurements of conductivity, pH and temperature showed that the chemistry of the concentrate was relatively constant in all experimental runs, see Appendix A.4. The pH and the conductivity changed during the FF process due to the insertion of air. The turbulence caused by the air leads to degassing of carbon dioxide which raises the pH and lowers the alkalinity of the effluent.

The increased removal obtained for the targeted short-chained PFASs when adding the surfactant to the FF process was statistical significant according to the T-test (Table 14-16), except for PFBA (C3). The higher removals obtained in the 2x minimum dose and the 3x minimum dose experiments, compared to the zero surfactant and the 1x minimum dose experiments, of PFPeA (C4), PFHxA (C5) and PFBS (C4) was statistical significant (Table 16-17). A statistical significance was obtained for the higher removal of PFBS (C4) in the 3x minimum dose experiment compared to 2x minimum dose. No statistical significance was found for PFPeA (C4) and PFHxA (C5) between the 2x minimum dose experiment and the 3x minimum dose experiment, thus the increase of the cationic surfactant impacts the reduction of individual short-chained PFASs differently.

The average removal of ∑short-chained PFASs was 77 % in the highest dose experiment (3x minimum dose), compared to 61 % in the experiment without any addition of surfactant (zero surfactant). An explanation behind the increase in removal, when applying the surfactant, could be the improvement in foam stability. The surfactant lowers the surface tension which increases the stability of the foam according to the Yung-Laplace equation (Equation 1), hence the duration of PFASs in the foam phase increases which facilitates the harvesting of the foam. PFBA (C3) was inefficiently removed in the FF process, and was not improved by the addition of the cationic surfactant. The main reason behind this finding could be the relatively short length of its perfluorocarbon chain compared to the other targeted PFASs. Shorter perfluorocarbon chain, with its lower hydrophobicity, decreases the chances of the surfactant (PFAS is a surfactant) in the solution to be expelled to the surface and interact in the foam formation.

The methodology in the pilot-scale could have been improved by investigating the optimal contact time and air-flow rate for the FF process. It was unfortunately not possible to execute these experiments due to the time and cost restrictions of the thesis. The values were instead

inspired from Kjellgren (2020), who evaluated the FF efficacy in removing PFASs from leachate water. The study used the same pilot equipment as this thesis. The results from Kjellgren (2020) indicated that a CT of 20 min would be superior to 10 and 5 min and that an air flow rate of 4 L/min and 6 L/min showed better results in terms of PFASs recovery compared to 2 L/min. This thesis used a CT of 10 min for time efficacy reasons and an air flow rate of 4 L/min, although it would have been interesting to test a CT of 20 min and an air-flow rate of 6 L/min aswell.

The volume of liquid harvested in the vacuum collector during the FF operation was between 9 and 12 % for the conducted experiments in the pilot-scale. These values included the water content inside the column at time zero, hence the fraction of foam volume and treated water volume was slightly underestimated. In reality, a larger volume would be expected for the foam, in the range of 15-20 % of total water volume.

No correlation was observed between the dose of surfactant and the amount of foam collected. The mass balance of PFASs collected in foam and effluent was < 100 % in all conducted experiments (Figure 22), however three of four experiments managed to collect ≥ 87 %. The amount of foam collected in the 1x minimum dose experiment was approximated due to a miss in the notations which could explain the low mass balance of 75 % observed. The aerosol experiment showed that a small amount of PFOS (C8) was collected in the water trap (Appendix A.9). Aerosol formation is one explanation behind the inefficient mass balance obtained.

The main error in the pilot-scale was the inefficient detection of PFBA (C3) and PFPeA (C4) in the tank water samples retrieved before each conducted experimental run. A significant fraction of the samples, reported concentrations below the LOR-value, thus an average value was used for the tank water samples containing PFBA (C3) and PFPeA (C4) in the removal calculations. PFASs concentration of all harvested samples in the pilot-scale are displayed in Appendix 2. PFBA (C3) had the highest LOR-value of all targeted compounds, which could explain the difficulty in detecting this molecule. Another reason for the low detection of these compounds could potentially be that the concentrate was inefficiently mixed in the 600 L container or electrostatic forces that interfered..

One more critical aspect of the pilot-scale was the manually maneuvering of the vacuum hose during the introduction of air in the colon. When air entered the colon, the volume of the waterbody increased significantly due to the volume of the bubbles, thus the hose was adjusted accordingly to collect the initial foam before it was held at a constant level as the water body reached steady-state. This procedure was hard to execute exactly the same for all conducted experiments which could have impacted the mass balance if some of the PFASs were not collected with the vacuum hose and instead got stuck on the walls in the colon.

5.3 Future studies

The findings from this study shows that the removal of short-chained PFASs are enhanced with the addition of a cationic surfactant in the FF process. The results opens up a lot of interesting questions for further investigations regarding the optimization of the FF system. It would be valuable to evaluate different types of surfactants in the pilot-scale setup, to fully understand if cationic surfactants truly are the best choice in terms of PFASs removal. Simulsol S 10, a nonionic surfactant, was another surfactant used in the laboratory-scale experiments which showed good indication of being effective in the removal of ∑short-chained PFASs. It was also the only surfactant that did not report any toxic implication to aquatic life in its safety data sheet. It would be interesting to investigate the removal efficiency of Simulsol S 10 in the pilot-scale FF process.

Another aspect would be to evaluate the optimal contact time and aeration flow rate in the FF process. Knowledge of the optimal operation parameter values would bring more understanding regarding the FF process truly potential in removing PFASs. It would also be interesting to use NF concentrates with varying PFASs compositions and concentrations to see if the trends observed in this study would hold.

The high efficacy showed in this thesis of the FF process alone in the removal of long-chained PFASs opens up the idea of a two-stage FF system. In the first stage, the long-chained PFASs are removed with only air, the effluent is then directed into a second FF chamber where surfactants are introduced to enhance the removal of short-chained PFASs. Finally, it would be good to replicate the laboratory-scale experiment with Montaline C 40 to establish that the screening methodology used in this thesis can be applied on new surfactants.

6. Conclusions

The aims of the thesis were encapsulated in three research questions

- Is foam fractionation an efficient method to remove PFASs from the concentrate from a two-stage nanofiltration membrane?

- Could surfactants be used to enhance the removal of PFASs in the foam fractionation process?

- Is the reduction of PFASs in the foam fractionation process affected by different concentrations of surfactants?

The results of the thesis showed that > 99 % of long-chained PFASs were reduced in all conducted experimental runs in the continuous FF process. The average reduction of short-chained PFASs was 61 % in the runs without any addition of the cationic surfactant, and 77 % in the experiment with the highest added dose. The average removal of $\sum_{11}$PFASs was 90 % without any addition of surfactant, whereas in the two highest dose experiments, 2x minimum dose and 3x minimum dose, the average reduction was 94 %. The results implies that the FF process is extremely efficient in removing long-chained PFASs from the concentrate, and that a cationic surfactant can successfully be applied to increase the removal of short-chained PFASs.

The addition of Montaline C 40, a cationic surfactant, increased the removal of short-chained PFASs substantially from 61 to 77 % in the continuous FF process. The removal of PFBA (C3), the shortest targeted perfluorinated compound, was not improved when adding the surfactant. Furthermore, the laboratory work indicated that different types of surfactants, not only cationic surfactants, were beneficial to increase the removal efficiency of the FF process. The results showed that surfactants can beneficially be used to enhance the removal of short-chained PFASs in the FF process.

The T-test showed statistical significance between higher dosing and increased removal of ∑short-chained PFASs. The lowest reductions of short-chained PFASs (61 %) was observed in the experiment with no addition of surfactant and the highest reduction (77 %) was obtained in the experiment with the highest dose. The results implied a positively correlation between the removal efficiency of ∑short-chained PFASs with higher dosing, although the relationship was not linear. The reduction of ∑short-chained PFASs in the 2x minimum dose experiment was 76% compared to the 77 % observed in the 3x minimum dose experiment.

7. References

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8. Appendices

A.1 List of harvested samples

Table 18: All samples harvested during the laboratory-scale experiments. The name of the sample, reference number, dose and Mole ratio of Surfactant/PFAS.

Surfactant	Name of sample	Number #	Dose (ml)	Mole ratio Surfactant/PFAS
Montaline C 40	Blank 1W	11	0	0
Montaline C 40	Blank 1F	12	0	0
Montaline C 40	1aF	13	0,3	1515
Montaline C 40	1aW	14	0,3	1515
Montaline C 40	1bF	15	0,6	3029
Montaline C 40	1bW	16	0,6	3029
Montaline C 40	1cW	17	1,5	7573
Montaline C 40	1cF	18	1,5	7573
Marlinat 242/28	Blank 2W	21	0	0
Marlinat 242/28	Blank 2F	22	0	0
Marlinat 242/28	2aF	23	0,25	1262
Marlinat 242/28	2aW	24	0,25	1262
Marlinat 242/28	2bF	25	0,5	2524
Marlinat 242/28	2bW	26	0,5	2524
Marlinat 242/28	2cW	27	1,25	6311
Marlinat 242/28	2cF	28	1,25	6311
Simulsol S 10	Blank 3W	31	0	0
Simulsol S 10	Blank 3F	32	0	0
Simulsol S 10	3aF	33	0,6	3029
Simulsol S 10	3aW	34	0,6	3029
Simulsol S 10	3bF	35	1,2	6058
Simulsol S 10	3bW	36	1,2	6058
Simulsol S 10	3cW	37	3	15146
Simulsol S 10	3cF	38	3	15146
LAS	Blank 4W	41	0	0
LAS	Blank 4F	42	0	0
LAS	4aF	43	0,6	3029
LAS	4aW	44	0,6	3029
LAS	4bF	45	1,2	6058
LAS	4bW	46	1,2	6058
LAS	4cW	47	3	15146
LAS	4cF	48	3	15146
Yes	Blank 5W	51	0	0
Yes	Blank 5F	52	0	0

Yes	5aF	53	0,3	-
Yes	5aW	54	0,3	-
Yes	5bF	55	0,6	-
Yes	5bW	56	0,6	-
Yes	5cW	57	1,5	-
Yes	5cF	58	1,5	-

Table 19: All samples harvested during the pilot-scale experiments. The name of the sample, reference number, dose and Mole ratio of Surfactant/PFAS used.

Surfactant	**Name of sample**	**Experimental ID**	**Dose (ml)**	**Mole ratio Surfactant/PFAS**
Montaline C 40	Tank 21	60	0	0
Montaline C 40	Column 21	61	0	0
Montaline C 40	5W 21	62	0	0
Montaline C 40	10W 21	63	0	0
Montaline C 40	20W 21	64	0	0
Montaline C 40	Foam 21	65	0	0
Montaline C 40	Tank 22	66	0	0
Montaline C 40	Column 22	67	0	0
Montaline C 40	5W 22	68	0	0
Montaline C 40	10W 22	69	0	0
Montaline C 40	20W 22	70	0	0
Montaline C 40	Foam 22	71	0	0
Montaline C 40	Tank 23	72	0	0
Montaline C 40	Column 23	73	0	0
Montaline C 40	5W 23	74	0	0
Montaline C 40	10W 23	75	0	0
Montaline C 40	20W 23	76	0	0
Montaline C 40	Foam 23	77	0	0
Montaline C 40	Tank 31	78	0,3	1425
Montaline C 40	Column 31	79	0,3	1425
Montaline C 40	5W 31	80	0,3	1425
Montaline C 40	10W 31	81	0,3	1425
Montaline C 40	20W 31	82	0,3	1425
Montaline C 40	Foam 31	83	0,3	1425
Montaline C 40	Tank 32	84	0,3	1425
Montaline C 40	Column 32	85	0.3	1425
Montaline C 40	5W 32	86	0.3	1425
Montaline C 40	10W 32	87	0.3	1425
Montaline C 40	20W 32	88	0.3	1425

Montaline C 40	Foam 32	89	0.3	1425
Montaline C 40	Tank 33	90	0.3	1425
Montaline C 40	Column 33	91	0.3	1425
Montaline C 40	5W 33	92	0.3	1425
Montaline C 40	10W 33	93	0.3	1425
Montaline C 40	20W 33	94	0.3	1425
Montaline C 40	Foam 33	95	0.3	1425
Montaline C 40	Tank 41	96	0.6	2850
Montaline C 40	Column 41	97	0.6	2850
Montaline C 40	5W 41	98	0.6	2850
Montaline C 40	10W 41	99	0.6	2850
Montaline C 40	20W 41	100	0.6	2850
Montaline C 40	Foam 41	101	0.6	2850
Montaline C 40	Tank 42	102	0.6	2850
Montaline C 40	Column 42	103	0.6	2850
Montaline C 40	5W 42	104	0.6	2850
Montaline C 40	10W 42	105	0.6	2850
Montaline C 40	20W 42	106	0.6	2850
Montaline C 40	Foam 42	107	0.6	2850
Montaline C 40	Tank 43	108	0.6	2850
Montaline C 40	Column 43	109	0.6	2850
Montaline C 40	5W 43	110	0.6	2850
Montaline C 40	10W 43	110	0.6	2850
Montaline C 40	20W 43	111	0.6	2850
Montaline C 40	Foam 43	112	0.6	2850
Montaline C 40	Tank 51	113	0.9	4275
Montaline C 40	Column 51	114	0.9	4275
Montaline C 40	5W 51	115	0.9	4275
Montaline C 40	10W 51	116	0.9	4275
Montaline C 40	20W 51	117	0.9	4275
Montaline C 40	Foam 51	118	0.9	4275
Montaline C 40	Tank 52	119	0.9	4275
Montaline C 40	Column 52	120	0.9	4275
Montaline C 40	5W 52	121	0.9	4275
Montaline C 40	10W 52	122	0.9	4275
Montaline C 40	20W 52	123	0.9	4275
Montaline C 40	Foam 52	124	0.9	4275
Montaline C 40	Tank 53	125	0.9	4275
Montaline C 40	Column 53	126	0.9	4275
Montaline C 40	5W 53	127	0.9	4275
Montaline C 40	10W 53	128	0.9	4275
Montaline C 40	20W 53	129	0.9	4275
Montaline C 40	Foam 53	130	0.9	4275

A.2 List of analysed PFAS

Table 20: Sampled PFASs executed by ALS. Each compound LOR-value and classification is displayed.

Name	Acronym	LOR	PFCA	PFSA	Precursor
Perfluoro+A1:D32-n-butanoic acid	PFBA	0.0020	x		
Perfluoro-n-pentanoic acid	PFPeA	0.0030	x		
Perfluoro-n-hexanoic acid	PFHxA	0.0030	x		
Perfluoro-n-heptanoic acid	PFHpA	0.0030	x		
Perfluorooctanoic acid	PFOA	0.0030	x		
Perfluorononanoic acid	PFNA	0.0030	x		
Perfluoro-n-decanoic acid	PFDA	0.0030	x		
Perfluorobutanesulfonic acid	PFBS	0.0030		x	
Perfluorohexanesulfonic acid	PFHxS	0.0030		x	
Perfluorooctanesulfonic acid	PFOS	0.0030		x	
Fluorotelomer sulfonate	6:2 FTS	0.0030			x
Perfluoro-n-undecanoic acid	PFUnDA	0.0030	x		
Perfluoro-n-dodecanoic acid	PFDoDA	0.0030	x		
Perfluoro-n-tridecanoic acid	PFTriDA	0.0030	x		
Perfluoro-n-tetradecanoic acid	PFTeDA	0.0030	x		
Perfluoropentane sulfonic acid	PFPeS	0.0030		x	
Perfluoroheptanesulfonic acid	PFHpS	0.0030		x	
Perfluorononane sulfonic acid	PFNS	0.0030		x	
Perfluorodecanesulfonic acid	PFDS	0.0030		x	
Perfluorodecane sulfonic acid	PFDoDS	0.0030		x	

Fluorotelomer sulfonic acid	4:2 FTS	0.00030			x
Fluorotelomer sulfonate	8:2 FTS	0.00030			x
Perfluorooctanesulfonamide 1	FOSA	0.00030			x
N-methyl perfluorooctane sulfonamide	MeFOSA	0.0020			x
N-ethyl perfluorooctane sulfonamide	EtFOSA	0.0020			x
N-methyl perfluorooctane sulfonamidoethanol	MeFOSE	0.0020			x
N-ethyl perfluorooctane sulfonamidoethanol	EtFOSE	0.0020			x
Perfluorooctane sulfonamidoacetic acid	FOSAA	0.0010			x
N-methylperfluorooctanesulfonamido acid	MeFOSAA	0.0010			x
N-ethylperfluorooctanesulfonamido acid	EtFOSAA	0.0010			x
7H-perflouroheptanic acid	HPFHpA	0.0010			
Perfluoro-3.7-dimethyloctanic acid	PF37DMOA	0.0010			

A.3 General Chemistry – Pilot

Table 21: General chemistry information of the concentrate used in the pilot experiments.

ELEMENT	SAMPLE	3x minimum	Zero surfactant	2x minimum	1x minimum
Sampling Date		2022-05-09	2022-04-11	2022-04-08	2022-04-07
Ca	mg/L	297	297	306	297
Mn	µg/L	2.8	1.52	1.2	0.94
Na	mg/L	68.4	65.7	67.7	65.8
K	mg/L	17.8	17.3	17.7	17.3
Fe	mg/L	0.00465	0.00231	0.00223	0.00263
Al	µg/L	7.31	7.64	7.46	8.32
Cu	µg/L	43.5	18.5	12.2	13.9
Mg	mg/L	62.3	60.7	62.2	60.7
Hardness	°dH	56	55.6	57.2	55.6
NO2, nitrite	mg/L	0.017	0.016	0.016	0.016

NO_2-N, nitrite nitrogen	mg/L	0.005	0.005	0.005	0.005
COD-Mn	mg/L	5.22	5.31	4.93	5
ammonia and ammonium (NH4)	mg/L	0.056	<0.050	<0.050	<0.050
ammonia-N, ammonium-N	mg/L	0.044	<0.040	<0.040	<0.040
Phosphate, PO4	mg/L	<0.040	<0.040	<0.040	<0.040
Phosphate phosphorus PO4-P	mg/L	<0.013	<0.013	<0.013	<0.013
NO3	mg/L	5.52	5.31	5.26	5.29
NO3-N	mg/L	1.25	1.2	1.19	1.2
Flourine	mg/L	4.01	3.55	3.54	3.53
Chlorine	mg/L	104	97.4	96.1	96.9
Sulphur SO4	mg/L	227	203	200	201
Measurement temp pH	°C	21.8	21.3	21	20.7
turbidity	FNU	0.75	0.59	0.54	0.6
conductivity	mS/m	141	168	156	159
pH		8.6	8.2	8.3	8.3
alkalinity	mg HCO3-/L	1010	1040	1050	1190

Table 22: General chemistry information of the column water. The samples were harvested during operation of the FF process.

ELEMENT	SAMPLE	3x minimum	Zero surfactant	2x minimum	1x minimum
Sampling Date		2022-05-09	2022-04-11	2022-04-08	2022-04-07
Ca. kalcium	mg/L	299	291	302	298
Mn. mangan	µg/L	3.28	1.58	1.15	1.02
Na. natrium	mg/L	67.8	64.1	67.6	64.9
K. kalium	mg/L	17.9	16.8	17.7	17.1
Fe. järn	mg/L	0.0089	0.00231	0.00213	0.00324
Al. aluminium	µg/L	7.6	7.71	8.05	8.02
Cu. koppar	µg/L	43.4	19.4	15.1	16
Mg. magnesium	mg/L	62.5	59	61.9	60.2
hårdhet	°dH	56.3	54.4	56.5	55.6
nitrit. NO2	mg/L	0.017	0.016	0.016	0.016
nitritkväve. NO2-N	mg/L	0.005	0.005	0.005	0.005
COD-Mn	mg/L	4.63	5	4.71	5.12
ammoniak och ammonium som NH4	mg/L	<0.050	<0.050	<0.050	<0.050

ammoniak- + ammoniumkväve	mg/L	<0.040	<0.040	<0.040	<0.040
fosfat. PO4	mg/L	0.051	<0.040	<0.040	<0.040
fosfatfosfor. PO4-P	mg/L	0.017	<0.013	<0.013	<0.013
nitrat. NO3	mg/L	5.64	5.27	5.93	5.96
nitratkväve. NO3-N	mg/L	1.27	1.19	1.34	1.34
fluorid	mg/L	4.11	3.51	3.66	3.7
klorid	mg/L	102	96.5	96.9	97.5
sulfat. SO4	mg/L	218	201	203	205
mättemperatur pH	°C	21.9	19.7	20.8	20.9
turbiditet	FNU	0.39	0.32	0.66	0.36
konduktivitet	mS/m	145	146	156	154
pH		8.5	8.5	8.5	8.5
alkalinitet	mg HCO3-/L	953		1030	1080

A.4 Temperature, pH and conductivity measurements – Pilot

Table 23: Temperature. pH and conductivity measurements made for each experimental run conducted

ID	*pH (before)*	C (µS/cm) (before)	Temp (C °) (before)	*pH (after)*	C (µS/cm) (after)	Temp (C °) (after)	Date
21	8.17	1909	11.6	8.46	1823	12.9	07-Apr
22	8.22	1893	11.5	8.48	1820	12.8	07-Apr
23	8.26	1884	11.4	8.53	1822	12.8	07-Apr
31	8.08	1902	Approsimate 11.5	8.43	1826	approximate 12.9	08-Apr
32	8.13	1903	Approximate 11.5	8.45	1831	approximate 12.9	08-Apr
33	8.13	1901	Approximate 11.5	8.45	1830	approximate 12.9	12-Apr
41	8.16	1900	11.6	8.54	1815	12.9	11-Apr
42	8.17	1903	11.5	8.48	1827	12.9	11-Apr
43	8.17	1901	11.6	8.53	1820	12.8	12-Apr
51	8.51	1852	11.7	8.61	1813	13.7	09-May
52	8.51	1845	11.8	8.60	1814	13.6	09-May
53	8.50	1841	11.7	8.60	1812	13.6	09-May

A.5 DI water - PFAS concentration

Pilot-scale

Table 24:PFAS content of the DI water collected during the pilot-scale experiments.

Element	**DI 3 8/4 (µg/L)**	**DI 4 11/4 (µg/L)**	**D1 5 7/4 (µg/L)**
PFBA	<0.0020	<0.0020	<0.0020
PFPeA	<0.00030	<0.00030	<0.00030
PFHxA	<0.00030	<0.00030	<0.00030
PFHpA	<0.00030	<0.00030	<0.00030
PFOA	<0.00030	<0.00030	<0.00030
PFNA	<0.00030	<0.00030	<0.00030
PFDA	<0.00030	<0.00030	<0.00030
PFBS	<0.00030	<0.00030	<0.00030
PFHxS	<0.00030	<0.00030	<0.00030
PFOS	<0.00030	<0.00030	<0.00030
6:2 FTSA	<0.00030	<0.00030	<0.00030
Sampling Date	**2022-04-08**	**2022-04-11**	**2022-04-07**

Lab-scale

Table 25:PFAS content of the DI water collected during the Lab-scalet experiments.

Element	**Bäcklösa. D1 water 1 592-1**	**Bäcklösa. D2 water 2 592-2**
PFBA	<0.0020	<0.0060
PFPeA	<0.00030	<0.00030
PFHxA	<0.00030	<0.00030
PFHpA	<0.00030	<0.00030
PFOA	<0.00030	<0.00030
PFNA	<0.00030	<0.00030
PFDA	<0.00030	<0.00030
PFBS	<0.00030	<0.00030
PFHxS	<0.00030	<0.00030
PFOS	<0.00030	<0.00030
6:2 FTSA	<0.00030	<0.00030
Sampling Date	**2022-03-08**	**2022-03-08**

A.6 Foam data - Pilot

Table 26: Collected amounts of foam for each experimental run conducted in the pilot. each experimental ID and name of experiment

Run	**Experimental ID**	**Experiment**	***Collected Foam (g)***
31	21	Zero surfactant	560
33	22	Zero surfactant	750
35	23	Zero surfactant	659
11	31	1x mini dose	800 (approximated)
12	32	1x mini dose	800 (approximated)
13	33	1x mini dose	814.34
21	41	2x mini dose	1022
22	42	2x mini dose	981.07
23	43	2x mini dose	660
41	51	3x mini dose	728.44
42	52	3x mini dose	801.02
44	53	3x mini dose	556

A.7 Calculations

A.7.1 Laboratory work – Stock solution calculations

MONTALINE C 40

Molweight calculations:

R=C12			
	Antal	M (g/mol)	Tot sum (g/mol)
C	**22**	12.0107	264.2354
H	**46**	1.00784	46.36064
O	**3**	15.999	47.997
N	**3**	14.0067	42.0201
Cl	**0**	35.453	0
Sum Molweight			**358.593**
R = C18			
	Antal	M (g/mol)	Tot sum (g/mol)
C	**28**	12.0107	336.2996
H	**58**	1.00784	58.45472
O	**3**	15.999	47.997
N	**3**	14.0067	42.0201
Cl	**0**	35.453	0
Sum Molweight			**442.751**
Average			**400.672**

Dose calculations

Stock solution 1	1000	ml
Molweight	400.672	g/mol

Wanted concentration in stock solution	0.00111	mol/l
Grams needed for 1 L	0.44474612	g
Active substance (%)	40	%
Grams needed of solution to have enough of active substance in 1 L	1.1118653	g
Density	1.105	g/ml
Amount needed in 1000 ml DI water for the stock solution	**1.006212941**	ml

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Dose calculations

Stock solution 1	1000	ml
Molweight	383	g/mol
Wanted concentration in stock solution	0.00111	mol/l
Grams needed for 1 L	0.42513	g
Active substance (%)	26.5	%
Grams needed of solution to have enogh of active substance in 1 L	1.604264151	g
Density	1.04	g/ml
Amount needed in 1000 ml DI water for the stock solution	**1.542561684**	ml

Simulsol S 10

Molweight calculations

R = C10H21			
	Number	Molweight	Tot sum
C	**16**	12.0107	192.1712
H	**32**	1.00784	32.25088
O	**6**	15.999	95.994
Sum Molweight			320.41608
R = C12H25			
	Number	Molweight	Tot sum
C	**18**	12.0107	216.1926
H	**36**	1.00784	36.28224
O	**6**	15.999	95.994
Sum Molweight			348.46884
Average sum			***334.442***

Dose calculations

R = C10H21			
	Number	Molweight	Tot sum
C	**16**	12.0107	192.1712
H	**32**	1.00784	32.25088
O	**6**	15.999	95.994
Sum Molweight			**320.41608**
R = C12H25			
	Antal	M	Tot sum
C	**18**	12.0107	216.1926
H	**36**	1.00784	36.28224
O	**6**	15.999	95.994
Sum Molweight			**348.46884**
Average sum			*334.442*

Linear alkylbenzensulfonic acid (LAS)

Molweight calculations

C10H21	Antal	M (g/mol)	Tot sum (g/mol)
C	**16**	12.0107	192.1712
H	**26**	1.00784	26.20384
O	**3**	15.999	47.997
S	**1**	32.065	32.065
Sum Molweight			**298.43704**
C13H27	Antal	M (g/mol)	Tot sum (g/mol)
C	**19**	12.0107	228.2033
H	**32**	1.00784	32.25088
O	**3**	15.999	47.997
S	**1**	32.065	32.065
Sum Molweight			**308.45118**
Average			**303.44411**

Dose calculations

Stock solution 1	1000	ml
Molweight	314.967	g/mol
Wanted concentration in stock solution (multiplied PFAS conc in 100ml with 10^6)	0.00111	mol/l
Grams needed for 1 l	0.34961332	g
Active substance (%)	97	%
Grams needed of solution to have enough of active substance in 1 L	0.360426103	g

Density	1.05	g/ml
Amount needed in 1000 ml DI water for the stock solution	0.343262955	ml

A.7.2 Surfactant/PFAS mole ratio

Pilot

Molar concentration (mol/L) calculations of PFAS in concentrate

Element	Mean Tank (ug/L)	Conc in sample (g/l)	Molweight (g/mol)	Average molarweight calculation (<0.01 is assumed to be 0.01)	C (mol/L)
PFBA	0.016285714	1.62857E-08	213.028	9.912323265	7.64487E-11
PFPeA	0.011571429	1.15714E-08	263.035	8.696259184	4.3992E-11
PFHxA	0.029818182	2.98182E-08	313.042	26.66955221	9.5253E-11
PFHpA	0	0	363.049	0	0
PFOA	0.0168	1.68E-08	413.056	19.826688	4.06725E-11
PFNA	0	0	463.063	0	0
PFDA	0	0	513.07	0	0
PFBS	0.0275	2.75E-08	299.089	23.49985	9.19459E-11
PFHxS	0.183666667	1.83667E-07	399.103	209.4340505	4.60199E-10
PFOS	0.06305	6.305E-08	499.117	89.91236243	1.26323E-10
6:2 FTSA	0	0	427.157	0	0
SUM:	*0.348691991*	3.48692E-07	4165.809	387.9510856	9.34834E-10

Montaline C 40

	1x minimum dos	2x minimum dos	3x minimum dos
Stock solution (mol/L)	0.00111	0.00111	0.00111
Added stock solution (L)	0.012	0.024	0.036
Added surfactant (mol)	0.00001332	0.00002664	0.00003996
Amount PFAS in 10 L (mol)	9.34834E-09	9.34834E-09	9.34834E-09
Surfactant/PFAS	**1425**	**2850**	**4275**

Lab-Scale

Molar concentration (mol/L) calculations of PFAS in concentrate

Element	Mean Tank (ug/L)	Conc in sample (g/l)	Molweight (g/mol)	Average molarweight calculation (<0.01 is assumed to be 0.01)	C (mol/L)
PFBA	0.015333333	1.53333E-08	213.028	9.332655238	7.1978E-11
PFPeA	0.013	0.000000013	263.035	9.769871429	4.94231E-11
PFHxA	0.03	0.00000003	313.042	26.83217143	9.58338E-11
PFHpA	0.005	0.00000005	363.049	5.186414286	1.37722E-11
PFOA	0.0133	1.33E-08	413.056	15.696128	3.2199E-11
PFNA	0.005	0.00000005	463.063	6.615185714	1.07977E-11
PFDA	0.005	0.00000005	513.07	7.329571429	9.74526E-12
PFBS	0.027	0.00000027	299.089	23.07258	9.02741E-11
PFHxS	0.161666667	1.61667E-07	399.103	184.3475762	4.05075E-10
PFOS	0.044233333	4.42333E-08	499.117	63.07888181	8.86232E-11
6:2 FTSA	0.005	0.00000005	427.157	6.102242857	1.17053E-11
SUM:	*0.324533333*	3.24533E-07	4165.809	357.3632784	8.79427E-10

Montaline C 40

	1x minimum dos	2x minimum dos	5x minimum dos
Stock solution (mol/L)	0.00111	0.00111	0.00111
Addition (L)	0.0003	0.0006	0.0015
Added surfactant (mol)	0.000000333	0.000000666	0.000001665
Amount PFAS in 250 ml (mol)	2.19857E-10	2.19857E-10	2.19857E-10
Surfactant/PFAS	**1515**	**3029**	**7573**

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	1x minimum dos	2x minimum dos	5x minimum dos
Stock solution (mol/L)	0.00111	0.00111	0.00111

Addition (L)	0.00025	0.0005	0.00125
Added surfactant (mol)	2.775E-07	0.000000555	1.3875E-06
Amount PFAS in 250 ml (mol)	2.19857E-10	2.19857E-10	2.19857E-10
Surfactant/PFAS	**1262**	**2524**	**6311**

Simulsol S 10

	1x minimum dos	2x minimum dos	5x minimum dos
Stock solution (mol/L)	0.00111	0.00111	0.00111
Addition (L)	0.0006	0.0012	0.003
Added surfactant (mol)	0.000000666	0.000001332	0.00000333
Amount PFAS in 250 ml (mol)	2.19857E-10	2.19857E-10	2.19857E-10
Surfactant/PFAS	**3029**	**6058**	**15146**

LAS

	1x minimum dos	2x minimum dos	5x minimum dos
Stock solution (mol/L)	0.00111	0.00111	0.00111
Addition (L)	0.0006	0.0012	0.003
Added surfactant (mol)	0.000000666	0.000001332	0.00000333
Amount PFAS in 250 ml (mol)	2.19857E-10	2.19857E-10	2.19857E-10
Surfactant/PFAS	**3029**	**6058**	**15146**

A.7.3 Mass balance - Pilot

	Zero surfactant	**1x minimum dose**	**2x minimum dose**	**3x minimum dose**
Mean concentration tank (µg/L)	0.368157	0.398357143	0.3576238	0.35089
Mean concentration in treated water (µg/L)	0.037348	0.02699	0.0214667	0.021534
Mean concentration Foam (µg/L)	3.063	2.379666667	2.6673333	3.144
Volume Foam (L)	0.656333	0.80478	0.88769	0.695153
Volume colonn (L)	2.29	2.29	2.29	2.29
CT (min)	10	10	10	10
Q (L/min)	0.229	0.229	0.229	0.229

Duration (min)	21	21	21	21
Total volume entering (L)	4.809	4.809	4.809	4.809
Absolute volume (L)	7.099	7.099	7.099	7.099
Absolut PFASs C (µg)	2.613548	2.827937357	2.5387714	2.490971
Absolute PFASs water (µg)	0.265132	0.19160201	0.1523919	0.152873
Absolute PFASs Foam (µg)	2.010349	1.91510814	2.3677651	2.185562
PFAS in water %	10%	7%	6%	61%
PFAS in foam	77%	68%	93%	88%

A.7.4 Dilution factor – LAB

Montaline C40

Flask	***Weight of flask (g)***	***Weight of liquid (g)***	***Weight when diluted (g)***	***Liquid captured (g)***	***Amount to ALS***	***Dilution factor***
Blank F	21.95	82.08	278.54	60.13	256.59	0.234342726
Blank W	22.07	200.29	283.87	178.22	261.8	0.680748663
1aF	21.97	81.81	278.86	59.84	256.89	0.232940169
1aW	23.96	204.85	282.15	180.89	258.19	0.700608079
1bF	22.01	92.88	276.62	70.87	254.61	0.278347276
1bW	22.77	194.8	278.24	172.03	255.47	0.673386308
1cF	21.73	87.42	274.96	65.69	253.23	0.259408443
1cW	21.02	197.37	281.01	176.35	259.99	0.678295319

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Flask	***Weight of flask (g)***	***Weight of liquid (g)***	***Weight when diluted (g)***	***Liquid captured (g)***	***Amount to ALS***	***Dilution factor***
Blank F	22.01	85.58	281.43	63.57	259.42	0.245046643
Blank W	21.79	194.1	280.57	172.31	258.78	0.665855167
2aF	21.84	95.61	281.87	73.77	260.03	0.283698035
2aW	22.08	193.2	280.97	171.12	258.89	0.660975704

2bF	22.09	85.47	272	63.38	249.91	0.2536113
2bW	21.79	190.61	282.65	168.82	260.86	0.647167063
2cF	22.01	82.43	283.17	60.42	261.16	0.231352428
2cW	21.83	192.49	277.49	170.66	255.66	0.667527185

Simulsol SL 10

Experiment	1x minimum	1x minimum	2x minimum	2x minimum	5x minimum	5x minimum	Zero surfactant	Zero surfactant
ELEMENT	W	F	W	F	W	F	F	W
PFBA (µg/L)	0.001	<0.010	0.001	<0.010	0.0097	<0.010	<0.010	0.001
PFPeA (µg/L)	0.0018	<0.010	0.00202	<0.010	0.00297	<0.010	<0.010	0.00207
PFHxA (µg/L)	0.00805	0.014	0.00764	0.017	0.00742	0.02	0.013	0.0103
PFHpA (µg/L)	0.0004	<0.010	0.00031	<0.010	<0.00030	<0.010	<0.010	0.00068
PFOA (µg/L)	0.00042	0.0117	0.00047	0.0102	0.0004	<0.0100	0.014	0.00047
PFNA (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
PFDA (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
PFBS (µg/L)	0.0153	0.01	0.0139	0.011	0.0122	0.014	<0.010	0.0165
PFHxS (µg/L)	0.00517	0.119	0.00448	0.116	0.00427	0.113	0.141	0.008
PFOS (µg/L)	0.00067	0.0306	0.00068	0.0175	0.00062	0.0127	0.0387	0.00074
6:2 FTS (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
SUM	0.0895	0.17	0.0733	0.143	0.0536	0.147	0.189	0.051

LAS

Experiment	1x minimum	1x minimum	2x minimum	2x minimum	5x minimum	5x minimum	Zero surfactant	Zero surfactant
ELEMENT	W	F	W	F	W	F	F	W
PFBA (µg/L)	0.0094	<0.010	0.0099	<0.010	0.0077	<0.010	<0.010	0.01

PFPeA (µg/L)	0.00763	<0.010	0.00742	<0.010	0.00266	<0.010	<0.010	0.0061
PFHxA (µg/L)	0.0124	0.012	0.013	0.011	0.0113	0.013	0.013	0.0107
PFHpA (µg/L)	<0.00120	<0.010	<0.00120	<0.010	0.00082	<0.010	<0.010	0.00062
PFOA (µg/L)	0.00132	0.0114	0.00146	0.0101	0.0011	0.0105	0.0116	0.00039
PFNA (µg/L)	<0.00120	<0.010	<0.00120	<0.010	<0.00030	<0.010	<0.010	<0.00030
PFDA (µg/L)	<0.00120	<0.010	<0.00120	<0.010	<0.00030	<0.010	<0.010	<0.00030
PFBS (µg/L)	0.0167	<0.010	0.0173	<0.010	0.0134	<0.010	<0.010	0.0155
PFHxS (µg/L)	0.0204	0.119	0.0242	0.108	0.0155	0.104	0.132	0.00697
PFOS (µg/L)	0.00128	0.0272	<0.00120	0.0143	0.0011	0.0193	0.032	0.00074
6:2 FTS (µg/L)	0.0204	<0.010	<0.00120	<0.010	<0.00030	<0.010	<0.010	<0.00030
SUM	0.0895	0.17	0.0733	0.143	0.0536	0.147	0.189	0.051

YES

Experiment	1x minimum	1x minimum	2x minimum	2x minimum	5x minimum	5x minimum	Zero surfactant	Zero surfactant
ELEMENT	W	F	W	F	W	F	F	W
PFBA (µg/L)	<0.0020	<0.010	<0.0020	<0.010	<0.0020	<0.010	<0.010	<0.0020
PFPeA (µg/L)	0.00168	<0.010	0.0019	<0.010	0.00192	<0.010	<0.010	0.00185
PFHxA (µg/L)	0.0102	0.012	0.0104	0.012	0.0101	0.015	0.01	0.0111
PFHpA (µg/L)	0.00077	<0.010	0.00092	<0.010	0.00068	<0.010	<0.010	0.00087
PFOA (µg/L)	0.00046	0.0108	0.00053	<0.0100	0.00057	0.011	0.0118	0.00054
PFNA (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
PFDA (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
PFBS (µg/L)	0.0174	<0.010	0.0163	<0.010	0.0166	0.01	<0.010	0.0176
PFHxS (µg/L)	0.00943	0.112	0.0117	0.098	0.00792	0.131	0.142	0.0112
PFOS (µg/L)	0.00094	0.0248	0.00033	<0.0100	0.00077	0.0175	0.0347	0.00057

6:2 FTS (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
SUM	0.0409	0.16	0.0421	0.11	0.0386	0.184	0.198	0.0437

A.8 – Raw data

A.8.1 Pilot

Run 23

	Tank	Column	5 min	10 min	20 min	Foam
PFBA (µg/L)	0.02	0.018	0.0119	0.0118	0.0123	0.021
PFPeA (µg/L)	0.012	0.011	0.00647	0.00669	0.00664	0.022
PFHxA (µg/L)	0.028	0.028	0.00408	0.0027	0.00295	0.201
PFOA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	0.064
PFOA (µg/L)	0.0154	0.016	<0.00030	<0.00030	<0.00030	0.146
PFNA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFDA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFBS (µg/L)	0.025	0.027	0.0134	0.0112	0.011	0.159
PFHxS (µg/L)	0.166	0.17	<0.00030	<0.00030	<0.00030	1.67
PFOS (µg/L)	0.0645	0.0625	<0.00030	<0.00030	<0.00030	0.65
6:2 FTS (µg/L)	<0.010	<0.010	0.00048	0.00091	0.00078	<0.010

Run 21

	Tank	Column	5 min	10 min	20 min	Foam
PFBA (µg/L)	<0.010	<0.010	0.0149	0.0145	0.0148	<0.010
PFPeA (µg/L)	<0.010	<0.010	0.00705	0.0068	0.00724	0.022
PFHxA (µg/L)	0.029	0.029	0.00498	0.00311	0.003	0.245
PFOA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	0.078
PFOA (µg/L)	0.0152	0.0168	<0.00030	<0.00030	<0.00030	0.196
PFNA	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010

(µg/L)						
PFDA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFBS (µg/L)	0.032	0.028	0.0129	0.0112	0.0113	0.14
PFHxS (µg/L)	0.196	0.196	0.00034	<0.00030	<0.00030	2.24
PFOS (µg/L)	0.0616	0.0612	0.00052	<0.00030	<0.00030	0.514
6:2 FTS (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010

Run 22

	Tank	**Column**	**5 min**	**10 min**	**20 min**	**Foam**
PFBA (µg/L)	<0.010	<0.010	0.0146	0.0162	0.0152	<0.010
PFPeA (µg/L)	<0.010	0.01	0.00654	0.00792	0.00754	0.02
PFHxA (µg/L)	0.029	0.03	0.00497	0.00348	0.00239	0.19
PFOA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	0.054
PFOA (µg/L)	0.016	0.016	<0.00030	<0.00030	<0.00030	0.149
PFNA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFDA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFBS (µg/L)	0.03	0.026	0.0104	0.00985	0.00849	0.127
PFHxS (µg/L)	0.197	0.203	<0.00030	<0.00030	<0.00030	1.81
PFOS (µg/L)	0.0562	0.0561	0.00032	0.0009	<0.00030	0.416
6:2 FTS (µg/L)	<0.010	<0.010	<0.00030	0.00044	<0.00030	<0.010

1x minimum dose:

Run 33

	Tank	**Column**	**5 min**	**10 min**	**20 min**	**Foam**
PFBA (µg/L)	<0.010	<0.010	0.0146	0.0162	0.0152	<0.010
PFPeA (µg/L)	<0.010	0.01	0.00654	0.00792	0.00754	0.02
PFHxA (µg/L)	0.029	0.03	0.00497	0.00348	0.00239	0.19
PFOA	<0.010	<0.010	<0.00030	<0.00030	<0.00030	0.054

(µg/L)						
PFOA (µg/L)	0.016	0.016	<0.00030	<0.00030	<0.00030	0.149
PFNA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFDA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFBS (µg/L)	0.03	0.026	0.0104	0.00985	0.00849	0.127
PFHxS (µg/L)	0.197	0.203	<0.00030	<0.00030	<0.00030	1.81
PFOS (µg/L)	0.0562	0.0561	0.00032	0.0009	<0.00030	0.416
6:2 FTS (µg/L)	<0.010	<0.010	<0.00030	0.00044	<0.00030	<0.010

Run 32

	Tank	**Column**	**5 min**	**10 min**	**20 min**	**Foam**
PFBA (µg/L)	0.012	<0.010	0.0146	0.0163	0.0166	<0.010
PFPeA (µg/L)	0.013	0.012	0.00701	0.00706	0.00642	0.032
PFHxA (µg/L)	0.033	0.034	0.00124	0.00085	0.00076	0.229
PFOA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	0.055
PFOA (µg/L)	0.0203	0.0201	<0.00030	<0.00030	<0.00030	0.135
PFNA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFDA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFBS (µg/L)	0.031	0.033	0.00532	0.00322	0.00324	0.201
PFHxS (µg/L)	0.215	0.218	<0.00030	<0.00030	<0.00030	1.47
PFOS (µg/L)	0.0715	0.0672	0.00038	<0.00030	<0.00030	0.416
6:2 FTS (µg/L)	0.012	<0.010	0.0146	0.0163	0.0166	<0.010

Run 31

	Tank	**Column**	**5 min**	**10 min**	**20 min**	**Foam**
PFBA (µg/L)	0.013	0.012	0.0155	0.0144	0.0155	<0.010
PFPeA (µg/L)	0.014	0.012	0.00692	0.00697	0.00689	0.033
PFHxA (µg/L)	0.036	0.035	0.00126	0.00075	0.0007	0.22

PFOA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	0.057
PFOA (µg/L)	0.0207	0.0321	<0.00030	<0.00030	<0.00030	0.129
PFNA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFDA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFBS (µg/L)	0.036	0.034	0.00472	0.00424	0.00362	0.217
PFHxS (µg/L)	0.223	0.218	<0.00030	<0.00030	<0.00030	1.34
PFOS (µg/L)	0.0762	0.128	0.00048	<0.00030	<0.00030	0.386
6:2 FTS (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010

2x minimum dose :

Run 42

µg/L	**Tank**	**Column**	**5 min**	**10 min**	**20 min**	**Foam**
	0.019	0.017	0.0107	0.0108	0.0116	0.022
PFBA (µg/L)	0.01	0.012	0.0047	0.0044	0.00427	0.043
PFPeA (µg/L)	0.027	0.026	0.00038	0.00034	0.00036	0.173
PFHxA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	0.046
PFOA (µg/L)	0.0146	0.0149	<0.00030	<0.00030	<0.00030	0.13
PFOA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFNA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFDA (µg/L)	0.025	0.025	0.00169	0.00179	0.00174	0.212
PFBS (µg/L)	0.151	0.147	<0.00030	<0.00030	<0.00030	1.75
PFHxS (µg/L)	0.0719	0.0645	0.00056	<0.00030	<0.00030	0.586
PFOS (µg/L)	<0.010	<0.010	0.00069	0.00101	0.00045	<0.010

Run 43

	Tank	**Column**	**5 min**	**10 min**	**20 min**	**Foam**
PFBA (µg/L)	<0.010	<0.010	0.0142	0.0145	0.0145	<0.010
PFPeA (µg/L)	<0.010	0.049	0.00475	0.00489	0.00441	0.01

PFHxA (µg/L)	0.03	0.275	0.00046	0.00036	0.00033	0.03
PFOA (µg/L)	<0.010	0.064	<0.00030	<0.00030	<0.00030	<0.010
PFOA (µg/L)	0.0163	0.148	<0.00030	<0.00030	<0.00030	0.0176
PFNA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFDA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFBS (µg/L)	0.026	0.252	0.0019	0.00182	0.00167	0.029
PFHxS (µg/L)	0.187	1.64	<0.00030	<0.00030	<0.00030	0.175
PFOS (µg/L)	0.0552	0.474	0.00044	<0.00030	<0.00030	0.0523
6:2 FTS (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010

Run 41

	Tank	**Column**	**5 min**	**10 min**	**20 min**	**Foam**
PFBA (µg/L)	<0.010	<0.010	0.0148	0.0144	0.0143	<0.010
PFPeA (µg/L)	0.01	0.011	0.00498	0.0048	0.00479	0.036
PFHxA (µg/L)	0.03	0.03	0.0004	0.0004	0.00035	0.186
PFOA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	0.042
PFOA (µg/L)	0.0166	0.0186	<0.00030	<0.00030	<0.00030	0.114
PFNA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFDA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFBS (µg/L)	0.027	0.028	0.00174	0.00172	0.00157	0.147
PFHxS (µg/L)	0.192	0.17	<0.00030	<0.00030	<0.00030	1.2
PFOS (µg/L)	0.0597	0.0537	0.00069	<0.00030	<0.00030	0.358
6:2 FTS (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010

3x minimum dose:

Run 51

	Tank	**Column**	**5 min**	**10 min**	**20 min**	**Foam**

PFBA (µg/L)	0.017	0.013	0.0133	0.0143	0.0143	<0.010
PFPeA (µg/L)	0.011	0.017	0.00498	0.0041	0.00411	0.064
PFHxA (µg/L)	0.03	0.03	0.00033	0.00034	0.00038	0.277
PFOA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	0.062
PFOA (µg/L)	0.0174	0.0262	<0.00030	<0.00030	<0.00030	0.131
PFNA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFDA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFBS (µg/L)	0.025	0.024	0.00158	0.00119	0.0012	0.268
PFHxS (µg/L)	0.186	0.201	<0.00030	<0.00030	<0.00030	1.46
PFOS (µg/L)	0.0741	0.0542	0.00087	0.00048	<0.00030	0.441
6:2 FTS (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010

Run 53

	Tank	**Column**	**5 min**	**10 min**	**20 min**	**Foam**
PFBA (µg/L)	0.017	0.0138	0.0144	0.0153	<0.010	<0.010
PFPeA (µg/L)	0.011	0.00492	0.00436	0.00466	<0.010	0.086
PFHxA (µg/L)	0.03	<0.00030	0.0003	0.00037	0.031	0.355
PFOA (µg/L)	<0.010	<0.00030	<0.00030	<0.00030	<0.010	0.081
PFOA (µg/L)	0.0144	<0.00030	<0.00030	<0.00030	0.0135	0.17
PFNA (µg/L)	<0.010	<0.00030	<0.00030	<0.00030	<0.010	<0.010
PFDA (µg/L)	<0.010	<0.00030	<0.00030	<0.00030	<0.010	<0.010
PFBS (µg/L)	0.025	0.00099	0.00083	0.00092	0.03	0.354
PFHxS (µg/L)	0.173	<0.00030	<0.00030	<0.00030	0.185	2.08
PFOS (µg/L)	0.0606	0.0009	0.00036	<0.00030	0.0488	0.326
6:2 FTS (µg/L)	<0.010	<0.00030	<0.00030	<0.00030	<0.010	<0.010

Run 52

	Tank	Column	5 min	10 min	20 min	Foam
PFBA (µg/L)	<0.020	<0.020	0.0146	0.0148	0.0142	<0.020
PFPeA (µg/L)	<0.010	<0.010	0.00482	0.00466	0.00336	0.049
PFHxA (µg/L)	0.028	0.024	0.00035	0.00038	0.00042	0.208
PFOA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	0.053
PFOA (µg/L)	0.0183	0.0163	<0.00030	<0.00030	<0.00030	0.176
PFNA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFDA (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010
PFBS (µg/L)	0.024	0.022	0.00109	0.00098	0.00101	0.215
PFHxS (µg/L)	0.152	0.157	<0.00030	<0.00030	<0.00030	1.8
PFOS (µg/L)	0.0513	0.0439	0.00055	0.00032	<0.00030	0.716
6:2 FTS (µg/L)	<0.010	<0.010	<0.00030	<0.00030	<0.00030	<0.010

A.8.2 LAB

Montaline C 40

Experiment	1x minimum	1x minimum	2x minimum	2x minimum	5x minimum	5x minimum	Zero surfactant	Zero surfactant
ELEMENT	W	F	W	F	W	F	F	W
PFBA (µg/L)	0.0041	<0.010	0.0045	0.005	<0.0080	0.0086	<0.010	0.0035
PFPeA (µg/L)	0.00736	<0.010	0.00539	0.005	0.00364	0.00152	<0.010	0.00743
PFHxA (µg/L)	0.00568	0.018	0.00218	0.022	0.0199	0.00169	0.012	0.0138
PFHpA (µg/L)	0.00015	<0.010	0.00015	0.005	0.00362	<0.00030	<0.010	0.00065
PFOA (µg/L)	0.00032	<0.010	0.0004	0.005	0.00753	0.00043	0.0138	0.00015
PFNA (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00120	<0.00030	<0.010	<0.00030
PFDA (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00120	<0.00030	<0.010	<0.00030

PFBS (µg/L)	0.0102	0.012	0.00495	0.017	0.022	0.003	<0.010	0.0186
PFHxS (µg/L)	0.00316	0.08	0.00179	0.1	0.0834	0.00272	0.125	0.00591
PFOS (µg/L)	0.00118	<0.010	0.00119	0.015	0.00648	0.00098	0.0439	0.00061
6:2 FTS (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00120	<0.00030	<0.010	<0.00030

Marlinat 242/28

Experiment	1x minimum	1x minimum	2x minimum	2x minimum	5x minimum	5x minimum	Zero surfactant	Zero surfactant
ELEMENT	W	F	W	F	W	F	F	W
PFBA (µg/L)	0.0105	<0.010	0.0097	<0.010	0.0092	<0.010	<0.010	0.0104
PFPeA (µg/L)	0.00749	<0.010	0.00736	<0.010	0.00279	<0.010	<0.010	0.00802
PFHxA (µg/L)	0.0109	0.013	0.0112	0.014	0.0104	0.016	0.013	0.0121
PFHpA (µg/L)	0.0006	<0.010	0.00081	<0.010	0.00058	<0.010	<0.010	0.0006
PFOA (µg/L)	0.00054	0.0131	0.0008	0.0108	0.00044	0.0109	0.0106	0.00046
PFNA (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
PFDA (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
PFBS (µg/L)	0.0155	<0.010	0.0169	<0.010	0.0133	0.011	0.01	0.018
PFHxS (µg/L)	0.00774	0.136	0.0126	0.127	0.00608	0.109	0.138	0.00609
PFOS (µg/L)	0.00083	0.0559	0.00115	0.0271	0.00072	0.0167	0.0331	0.00069
6:2 FTS (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
SUM	0.0541	0.218	0.0605	0.179	0.0435	0.164	0.205	0.0564

Simulsol SL 10

Experiment	1x minimum	1x minimum	2x minimum	2x minimum	5x minimum	5x minimum	Zero surfactant	Zero surfactant
ELEMENT	W	F	W	F	W	F	F	W
PFBA (µg/L)	0.001	<0.010	0.001	<0.010	0.0097	<0.010	<0.010	0.001

PFPeA (µg/L)	0.0018	<0.010	0.00202	<0.010	0.00297	<0.010	<0.010	0.00207
PFHxA (µg/L)	0.00805	0.014	0.00764	0.017	0.00742	0.02	0.013	0.0103
PFHpA (µg/L)	0.0004	<0.010	0.00031	<0.010	<0.00030	<0.010	<0.010	0.00068
PFOA (µg/L)	0.00042	0.0117	0.00047	0.0102	0.0004	<0.0100	0.014	0.00047
PFNA (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
PFDA (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
PFBS (µg/L)	0.0153	0.01	0.0139	0.011	0.0122	0.014	<0.010	0.0165
PFHxS (µg/L)	0.00517	0.119	0.00448	0.116	0.00427	0.113	0.141	0.008
PFOS (µg/L)	0.00067	0.0306	0.00068	0.0175	0.00062	0.0127	0.0387	0.00074
6:2 FTS (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
SUM	0.0895	0.17	0.0733	0.143	0.0536	0.147	0.189	0.051

LAS

Experiment	1x minimum	1x minimum	2x minimum	2x minimum	5x minimum	5x minimum	Zero surfactant	Zero surfactant
ELEMENT	W	F	W	F	W	F	F	W
PFBA (µg/L)	0.0094	<0.010	0.0099	<0.010	0.0077	<0.010	<0.010	0.01
PFPeA (µg/L)	0.00763	<0.010	0.00742	<0.010	0.00266	<0.010	<0.010	0.0061
PFHxA (µg/L)	0.0124	0.012	0.013	0.011	0.0113	0.013	0.013	0.0107
PFHpA (µg/L)	<0.00120	<0.010	<0.00120	<0.010	0.00082	<0.010	<0.010	0.00062
PFOA (µg/L)	0.00132	0.0114	0.00146	0.0101	0.0011	0.0105	0.0116	0.00039
PFNA (µg/L)	<0.00120	<0.010	<0.00120	<0.010	<0.00030	<0.010	<0.010	<0.00030
PFDA (µg/L)	<0.00120	<0.010	<0.00120	<0.010	<0.00030	<0.010	<0.010	<0.00030
PFBS (µg/L)	0.0167	<0.010	0.0173	<0.010	0.0134	<0.010	<0.010	0.0155
PFHxS (µg/L)	0.0204	0.119	0.0242	0.108	0.0155	0.104	0.132	0.00697

PFOS (µg/L)	0.00128	0.0272	<0.00120	0.0143	0.0011	0.0193	0.032	0.00074
6:2 FTS (µg/L)	0.0204	<0.010	<0.00120	<0.010	<0.00030	<0.010	<0.010	<0.00030
SUM	0.0895	0.17	0.0733	0.143	0.0536	0.147	0.189	0.051

YES

Experiment	1x minimum	1x minimum	2x minimum	2x minimum	5x minimum	5x minimum	Zero surfactant	Zero surfactant
ELEMENT	W	F	W	F	W	F	F	W
PFBA (µg/L)	<0.0020	<0.010	<0.0020	<0.010	<0.0020	<0.010	<0.010	<0.0020
PFPeA (µg/L)	0.00168	<0.010	0.0019	<0.010	0.00192	<0.010	<0.010	0.00185
PFHxA (µg/L)	0.0102	0.012	0.0104	0.012	0.0101	0.015	0.01	0.0111
PFHpA (µg/L)	0.00077	<0.010	0.00092	<0.010	0.00068	<0.010	<0.010	0.00087
PFOA (µg/L)	0.00046	0.0108	0.00053	<0.0100	0.00057	0.011	0.0118	0.00054
PFNA (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
PFDA (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
PFBS (µg/L)	0.0174	<0.010	0.0163	<0.010	0.0166	0.01	<0.010	0.0176
PFHxS (µg/L)	0.00943	0.112	0.0117	0.098	0.00792	0.131	0.142	0.0112
PFOS (µg/L)	0.00094	0.0248	0.00033	<0.0100	0.00077	0.0175	0.0347	0.00057
6:2 FTS (µg/L)	<0.00030	<0.010	<0.00030	<0.010	<0.00030	<0.010	<0.010	<0.00030
SUM	0.0409	0.16	0.0421	0.11	0.0386	0.184	0.198	0.0437

Tank water – Lab

PFBA (µg/L)	0.01	0.019	0.017
PFPeA (µg/L)	0.012	0.013	0.014
PFHxA (µg/L)	0.031	0.028	0.031
PFHpA (µg/L)	0.005	0.005	0.005
PFOA (µg/L)	0.0126	0.0137	0.0136
PFNA (µg/L)	0.005	0.005	0.005
PFDA (µg/L)	0.005	0.005	0.005
PFBS (µg/L)	0.028	0.026	0.027
PFHxS (µg/L)	0.155	0.172	0.158
PFOS (µg/L)	0.0278	0.0547	0.0502

6:2 FTSA (µg/L)	0.005	0.005	0.005
Sum (µg/L)	0.2964	0.3414	0.3308
Sampling Date		2022-04-11	2022-04-07

A.9 Aerosol experiment

The hose was placed in the 5W water trap between 0-5 min. The hose was placed in the 10W water trap between 5-10 min and the hose was then placed in the 20W water trap between 10-20 min.

Aerosol 1

		5W	10W	20W
perfluorbutansyra (PFBA)	µg/L	<0.0020	<0.0020	<0.0020
perfluoropentansyra (PFPeA)	µg/L	<0.00030	<0.00030	<0.00030
perfluorhexansyra (PFHxA)	µg/L	<0.00030	<0.00030	<0.00030
perfluoroheptansyra (PFHpA)	µg/L	<0.00030	<0.00030	<0.00030
perfluoroktansyra (PFOA)	µg/L	<0.00030	<0.00030	<0.00030
perfluorononansyra (PFNA)	µg/L	<0.00030	<0.00030	<0.00030
perfluorodekansyra (PFDA)	µg/L	<0.00030	<0.00030	<0.00030
perfluorbutansulfonsyra (PFBS)	µg/L	<0.00030	<0.00030	<0.00030
perfluorhexansulfonsyra (PFHxS)	µg/L	<0.00030	<0.00030	<0.00030
perfluoroktansulfonsyra (PFOS)	µg/L	0,00074	0,00038	0,00037
6:2 FTS fluortelomersulfonat	µg/L	<0.00030	<0.00030	<0.00030

Aerosol 2

		5W	10W	20W
perfluorbutansyra (PFBA)	µg/L	<0.0020	<0.0020	<0.0020
perfluoropentansyra (PFPeA)	µg/L	<0.00030	<0.00030	<0.00030
perfluorhexansyra (PFHxA)	µg/L	<0.00030	<0.00030	<0.00030
perfluoroheptansyra (PFHpA)	µg/L	<0.00030	<0.00030	<0.00030
perfluoroktansyra (PFOA)	µg/L	<0.00030	<0.00030	<0.00030
perfluorononansyra (PFNA)	µg/L	<0.00030	<0.00030	<0.00030
perfluorodekansyra (PFDA)	µg/L	<0.00030	<0.00030	<0.00030
perfluorbutansulfonsyra (PFBS)	µg/L	<0.00030	<0.00030	<0.00030
perfluorhexansulfonsyra (PFHxS)	µg/L	<0.00030	<0.00030	<0.00030
perfluoroktansulfonsyra (PFOS)	µg/L	0,00072	0,00039	0,00037
6:2 FTS fluortelomersulfonat	µg/L	<0.00030	<0.00030	<0.00030