

# Teknologiudviklingsprojekt

Undersøgelser af muligheden for rensning af PFAS i vand ved hjælp af fraktionering baseret på ozon mikrobobler

Den Syddanske Udviklingspulje

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Dato: 26. september 2023

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**Projektet er finansieret med puljemidler fra Den Syddanske Udviklingspulje for rent vand og jord**

### **Ansvarsfraskrivelse:**

Region Syddanmark vil, når lejligheden gives, offentliggøre rapporten som er finansieret med puljemidler fra "Den Syddanske Udviklingspulje for rent vand og jord".

Det skal bemærkes, at offentliggørelse af rapporten ikke nødvendigvis betyder, at Region Syddanmark er enig i rapportens indhold og konklusioner, men er udelukkende med henblik på at dele viden om teknologiudviklingen på jordforureningsområdet.

## 1 Indledning

NIRAS har i samarbejde med DTU Sustain og Arcadis US udført et teknologiudviklingsprojekt, hvor brugen af skumfraktionering i forbindelse med rensning af grundvand for udvalgte PFAS forbindelser er undersøgt. Arbejdet er udført i perioden Januar-Juni 2023 og er primært udført af Mónika Büki som led i hendes M.Sc. afgangprojekt på DTU Sustain i foråret 2023. NIRAS har stået for den praktiske koordinering med Region Syd ved Steffen Gram Lauridsen – herunder fremskaffelse af PFAS forurenede grundvand til brug ved forsøgene.

I det følgende afsnit er der givet et kort resumé på dansk af det gennemførte projekt. For yderligere detaljer henvises til det udførte eksamensprojekt, Bilag 1.

## 2 Baggrund og formål

Poly- og perfluorerede stoffer (PFAS) er tusindvis af persistente og giftige stoffer, som har været meget anvendt i mange forskellige produkter på grund af deres egenskaber. En af de vigtigste anvendelser har været anvendelsen af filmdannende brandslukningsskum (AFFF), som blev anvendt på militær- og brandøvelsessteder samt oliebrande. Anvendelsen af AFFF resulterede i kraftigt forurenede jord og grundvand, og der er mere end 200 registrerede PFAS-forurenede grunde i Danmark.

Baggrunden for projektet er, at man i nogle år har anvendt aktiv kul til at rense for PFAS i vand, og der er efterhånden opsamlet en del viden om fordele og ulemper ved metoden. I løbet af de seneste 2-3 år er fokus kommet på at anvende resiner (fx syntetiske anion ionbyttere) til at fjerne PFAS i vand. Efterhånden er der også opnået nogle driftserfaringer med denne metode.

En af problemstillingerne for begge metoder er, at vandet typisk kræver en forbehandling for at fjerne eventuelle andre molekyler / partikler, før det ledes til de aktive kulfiltre / resinanlæg, idet fx forekomsten af jern, suspenderet stof, andre forureningsstoffer etc. vil kunne reducere effekten af kul / resiner væsentligt og dermed levetiden af dem.

Skumfraktionering (SAFF) er en forholdsvis ny rensningsmetode til fjernelse af PFAS i vand. SAFF separerer de overfladeaktive PFAS ved at adsorbere dem fra vandet til grænsefladen mellem luft og vand i de stigende bobler, hvilket producerer skum, som indeholder PFAS. Dermed opnås der et mindre volumen af PFAS beriget skum der skal efterbehandles. Fjernelse af kortkædede PFAS forbindelser (færre end seks kulstofatomer i C-F kæden) er dog fortsat udfordrende, hvorfor der er behov for yderligere undersøgelser for at afklare potentialet og optimering for skumfraktionering til fjernelse af de kortkædede PFAS.

Formålet med projektet var at undersøge og optimere skumfraktionering på PFAS forurenede grundvand ved at anvende forskellige typer af overfladeaktive stoffer (anioniske (SDS), zwitterioniske (CAPB) og kationiske (DTAC)) og blandinger heraf, herunder at evaluere fjernelsen af PFAS fra grundvandet og reduktionen af det volumen der efterfølgende skal behandles (den PFAS berigede skum). Derudover blev det også undersøgt, hvorvidt PFAS fjernelsen kunne øges ved en øgning af ionstyrken i grundvandet via tilsætning af inorganiske salte eller præozonering af grundvandet til forbedring af skumdannelsen.

### 3 Resumé

Indledningsvist blev der designet og optimeret en forsøgsoptstilling til behandling af 600 mL grundvand med prøvetagning af både det behandlede grundvand og det PFAS berigede skum, hvorved fjernelseseffektivitet fra grundvandet og berigelsesfaktor af skummet kunne bestemmes.

I forhold til andre vandtyper (f.eks. spildevand og overfladevand) kan koncentrationen af PFAS i forurenede grundvand (typisk ng/l til µg/l) være for lav til at resultere i den for teknologien nødvendige skumdannelse. Indholdet af andet opløst organisk materiale i vandet, der kan forårsage skumdannelse, er ligeledes lavt og/eller hurtigt nedbrydeligt. Grundvandet i dette projekt er hentet i felten, men bragt hjem til forsøgsoptstillingen i laboratoriet. Her blev det observeret, at skumdannelsen var ikke eksisterende efter 3-4 dages oplagring. Dette var gældende for begge de lokaliteter, hvor grundvand blev hentet fra. Det har derfor i projektet været nødvendigt at anvende overfladeaktive stoffer til at fremme skumdannelsen. Både kationiske og zwitterioniske overfladeaktive stoffer er i andre sammenhænge set at kunne øge fjernelsen af de kortkædede PFAS. De kationiske overfladeaktive stoffer er dyrere og mere toksiske, hvorved minimal tilsætning er ønskværdig. DTAC blev udvalgt som et potentielt bionedbrydeligt og relativt mindre toksisk alternativ blandt de kationiske overfladeaktive stoffer.

Resultaterne viste, at anvendelsen af overfladeaktive stoffer kunne øge fjernelsen af PFAS betydeligt. Den højeste fjernelse blev opnået med en blanding af kationiske og zwitterioniske overfladeaktive stoffer, som effektivt fjernede alle PFAS, herunder kortkædede forbindelser. To blandingsforhold blev testet (forhold 1:1 og 1:9), hvor forsøgene viste, at der efter 10 minutter var mindre end 3% forskel i fjernelsen af PFAS fra vandet. Opkoncentreringen af PFAS blev imidlertid mere end tredoblet ved at reducere fraktionen af de kationiske overfladestoffer, da de zwitterioniske overfladestoffer producerede et meget tørt og stabilt skum, og at det volumen af skum, som indeholdt PFAS, dermed blev væsentligt reduceret.

Den beskedne forskel i fjernelsen for de to forskellige blandingsforhold indikerer, at der er potentiale for at reducere den kationiske fraktion yderligere. Dette er ønskværdigt, da de kationiske overfladeaktive stoffer som nævnt er toksiske, samt desuden er betydeligt dyrere end de an- og zwitterioniske overfladeaktive stoffer. Det bør desuden undersøges i hvor høj grad de tilsatte overfladeaktive stoffer fjernes med skummet, da det ikke er ønskværdigt, at have en restfraktion i det behandlede grundvand.

Det blev observeret, at præozonering ikke forbedrede skumdannelse. Desuden var der tegn på, at præozoneringen kunne omdanne PFAS-forstadier (precursorer) til andre målbare PFAS, da der blev observeret mindre fjernelse af nogle af PFAS forbindelserne (PFBS, PFHpA og PFDoDA) end uden præozoneringen.

Forsøgene viste desuden, at en øget ionstyrke (10 mM Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> eller Ca<sup>2+</sup>) ikke øgede fjernelse af PFAS yderligere ved samtidig anvendelse af en SDS- og CAPB-blanding. Dette var sandsynligvis på grund af konkurrencen mellem den anioniske funktionelle gruppe på PFAS forbindelsen og de tilsatte anioner fra saltene. Der blev imidlertid observeret en mindre positiv effekt på fjernelsen af PFHpA (C7) med divalent kationtilsætning, men en reduceret fjernelse af PFBS (C4) ved alle tilsatte kationer.

Endelig afslørede en omkostningsanalyse af de overfladeaktive stoffer, at forholdet 1:9 mellem den zwitterioniske og kationiske blanding er det mest omkostningseffektive i forhold til de priser, der er på laboratorie- og kommercielle kemikaliepriser. Omkostningsanalysen har taget udgangspunkt i en fuldstændig fjernelse af PFAS baseret på en simpel lineær sammenhæng mellem den tilsatte mængde overfladeaktivt stof

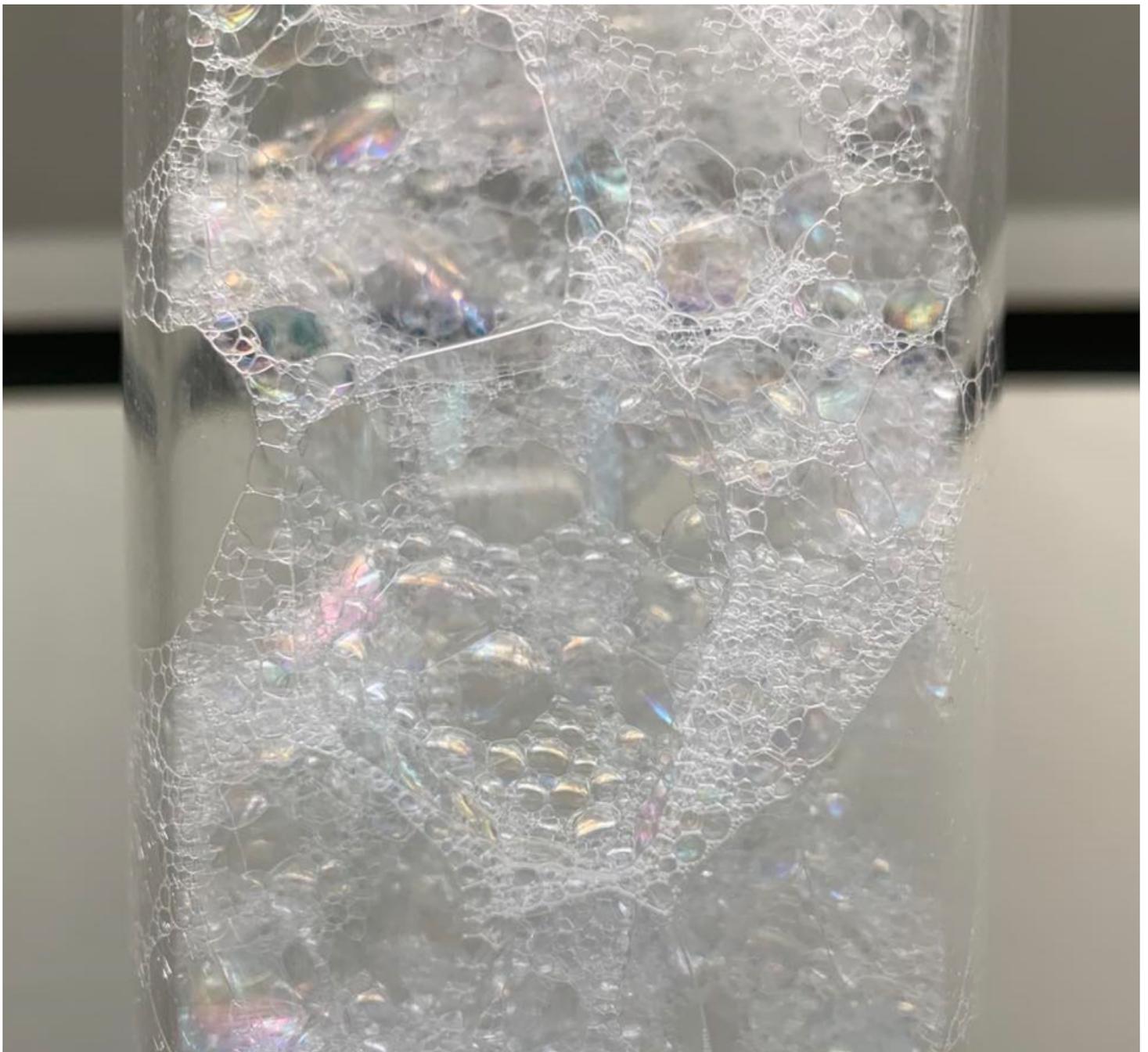
og fjernelsen af PFAS. Dermed skal der anvendes mindre mængder jo mere effektiv den specifikke blanding er. Den pågældende blanding er den næstmest effektive, men indeholder betydeligt mindre DTAC, der er det dyreste af stofferne. Analysen inkluderede ikke, at der ved det pågældende forhold (1:9), også blev produceret det mest PFAS berigede skum, hvorved der opnås det mindste volumen der skal efterbehandles (og dermed lavere omkostninger).

Projektet viste, at det var muligt at fjerne PFAS fra grundvandet ved skumfraktionering, og at der er forskellige muligheder for at øge og optimere skumfjernelsen. Forsøgene viste dog også, at det kræver yderligere forsøg og undersøgelser for at finde de optimale forhold. Anvendelsen af overfladeaktive stoffer var i laboratoriet helt afgørende for fjernelsen af PFAS fra grundvandet, når dette ikke havde den rette kemiske sammensætning til at resultere i skumdannelse. Det er dog muligt, at behandling af friskoppumpet grundvand direkte på lokalitet i højere grad vil kunne udnytte et begrænset potentiale for skumdannelse, hvilket i projektet blev observeret for grundvandet før oplagring i laboratoriet. Ved yderligere afprøvning af metoden til grundvand kan forsøg i felten derfor være en fordel.

# Optimization of foam fractionation-induced PFAS removal from contaminated groundwater: Evaluating the effect of cosurfactant type, ionic strength and ozone addition

Master's Thesis

Mónika Büki





**Optimization of foam fractionation-induced PFAS removal from contaminated groundwater: Evaluating the effect of cosurfactant type, ionic strength and ozone addition**

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By  
Mónika Büki

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## **Preface**

The present master's thesis has been prepared from January until July 2023 at the Section of Water Technology and Processes, Department of Environmental and Resource Engineering, at the Technical University of Denmark. The thesis corresponds to 30 ECTS points and is conducted as partial fulfilment of the degree Master of Science in Environmental Engineering, Specialization in Environmental Chemistry.

The project was supervised by

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Anders G. Christensen (Expertise Director, Niras A/S).

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23.06.2023



## Abstract

Poly- and perfluorinated substances (PFAS) are thousands of persistent and toxic chemicals, which have been widely used in many commercial and household products due to their beneficial properties. One of their main applications is aqueous film-forming foams (AFFF), which were applied against hydrocarbon fires at military and fire training sites. These activities resulted in highly contaminated areas worldwide, and there are more than 200 registered PFAS-contaminated sites in Denmark. PFAS contamination can leach into and be transported with groundwater, which poses a threat to groundwater drinking water resources, which Denmark greatly relies on.

For the remediation of PFAS-contaminated waters activated carbon, ion exchange resins and foam fractionation (FF) are widely employed. Foam fractionation is an emerging sustainable and cheap treatment alternative for PFAS treatment. FF separates the surface active PFAS by adsorbing them from the water to the air-water interface of rising bubbles, producing a PFAS-rich foam which is harvested and needs further treatment. However the removal of short-chain compounds stays challenging and non-foaming waters cannot utilise the advantages of this technology, therefore there is an urge for additional studies investigating the potential of foam improvement and optimization for short-chain PFAS removal.

The aim of this study was to optimize foam fractionation on a non-foaming Danish groundwater by applying different types of surfactants and their mixtures (anionic (SDS), zwitterionic (CAPB) and cationic (DTAC)), evaluating the induced PFAS removal and assessing the effect of preozonation on foamability. Additionally, the PFAS removal of the combined application of increased ionic strength and cosurfactants was also evaluated. The results showed, that the applied surfactant type affects the PFAS removal. The highest removal was achieved with the mixture of cationic and zwitterionic surfactants, which efficiently removed all target PFAS including short-chain compounds. Two ratios of the mixture were tested (1:1 and 1:9) and it was found that there is less than 3% difference in their removal performance after 10 minutes. However, the enrichment increased more than three times by reducing the fraction of the DTAC, as the CAPB produced a very dry foam. As a result, 97.4% contaminated volume reduction was achieved. The results also indicate that there is potential to further decrease the cationic fraction, which reduces cost and toxicity. In addition, it was observed that preozonation did not improve foaming and potentially transformed PFAS precursors to target species, as retained removal was observed for PFBS, PFHpA and PFDoDA. Furthermore, increased ionic strength (10 mM of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> or Ca<sup>2+</sup>) was found not to further elevate the total removal with the application of an SDS and CAPB mixture. Most likely due to the competitive sorption of PFAS with other anions to the air-water interface. However, a slight positive effect on the removal of PFHpA was observed with divalent cation addition and worsened removal of PFBS with all added cations. Additionally, the surfactant cost analysis revealed that the 1:9 ratio of the zwitterionic and cationic mixture is the most cost-effective, considering both laboratory and commercial reagent prices. This reinforces the effectiveness of this mixture compared to the tested alternatives.



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I would also like to thank Steffen Gram Lauridsen (Environmental Engineer, Region Syd-danmark) for sampling the groundwater from Vandel Airport and Mikael Emil Olsson (Analytical Chemist, DTU Sustain) for introducing me to the analytical measurement of PFAS and data treatment. Additionally, I am grateful for the help from Jens Schaarup Sørensen (Technician, DTU Sustain) and Tajs Brøndal Nielsen (Technician, DTU Sustain) who helped me build the experimental setup and for the help received from the Water Technology and Processes research group.

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## Abbreviations

6:2 FTS	6:2 Fluorotelomer sulfonic acid
AFFF	Aqueous film forming foams
BTEX	Benzene, toluene, ethylbenzene, and xylene
$C_0$	Initial PFAS concentration
CAPB	Cocamidopropyl betaine
Cfoam	Foam PFAS concentration
CMC	Critical Micelle concentration
CTAB	Cetyltrimethylammonium bromide
DEPA	Danish Environmental Protection Agency
DOC	Dissolved Organic Carbon
DTAB	Dodecyl Trimethyl Ammonium Bromide
DTAC	Dodecyl Trimethyl Ammonium Chloride
E	Enrichment factor
FFF	Fire fighting foams
GAC	Granulated Activated Carbon
GW	Groundwater
HDPE	High density polyethylene
HPLC-MS/MS	High pressure liquid chromatography with tandem mass spectroscopy
HPMC	Hydroxypropyl methylcellulose
IER	Ion exchange resin
IS	Ionic strength
LAS	Linear Alkylbenzene Sulfonate
logK <sub>oc</sub>	Logarithmic organic carbon to water partition coefficient
MB	Mass balance
MRM	Multiple Reactions Monitoring
NOM	Natural Organic Matter
NVOC	Non-Volatile Organic Carbon
OECD	Organisation for Economic Co-operation and Development
OTAB	Octadecyltrimethylammonium bromide
PFAA	Perfluoroalkyl acids
PFAS	Per- and polyfluorinated substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonate
PFCA	Perfluoroalkyl carboxylic acids
PFDA	Perfluorodecanoic acid
PFDS	Perfluorodecane sulfonic acid
PFD <sub>o</sub> DA	Perfluorododecanoic acid
PFD <sub>o</sub> S	Perfluorododecane sulfonate
PFHpA	Perfluoroheptanoic acid
PFHpS	Perfluoroheptanesulfonic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexanesulfonic acid
PFNA	Perfluorononanoic acid
PFNS	Perfluorononanesulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFOSA	Perfluorooctanesulfonamide
PFPeA	Perfluoropentanoic acid
PFPA	Perfluoropropionic acid
PFPS	Perfluoropropanesulfonic acid

## Abbreviations

PFSA	Perfluorinated Sulfonic acids
PFTTrS	Perfluorotridecanesulfonic acid
PFTTrDA	Perfluorotridecanoic acid
PFUnS	Perfluoroundecane sulfonate
PFUnDA	Perfluoroundecanoic acid
R %	Removal %
RAS	Recirculated Aquaculture System
SB3-12	N-Dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate
SD	Standard deviation
SDS	Sodium Dodecyl Sulfate
SPE	Solid phase extraction
TBAB	Tetrabutylammonium bromide
$t_r$	Residence time
WWTP	Wastewater treatment plant

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# 1 Introduction

The term poly- and perfluorinated substances (PFAS) describes thousands of synthetic molecules with varying chemical structures (Z. Wang et al., 2021). These compounds' shared characteristic is the C-F bond, which is the strongest bond in organic chemistry (O'hagan, 2008). As a result, they have industrially favourable properties including non-reactivity, good thermal conductivity, hydrophobicity, heat-bearing characteristics, non-flammability and the ability to prevent corrosion and lower surface tension (Glüge et al., 2020).

Subsequently, these substances were applied in many industrial, commercial and household products from the 1940s such as cook- and baking ware, water-repellent textiles and surfaces, food packaging and fire-fighting foams (FFF) (Glüge et al., 2020). Due to their resistance to degradation, PFAS are referred to as "forever chemicals" (Allen, 2018), in addition, they have a tendency for bioaccumulation and are toxic (Cousins et al., 2020; Z. Wang et al., 2017). PFAS can accumulate in plants and animals, thus posing a risk for humans via the food chain (Sunderland et al., 2019).

Aqueous film-forming foams (AFFF) were used in large quantities at military sites, airports and fire training areas (Volchek & Brown, 2015) and various studies identified AFFF-applying sites as the main sources of PFAS in the neighbouring environment (Ahrens et al., 2015; Baduel et al., 2015; Dauchy et al., 2017; Solla et al., 2012). In Denmark, there are 228 registered AFFF-contaminated sites from past military and firefighting activities (Miljøstyrelsen, 2023).

PFAS contamination can leach to the groundwater and be further transported, posing a risk to drinking water supplies (Sunderland et al., 2019). In recent years PFAS attracted a lot of attention and authorities were urged to set regulations to prevent the further spread of contamination and protect human health (Abunada et al., 2020). PFOS, PFOA, their salts and related compounds are listed among the Persistent Organic Pollutants (POPs) (ECHA, 2023). In addition, Denmark was the first country to ban PFAS in food packaging from 2020 (Trager, 2019). Since 2021, 2 ng/L threshold is established for the sum of PFOA, PFOS, PFNA and PFHxS in drinking- and groundwater with an additional 0.1  $\mu\text{g}$  restriction for the sum of 12 and 22 other PFAS, respectively (Miljøministeriet, 2021; Miljøstyrelsen, 2021a, 2021b).

As PFAS are resistant to natural and chemical degradation, it is highly challenging to remediate PFAS-contaminated sites (Darlington et al., 2019). Recently, remediation technologies have been developed for sufficient groundwater treatment, such as ion exchange resins, activated carbon adsorption and foam fractionation (FF). However, all three technologies have limitations such as difficulties with short-chain PFAS removal (Ambaye et al., 2022; Buckley et al., 2022b). Foam fractionation is a promising sustainable alternative due to its simple and cost-efficient operation (Burns et al., 2021), often followed by a polishing treatment step (Buckley et al., 2022b; Burns et al., 2021). Currently, various articles assess the optimization potential to reach better PFAS removal including the short-chain compounds. Salt addition and cosurfactant application are among the most studied areas, which are proven to improve the removal from diverse water matrixes (Buckley et al., 2022a; Vo et al., 2023). However, there is high demand for additional studies and the development of technological applications with a focus on non-foaming PFAS-contaminated waters and short-chain PFAS removal improvement.

The aim of this project is to optimize foam fractionation on a non-foaming PFAS-contaminated groundwater by first constructing a laboratory-scale foam fractionation setup, and then developing an experimental method according to previous literature studies. Based on results obtained from a series of laboratory experiments, observations and calculations, the objectives to be reached are:

- to assess PFAS removal by the application of different co-foaming agents and mixtures such as anionic, cationic and zwitterionic with a primary focus on short-chain PFAS removal
- to make recommendations for future surfactant application based on short-chain removal ability, contaminant foam enrichment, volume reduction and reagent expense
- to evaluate the effect of the joint application of increased ionic strength and anionic and zwitterionic surfactant mixture on target and total PFAS removal
- to examine the impact of groundwater preozonation for foam production improvement

## 2 Theory

### 2.1 PFAS occurrence and associated risks

#### 2.1.1 Main sources and adverse health effects

According to the definition by Z. Wang et al. (2021) "any chemical with a perfluorinated methyl group ( $-CF_3$ ) or a perfluorinated methylene group ( $-CF_2-$ ) is a PFAS". Currently, there are 4730 chemicals listed on OECD's PFAS list (OECD, 2023a). PFAS are divided into two main categories, fluoropolymers such as Teflon (Dhanumalayan & Joshi, 2018) and non-polymers such as perfluoroalkyl acids (PFAA), which are applied in fire fighting foams, fluoropolymer and water-repellent textile and paper production (Glüge et al., 2020). PFAA and their precursors are considered the most toxic PFAS group and are among the most common PFAS (Glüge et al., 2020). Perfluoroalkyl carboxylic acids (PFCA) and sulfonic acids (PFSA) are PFAA and can either have short or long alkyl chain (Ambaye et al., 2022). Long-chain compounds and precursors have carbon chain lengths above 8 (C8-PFCA) and 6 (C6-PFSA), otherwise, they are considered short-chain PFAS (OECD, 2023b). However, in the literature, usually all PFAS below C8 alkyl chain is referred to as short-chain PFAS (Gellrich et al., 2013)

Chronic exposure to PFAS in adults can cause -among many other- thyroid and hormonal changes, cancer (breast, kidney, prostate, and liver), reduced liver function, cardiovascular disorder, obesity and reproductive disturbance. In children, PFAS can induce premature or stillbirth, birth defects, neuro-developmental deficiencies, asthma and hormonal disturbance and others (Anderko & Pennea, 2020; Garg et al., 2020). Additionally, both PFOS and PFOA can manipulate the response mechanism of antibodies, hence they are considered immune hazards (NTP, 2016; L. Zhang et al., 2023)

#### 2.1.2 PFAS in the environment

Due to the wide application of PFAS, contamination in the environment can be a result of various sources (Abunada et al., 2020). The spread of PFAS-accumulated wastewater sludge on agricultural fields can result in diffuse leaching into the ground (Garg et al., 2020), while the application of AFFF on a site is characterised as a point source (Abunada et al., 2020). Moreover, PFAA and precursors can enter the environment from fluoropolymer-producing factories, where they are applied as aids for the polymerization (Glüge et al., 2020). PFAS precursors can be partially degraded and form highly stable and persistent PFAS end products (Z. Wang et al., 2017), for example, fluorotelomer alcohols can be degraded to perfluoroalkyl carboxylic acids (Cousins et al., 2020).

It was estimated that in Germany the average daily human intake of PFOS and PFOA from drinking water was 0.17 and 0.21 ng/kg body weight, respectively (Gellrich et al., 2013). The same study showed that short-chain compounds were the dominant PFAS in drinking water, which can be explained by them being more mobile and having less tendency for sorption (Gellrich et al., 2013). This phenomenon was also observed during the monitoring of a PFAS-contaminated Swedish drinking water aquifer, where PFHxS was detected the furthest downgradient from the source zone, even though PFOS was present in the highest concentration there (Sörengård et al., 2022). Another study showed that in Dutch drinking water, the dominant PFAS is ultrashort-chain (C2-C3) with 300-1100 ng/L followed by short-chain PFAS with 0.4-95.1 ng/L (Sadia et al., 2023). It was found that PFCA, PFSA and precursor ( $>C_4$ ) levels were higher in drinking water from surface water compared to groundwater, however, the ultra-short-chain PFAS content was similar

in both cases (Sadia et al., 2023). The higher mobility of short-chain compounds -in contrast to the long-chain ones- was also observed after landfill leachate treatment (Yin et al., 2017) and wastewater treatment (Arvaniti et al., 2014). PFAS sorption to sediment particles depends on the organic carbon content of the soil and the organic carbon to water coefficient (Koc) of the molecule. logKoc values of different PFAS species were modelled (Rayne & Forest, 2009) and determined experimentally (Pereira et al., 2018) in soils, both studies observed logKoc increase with increasing chain length, indicating the greater soil partitioning potential of long-chain PFAS (Pereira et al., 2018; Rayne & Forest, 2009). Additionally, Gao et al. (2019) showed that PFSA sorbed faster compared to PFCA due to their variation in polarity and hydrophobicity originating from structural differences.

### 2.1.3 PFAS legislation in Denmark and in the EU

Denmark's PFAS regulation precedes other countries' legislation in Europe. In 2021, the Danish Environmental Protection Agency (DEPA) established strict water quality requirements, presented in Table 2.1 and banned PFAS-containing food packaging from 2020 (Trager, 2019).

Perfluorinated carboxylic acid with chain-length of C9-C14 and their precursors are restricted in the European Union since February 2023 (ECHA, 2023). Danish, Swedish, Norwegian, German and Dutch authorities handed in a proposal to the European Chemical Agency for extensive restriction of PFAS (Sonne et al., 2023). Moreover, the proposal to ban FFF is also under consideration (ECHA, 2023). Perfluorooctanesulfonic acid (PFOS), Perfluorooctanoic acid (PFOA) and their salts and related compounds are banned under the European Union's Persisted Organic Pollutants (POPs) Regulation since 2009 and 2020, respectively. Perfluorohexanesulfonic acid (PFHxS) its salts and related compounds will be included from the end of 2023. In addition, long-chain (C9 to C21) carboxylic acids (PFCAs) are currently being evaluated for restriction (ECHA, 2023).

Table 2.1: Danish groundwater quality criteria (Miljøstyrelsen, 2021a).

Compounds	Quality criteria [ $\mu\text{g/L}$ ]
Sum of PFBS, PFPS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFUnS, PFDoS, PFTrS, PFOSA, 6:2 FTS, PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA	0.1
Sum of PFOA, PFOS, PFNA, PFHxS	0.002

### 2.1.4 AFFF contaminated sites

AFFF mixtures were utilized in large amounts at military bases, airports and firefighting facilities (Reinikainen et al., 2022), where AFFF are applied against hydrocarbon fires such as fuel and oil (Moody & Field, 2000), presented in Figure 2.1. In addition, due to their structure, PFAS can withstand extreme heat without breaking down, while forming a film layer and preventing fire re-ignition (Volchek & Brown, 2015). Commercially available AFFF is a mixture of various chemicals. Their exact composition is unknown, however, they generally consist of fluorinated surfactants from C4 to C12 alkyl chain length, hydrocarbon surfactants, solvents, and thickeners (Volchek & Brown, 2015). PFOS was extensively used in AFFF mixtures (Volchek & Brown, 2015) until its restrictions under the Stockholm Convention in 2009 (ECHA, 2023). Subsequently, it is substituted with other polyfluorinated surfactants (Hetzer et al., 2014), such as short-chain PFAS (F. Li et al., 2020) which are still compounds of concern (Hetzer et al., 2014). Additionally, a

higher concentration of short-chain PFAS is required to achieve the same decrease in surface tension (Brusseau & Glubt, 2021).



Figure 2.1: Application of AFFF during fire training (“Piqsels.com”, 2023).

Due to the wide and large amount of application, AFFF are the main source of PFAS-contaminated sites (Reinikainen et al., 2022) and as they were used at airports, military and fire training areas, cocontaminants such as chlorinated solvents, fuel and oil and other surfactants are commonly present at the AFFF-impacted sites (Moody & Field, 2000). In the unsaturated zone, PFAS can sorb in the air-water interface and on the surface of soil particles, which can result in above 50% mass holdup (Wallis et al., 2022). It was shown, that infiltration intensity (Høisæter et al., 2019), pH, cation and organic matter content of the soil have an important role in the sorption mechanism (Pereira et al., 2018), hence influencing PFAS leaching to the groundwater (Bierbaum et al., 2023). PFAS in the groundwater can be further transported thus, posing a threat to drinking water resources (Banzhaf et al., 2017). As Denmark’s drinking water supply relies 99% on groundwater (Miljøstyrelsen, 2001), the remediation of PFAS-contaminated sites and groundwater protection are particularly important.

## 2.2 PFAS-contaminated groundwater remediation

Recently, technologies have been emerging for PFAS-contaminated water remediation. Destructive and non-destructive (separation) treatments are two of the most common approaches (Yadav et al., 2022). Plasma destruction and high-temperature incineration are among the destruction methods, which permanently destroy PFAS (Ambaye et al., 2022). Water remediation with the application of sorbents is widely applied for PFAS water treatment (Yadav et al., 2022). Typical sorbents are granulated activated carbon (GAC), ion exchange resins (IER) and other polymers (Ambaye et al., 2022). PFAS remediation using GAC and ion-exchange resins have been intensively studied (McGregor, 2020). Ion exchange resins are considered the preferred option for PFAS treatment, as the resin can be regenerated, and have better absorption ability including short-chain PFAS (Murray et al., 2021). However, sorbent technologies can have high capital and treatment costs and in some cases, the spent sorbent needs disposal (Murray et al., 2021). Foam fractionation provides a sustainable and cost-effective alternative for PFAS removal from water (Burns et al., 2021).

### 2.2.1 PFAS foam fractionation

During the foam fractionation process, surface active molecules adsorb in the air-water interface of gas bubbles, which are rising through the contaminated water column. The concentrated hydrophobic molecules form a foam on top of the bulk liquid (Burns et al., 2021). A few of the biggest advantages of foam fractionation are the low operation cost, low energy consumption and significant contaminated volume reduction (Burns et al., 2021). This technology has been successfully applied for other purposes in different matrices, such as protein skimming in recirculating aquaculture system (RAS) water (Buckley et al., 2022b; de Jesus Gregersen et al., 2021). Various studies have investigated PFAS foam fractionation on laboratory, pilot and full scale. Spiked MilliQ or tapwater samples, groundwater and landfill leachate can be found among the treated water types. It has been reported in many cases that long-chain molecules are more efficiently removed compared the short-chain molecules, due to their higher hydrophobicity (Meng et al., 2018; Y. Wang et al., 2023). After foam fractionation, 78% contaminated volume reduction can be achieved (Robey et al., 2020). The concentrated foam needs further treatment (Smith et al., 2022) by destructive technologies, such as sonochemical or thermal degradation (Garg et al., 2021). In addition, Burns et al. (2021) treat the foam with secondary and tertiary foam fractionation, to obtain a minimal volume. In literature studies, foam fractionation is conducted in batch mode (Meng et al., 2018), continuous mode (Smith et al., 2023; Smith et al., 2022) or multiple-stage operation (Burns et al., 2021). Figure 2.2 shows the schematic diagram of a continuous foam fractionator. The rising bubbles drive the foam production, which can be harvested on the top. The PFAS concentration is the highest in the produced foam, while the outflow has the lowest PFAS content (Smith et al., 2022).

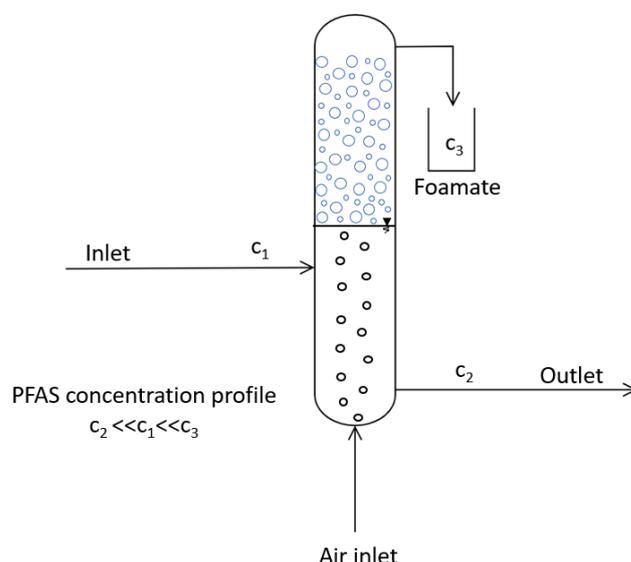


Figure 2.2: Schematic diagram of a continuous foam fractionator adapted from Smith et al. (2022).

#### The short-chain PFAS challenge and influential factors on removal

As a result of their higher solubility and less surface activity (Meng et al., 2018; Y. Wang et al., 2023), the low removal of short-chain compounds is observed in many studies (Buckley et al., 2022a; Burns et al., 2021; Dai et al., 2019; Meng et al., 2018; Robey et al., 2020; Smith et al., 2023; Smith et al., 2022; Y. Wang et al., 2023). Due to their persistent insufficient removal, many studies suggest a polishing step after foam fractionation, such

as activated carbon, ion exchange or membrane filtration (Buckley et al., 2022b; Burns et al., 2021; Smith et al., 2023).

In general, PFSA is removed better than PFCA (Smith et al., 2023), as sulfonic acids are more hydrophobic and thus they sorb better in the air-water interface (Dai et al., 2019; Smith et al., 2022; Y. Wang et al., 2023). In studies conducted by McCleaf et al. (2021) and Meng et al. (2018), it was observed that the individual PFAS removal is dependent on their initial concentration and removal decrease was found when treating increasing concentration of PFOS (Meng et al., 2018). Generally, PFAS removal depends on the water chemistry, such as dissolved organic carbon (DOC), metal ion content, conductivity (McCleaf et al., 2021) and PFAS composition (Smith et al., 2022). If the longer chain PFAS are dominant the influent the total removal will be lower due to less efficient elimination of short-chain molecules (Smith et al., 2022). The presence of Natural Organic Matter (NOM) enhances the removal due to the emergence of more hydrophobic PFAS-NOM complexes, which sorb better to the air-water interface (Y. Wang et al., 2023). Moreover, thickener (water-soluble polymer) addition such as hydroxypropyl methylcellulose (HPMC) also has a positive effect on removal due to its surface lowering properties, which supports foaming (Y. Wang et al., 2023). During foam fractionation, aerosols can be produced (McCleaf et al., 2023; Smith et al., 2022), containing mostly short-chain PFAS as they have a higher tendency to migrate to the air (Smith et al., 2022). This can result in mass balance (MB) losses (Smith et al., 2022). In addition, the presence of suspended solids may impact the foam stability by preventing it to burst, which would block aerosol production into the air (Smith et al., 2023). Furthermore, MB>100% can be the result of precursor transformation and MB below 100% can be a result of PFAS sorption on organic matter, iron and aluminium ions (Smith et al., 2023). Additionally, MB variations can be also caused by analytical uncertainties (Smith et al., 2023).

#### **The effect of operation parameters**

During foam fractionation, the operating parameters, such as air-flow and bubble size (Buckley et al., 2022b), substantially impact the removal efficiency (Buckley et al., 2022a). During foam fractionation experiments, the PFAS removal increased with increasing flow rate (Dai et al., 2019; Y. F. Li et al., 2021; McCleaf et al., 2021; Meng et al., 2018; Y. Wang et al., 2023), due to increased bubble surface area and thus higher partitioning to the water-air interface (Y. F. Li et al., 2021). Additionally, a smaller bubble size results in a higher surface area for contaminant sorption, which results in removal improvement (Buckley et al., 2022b). However, there is an optimum flow rate above which the efficiency does not change (McCleaf et al., 2021).

The enrichment factor (E) -the ratio between initial and foam concentrations- decreased, as the rising foam had less time to dewater, which resulted in more foamate (McCleaf et al., 2021; Y. Wang et al., 2023). Y. Wang et al. (2023) defines this phenomenon as "convective liquid carry over". This can result in the lack of contact time, hence worsened removal for some compounds, such as PFOS (Y. Wang et al., 2023). In addition, the height of the water column was observed not to have a significant effect (1%) on the removal efficiency (McCleaf et al., 2021), which did also not decrease by changing from batch mode to continuous operation mode (Smith et al., 2022). Regarding continuous systems, a residence time ( $t_r$ ) of ~20 minutes is suggested by many studies (Buckley et al., 2022a; Burns et al., 2021; Y. F. Li et al., 2021; Smith et al., 2023; Smith et al., 2022; Vo et al., 2023), as it was observed that the removal did not increase notably with longer contact time Smith et al. (2023). Table 2.2 presents the applied technological parameters from the above-mentioned publications.

Table 2.2: Parameters of literature studies including treated water type, treated volume, gas flow, experiment type and setup material (Abbreviations: residence time ( $t_r$ ), standard litre per minute (slpm), groundwater (GW), High-density polyethylene (HDPE), wastewater treatment plant (WWTP), calculated value (cal)).

Publication	Water type	Volume [L]	Gas flow [L/min]	Duration [min]	Experiment type	Setup material
Buckley et al., 2022a	Simulated wastewater Groundwater	8	~5.2 (slpm)	60	Semi-batch	Acrylic plastic
Buckley et al., 2023	Simulated wastewater	8	~5.2 (slpm)	30-60	Semi-batch	Acrylic plastic
Meng et al., 2018	Diluted AFFF concentrate	0.6 L	0.050-0.125	120	Batch experiments	Polymethyl methacrylate
Dai et al., 2019	Tapwater diluted FFF	14	10, 20 and 30	10 and 40 ( $t_r$ )	Pilot scale benchtop tests	Not specified
Vo et al., 2023	Landfill leachate	9	8.5	60	Batch experiment	Acrylic plastic
Smith et al., 2022	Landfill leachate	46 (cal)	5-20	10-30 ( $t_r$ )	Benchmark batch and continuous tests	Polypropylene
Y. F. Li et al., 2021	Simulated wastewater	0.5	0.3	60	Batch experiments	Polyethylene
Y. Wang et al., 2023	Spiked deionized water Landfill leachate AFF contaminated Groundwater WWTP effluent	1.4-2	4, 7, 10 and 15	2	Batch experiments	Acrylic plastic
McCleaf et al., 2023	Drinking water (from GW) nanofiltration concentrate	0.25, 7.1	1.7 and 4	2-3 and 10 ( $t_r$ )	Laboratory batch and continuous tests	Acrylic plastic
Smith et al., 2023	Mixture of AFF-contaminated surface runoff groundwater process water	208 (cal)	3.5-16	60	Pilot scale continuous experiments	ECT2 system ("ECT2", 2023)
McCleaf et al., 2021	Landfill leachate	1.2 and 2.4	3500-7000 and 10500 (L/min* $m^2$ )	60	Batch and continuous experiments	Acrylic plastic
Robey et al., 2020	Landfill leachate	0.75	2.6	Until foaming stopped blank test for 15	Mass labelled tracer Batch experiments	Glass beaker
Burns et al., 2021	Groundwater	2500	Not specified	21	Semi-batch	HDPE
Lee et al., 2017	PFOA and PFOS spiked deionized water	0.37	7.5	5	Batch-type column	Polyethylene

### **The effect of ionic strength (IS) from salt addition and pH change**

Among operation parameters, water chemistry, such as ionic strength and pH have a notable effect on the removal efficiency. Many studies report improved removal with increased ionic strength (Buckley et al., 2022a; McCleaf et al., 2021; Meng et al., 2018; Smith et al., 2023; Y. Wang et al., 2023). The positive effect appeared to have a maximum above which the removal did not elevate (McCleaf et al., 2021). Y. Wang et al. (2023) made the same observation, where 10 mM salt ( $\text{CaCl}_2$  and  $\text{NaNO}_3$ ) concentration is found as optimum. The presence of salts lessens the electrostatic repulsion between PFAS head groups, which improves the adsorption to the air-water interface (Buckley et al., 2022a; Y. Wang et al., 2023). Increased IS decreases the solubility of PFAS, which enhances its adsorption on the bubble surfaces, moreover, it decreases the bubble size and supports their stability by increasing the electrostatic repulsions between bubbles, hence hindering their merging and bursting (Meng et al., 2018; Y. Wang et al., 2023).

In the work of Buckley et al. (2022a), the removal of PFHxS, PFOA and PFOS improved with the addition of 10 mM concentrations of sodium, potassium or magnesium. However, the presence of calcium had a negative effect due to its complexation with the applied cosurfactant (Sodium dodecyl sulfate, SDS) and forming  $\text{Ca}(\text{DS})_2$ , which hindered foaming (Buckley et al., 2022a). The improvement in removal was observed to be proportional to the charge density of the applied cations (Buckley et al., 2022a). Among the discussed cations, the charge density follows the order of  $\text{Mg}^{2+} > (\text{Ca}^{2+}) > \text{Na}^+ > \text{K}^+$  (Rayner-Canham & Overton, 2009).

Another study showed that the addition of iron chloride coagulant elevates PFAS removal (McCleaf et al., 2021), as iron neutralizes the negatively charged functional groups of PFAS, thus increasing their hydrophobicity resulting in better incorporation in the foam (McCleaf et al., 2021; Y. Wang et al., 2023). PFOS removal was evaluated using 11.5 mM of  $\text{Fe}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$  or  $\text{K}^+$ , which resulted in removal of 99.5%, 99.0%, 90.2%, 28.9%, 25.2% and 3.1%, respectively. Hence, it was found that trivalent ions with higher charge density result in better removal than di- and monovalent cations (Lee et al., 2017).

When using an anionic surfactant -such as SDS- as cofoaming agent, salt addition lowers its critical micelle concentration (CMC) (Buckley et al., 2022a). CMC is a unique property of a surfactant, which expresses the concentration at which micelles start to form (Reth et al., 2011). Additionally, elevated  $\text{Na}^+$  concentration neutralises the repulsion between the head groups of PFAS and SDS. As a consequence, smaller surfactant micelles are formed, which provides more surface area for PFAS to incorporate, hence the removal is improved (Buckley et al., 2022a). A study conducted by Y. Wang et al. (2023) showed, that the removal did not show further improvement when adding salts together with either NOM or HPMC, which suggests that the effect of NOM and HPMC outnumbers the ionic strength's.

Considering the effect of pH, both increasing and decreasing the pH result in elevated ionic strength, due to the higher concentration of  $\text{OH}^-$  or  $\text{H}^+$  ions (Y. Wang et al., 2023). Meng et al. (2018) observed that alkaline pH was more effective for PFAS removal, as  $\text{H}^+$  ions in the acidic solution can neutralize the negatively charged bubbles and decrease their stability. However, Y. Wang et al. (2023) noted better removal at acidic pH as the CMC is lowered in the presence of elevated  $\text{H}^+$  ion concentration.

### **The effect of co-foaming agent addition**

For non-foaming PFAS-contaminated waters, it is necessary to apply cosurfactants/ co-foaming agents, as PFAS in low concentrations are not able to form foam (Buckley et al., 2023). Foam fractionation studies are emerging with the utilization of different types of co-foaming agents. The addition of surfactants decreases the surface tension and increases

the stability of bubbles, hence better removal is achieved, as the PFAS-containing bubbles do not burst while rising (Meng et al., 2018). Among the applied surfactants, there are anionic, non-ionic, zwitterionic and cationic ones. The addition of cationic and zwitterionic surfactants is proven to significantly elevate the PFAS removal including short-chain species (Buckley et al., 2023; Y. F. Li et al., 2021; McCleaf et al., 2023; Vo et al., 2023).

Figure 2.3 presents the removal mechanism of PFAS with different types of cosurfactants present in the solution. There is no interaction between PFAS and surfactant head groups when using a nonionic type (Vo et al., 2023). When using an anionic surfactant (e.g SDS) which has the same charge as PFAS head groups, it might lower the sorption coefficient of PFAS due to the repulsion between their charges, however by providing sufficient bubble surface area for sorption this process can be averted (Vo et al., 2023). Cationic surfactant can form a pair with the negatively charged PFAS, hence increasing the molar volume and consequently strengthening the pair's hydrophobicity which results in better sorption on air bubbles (Vo et al., 2023). Zwitterionic surfactants have a positive charge along with a negative one, which has similar effects to cationic surfactants, thus enhancing PFAS absorption to the air-water interface (Vo et al., 2023). The application of cationic or zwitterionic surfactant can provide a sufficient solution for short-chain PFAS removal (Vo et al., 2023).

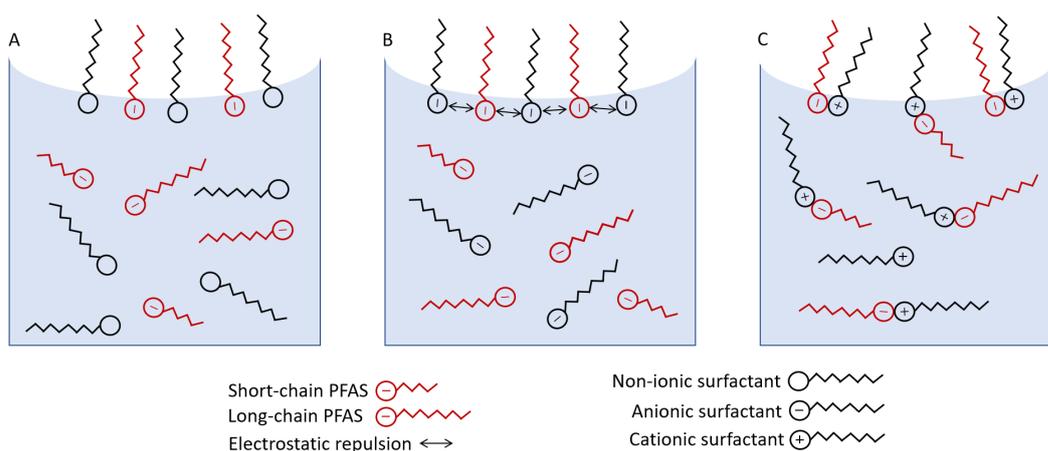


Figure 2.3: PFAS and surfactant interactions adapted from Buckley et al. (2023). The Figure visualizes (A) no interaction between surfactant (non-ionic) and PFAS head groups, (B) repulsions between the anionic surfactant and PFAS heads, (C) attraction between positive cationic heads and negative PFAS functional groups.

Table 2.3 summarizes the reviewed co-foaming agents and their types from literature. The best removal is obtained by using a cationic surfactant, followed by anionic and non-ionic surfactants, respectively (McCleaf et al., 2023). Similarly, Buckley et al. (2023) noted that the application of the cationic surfactant, Cetyltrimethylammonium bromide (CTAB) resulted in the complete removal of all focus substances (Buckley et al., 2023). The second-best removal was achieved with zwitterionic surfactant followed by non-ionic and anionic, respectively (Buckley et al., 2023). However, efficient removal of long-chain PFAS can be achieved without the addition of cationic surfactant (McCleaf et al., 2023; Vo et al., 2023). In addition, it is highlighted that PFBA (McCleaf et al., 2023; Vo et al., 2023) and PFPeA (Vo et al., 2023) are still challenging to remove even with cationic surfactants, while (Buckley et al., 2023) achieved sufficient removal for PFBA.

Table 2.3: Applied cosurfactants and their types from previous studies, Linear (L) and branched (B) alkyl chain types are presented.

<b>Publication</b>	<b>Applied cosurfactant</b>	<b>Surfactant type</b>
McCleaf et al. (2023)	MONTALINE™ C 40 (Cocamidopropyl Betainamide MEA Chloride)	cationic (L)
Vo et al. (2023) Buckley et al. (2023) Y. F. Li et al. (2021)	Cetyltrimethylammonium bromide (CTAB)	cationic (L)
Y. F. Li et al. (2021)	Dodecyl-trimethyl-ammonium bromide (DTAB)	cationic (L)
Y. F. Li et al. (2021)	Tetra-n-butyl-ammonium bromide (TBAB)	cationic (B)
Y. F. Li et al. (2021)	N-octyl-trimethyl-ammonium bromide (OTAB)	cationic (L)
McCleaf et al. (2023)	Marlinat™ 242/28 (Sodium Laureth Sulfate)	anionic (L)
McCleaf et al. (2023)]	Linear alkylbenzene sulfonate (LAS)	anionic (L)
Vo et al. (2023) Buckley et al. (2023) Buckley et al. (2022a) Y. F. Li et al. (2021)	Sodium dodecyl sulfate (SDS)	anionic (L)
McCleaf et al. (2023)	SIMULSOL™ SL 10 (Alkylpolyglucoside)	non-ionic (L)
Meng et al. (2018)	N-Octyl- $\beta$ -D-glycopyranoside	non-ionic (L)
Vo et al. (2023) Buckley et al. (2023)	Triton X-100	non-ionic (L)
Vo et al. (2023) Buckley et al. (2023)	N-Dodecyl-N,N-dimethyl- 3-ammonio-1-propanesulfonate (SB3-12)	zwitterionic (L)
Smith et al. (2023)	Neutral Hand Dishwash	mixture of anionic, zwitterionic and non-ionic

When applying anionic surfactants such as SDS (Buckley et al., 2023; Y. F. Li et al., 2021; Vo et al., 2023) or Linear alkylbenzene sulfonate (LAS) (McCleaf et al., 2023) the removal was reported to be the lowest, furthermore, McCleaf et al. (2023) observed 3% less removal with LAS compared to experiments without any surfactants.

Increased removal with an increased surfactant dose is found by McCleaf et al. (2023). The addition of non-ionic surfactant elevated the removal and also the foam volume (Meng et al., 2018). On the other hand, removal did not increase with increasing concentration of cationic surfactant (Y. F. Li et al., 2021), moreover Smith et al. (2023) also noted that the increase in soap dose did not result in notably better removal, but leads to a higher foam fraction, suggesting that there is an optimal dose of the surfactants (Y. F. Li et al., 2021). The geometric shape and the chain length of the surfactant's tail also influence the removal, as the use of branched (B) surfactant resulted in the lowest removal of PFOA (C8) and with linear chained (L) OTAB (C8) the removal was the fastest, which has the same alkyl-chain length as PFOA (Y. F. Li et al., 2021). This suggests that surfactant molecules with the same alkyl chain length of target PFAS form micelles more easily (Y. F. Li et al., 2021). Y. F. Li et al. (2021) reported less efficient removal with the combined application of increased IS and cationic surfactant. It is argued that anions can compete

with PFAS for the sorption in the air-water interface, which causes decreased removal (Y. F. Li et al., 2021). However, when enhancing the IS while applying anionic surfactant, the effect of the counter ion of the added salt does not play an important part in PFAS removal (Buckley et al., 2022a; Dutkiewicz & Jakubowska, 2002). It is emphasized that cationic and zwitterionic surfactants are expensive compared to other alternatives (Vo et al., 2023) and are toxic (McCleaf et al., 2023; Vo et al., 2023). However, it suggested that if the residual water is treated with biotreatment or oxidation processes (Vo et al., 2023), the surfactant will not cause an issue due to its proper degradability (McCleaf et al., 2023; Vo et al., 2023).

### The effect of ozone

In a pilot scale study by Dai et al. (2019) foam fractionation alone removed 81.3% of total PFAS, however, ~95% of total PFAS removal was achieved with ozonated air. Even though ozonated air improved the removal of long-chain compounds, it was found to be ineffective for short-chain molecules (Dai et al., 2019). As ozone could not oxidize the PFAS species because of the high energy required to break the C-F bond, the removal elevation is due to the great amount of electron binder hydroxyl radicals on the surfaces of ozonated bubbles (Dai et al., 2019), as presented on Figure 2.4. These radicals are able to attach to the carboxylic or sulfonic group of PFCA and PFSA, thus improving their removals (Dai et al., 2019).

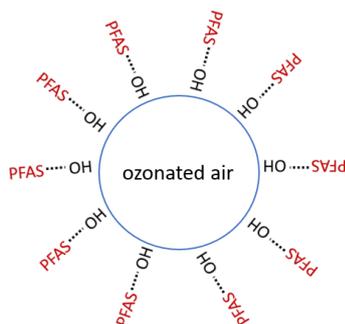


Figure 2.4: Removal mechanism of PFAS with ozonated air (adapted from Dai et al. (2019)). Hydroxyl radicals on ozonated air bubbles attach to the negatively charged functional groups in PFAS resulting in better adsorption in the air-water interface.

Additionally, combined treatment of UV/ozone increases the amount of short-chain PFCA in the water, likely due to the transformation of precursors (Dai et al., 2019). Moreover, 6:2 FTS was measured in the foam despite not being detected in the influent or effluent (Dai et al., 2019).

Furthermore, an Australian company, EVO CRA, developed the Ozofractionative Catalysed Reagent Addition (OCRA) patented technology, which utilizes ozone gas for foam fractionation and provides sufficient PFAS removal including co-contaminants and PFAS precursor (EVO CRA, 2016).

The combination of ozonation and foam fractionation is widely applied in recirculating aquaculture systems for the removal of the accumulated organic matter (de Jesus Gregersen et al., 2021; Park et al., 2011). Ozone breaks down the complex organic molecules, therefore the foaming is expected to improve, which was observed in studies when treating RAS water (Park et al., 2011). The application of ozone increases the number of hydrophilic species in the water (Świetlik et al., 2004). Hence, presumably due to altering characteristics in organic matter, elevated foam production can be achieved, which increases with ozonation time (Park et al., 2011).

## 3 Methodology

### 3.1 Site description (Vandel Airport)

Vandel Airport is located close to Billund in the Region of Southern Denmark. The area was used by the military from 1943/44 until 2001/2003. In 1960, a fire station was built on the site including a fire training ground with a nearby foam extinguisher storage. The fire extinguisher liquid was stored in 200 L plastic drums, around 2000 L in total. Fire trainings have been held regularly on the site, hence fuel and extinguishing agents were dispersed to the ground and have contaminated the groundwater (COWI, 2022). The monitoring well at the fire training area (B101-2, 28 m) with the second highest PFAS concentration at the site (COWI, 2022) was sampled by the Region of Southern Denmark. The well with the highest contamination was dry and could not be sampled. The measured sum of 4 and 22 PFAS species exceeded the groundwater criteria by 1400 and 32 times, respectively (COWI, 2022). There is oil and BTEX contamination present at the site, and B101 is affected by 12  $\mu\text{g/L}$  C5-C35 oil contamination, which is 3  $\mu\text{g/L}$  above the quality criteria (COWI, 2022).

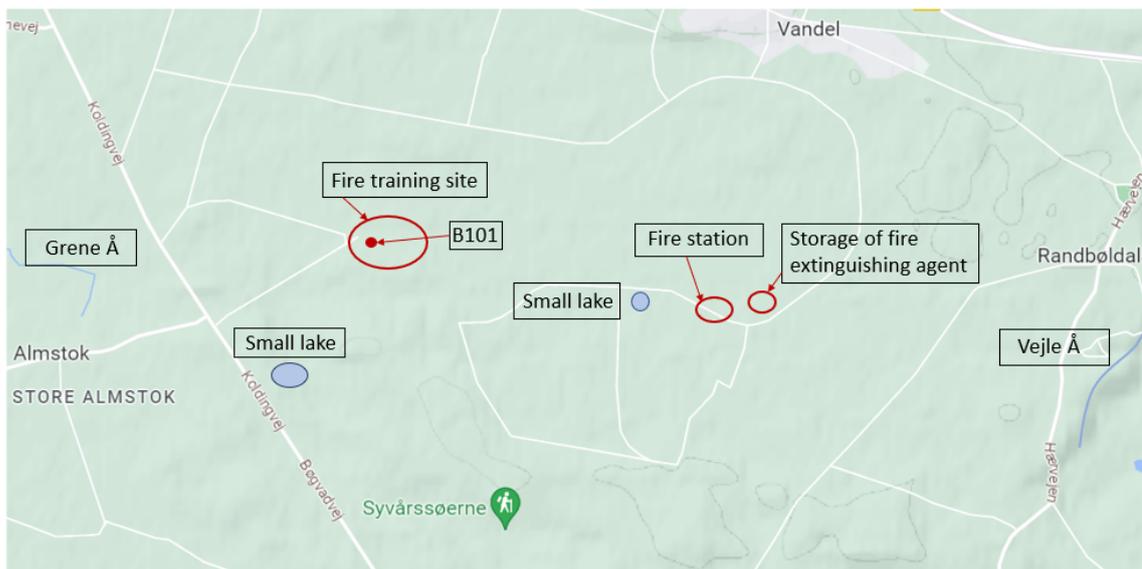


Figure 3.1: Map of Vandel Airport and location of the former fire training area based on COWI (2022).

The nearest drinking water well is located 2000 m north, while the direction of groundwater flow is east. The nearest waterbodies to the fire training site are two small lakes and a nearby stream (Grene Å) located 230 m and 2400 m away, respectively, both in the western direction. The report highlights that the surrounding waterbodies are at a bigger risk in terms of contamination transport, compared to the nearby waterworks (COWI, 2022). General water chemistry parameters and commercially performed PFAS analysis results are presented below in Table 3.1.

Table 3.1: Commercially measured PFAS concentrations (COWI, 2022) and general water chemistry parameters (measured during the project) of the Vandel water (NVOC was measured to be lower than the DOC, likely due to measurement uncertainties.)

Parameter/ compound	Value
pH	6.9
Conductivity [ $\mu$ S/cm]	75.4
Total hardness [mg/L]	7.2
Total alkalinity [eq/ml]	0.3
NVOC [mg/L]	2.5
DOC [mg/L]	2.6
PFPeA [ng/L]	94.0
PFPeS [ng/L]	16.0
PFHxA [ng/L]	160.0
PFHxS [ng/L]	600.0
PFHpA [ng/L]	35.0
PFHpS [ng/L]	72.0
PFOA [ng/L]	250.0
PFOS [ng/L]	2800.0
6:2 FTS [ng/L]	34.0

## 3.2 Experimental methodology development

### 3.2.1 Experimental setup design

The experimental setup is designed for batch experiments and is depicted on Figure 3.2. It consists of a polymethyl methacrylate column, which was modified with another tube attachment to ensure the bypass of the continuously produced foam. The column is 72.7 cm high and its internal diameter is 5.5 cm. 600 mL of groundwater was treated during the experiments. The column was fixed to a laboratory stand, which enabled the introduction of the gas and the co-foaming agent from the bottom. Both outlets were closed with a check valve stopping the back-flow of water from the column. A ball valve is connected to the column to discharge the treated water after an experiment to avoid mixing with the foam above. The co-foaming agent was added continuously with a peristaltic pump (BT100-2J, Longer pump, 0.0002 mL/min-380 mL/min flow range). The pump was calibrated and documented in Table A.1 in the Appendix. The gas flow was measured with a Brooks Instrument flowmeter (0.1-0.5 L/min flow range), connected to the laboratory air tap available in the fume hood. A stainless steel bubble stone was applied for bubble dispersion, which produced bubbles with  $\sim 1$  mm diameter.

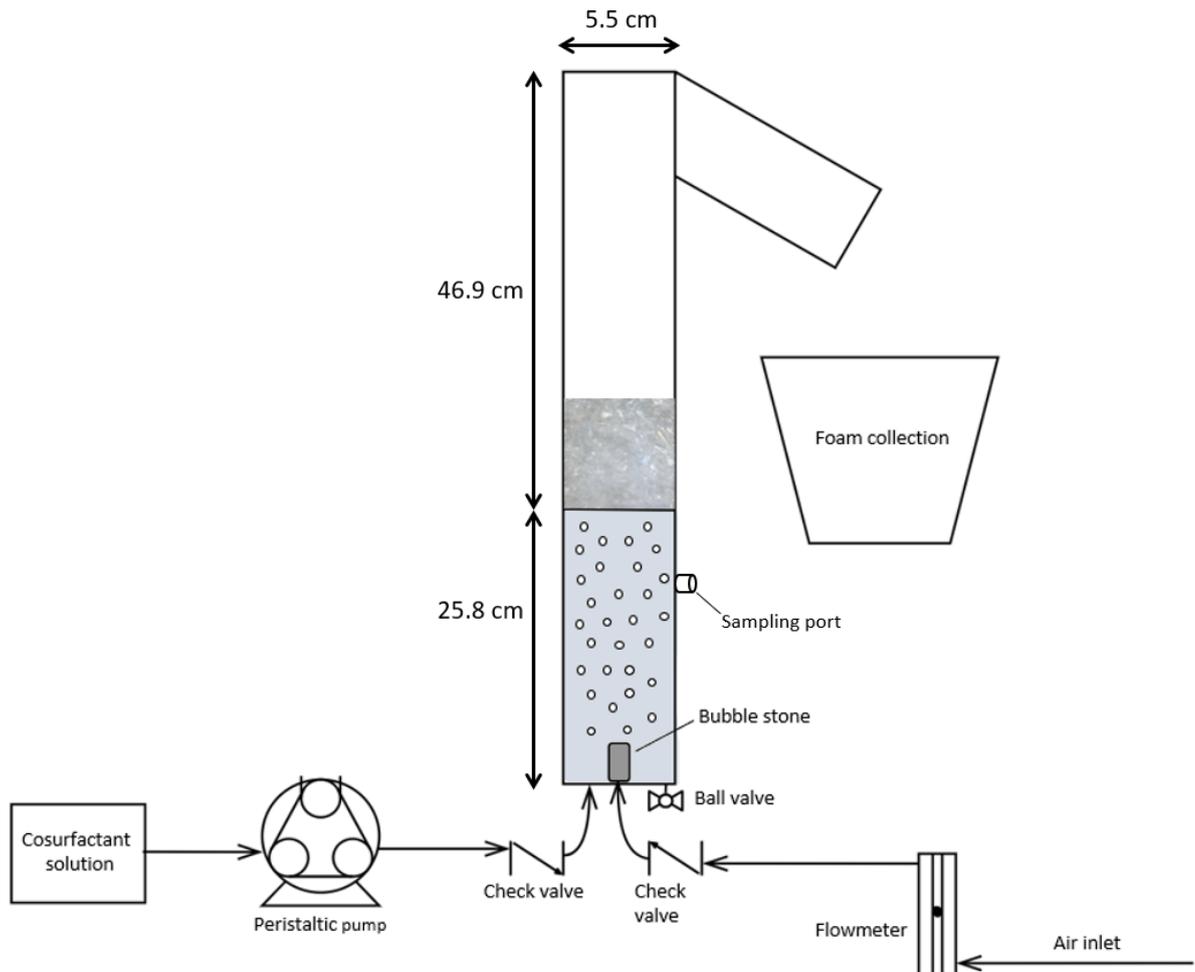


Figure 3.2: Developed experimental setup suitable for batch experiments.

### Blank and sorption tests

Blank and sorption tests were carried out before starting the laboratory experiments, to ensure that the setup does not leach and sorb PFAS. To perform the leaching test, 500 ml of MilliQ water was poured into the setup and left for 2 hours, which is two times higher than the duration of a performed experiment. No leaching was found as all target PFAS were below the quantification limit. Similarly, for the sorption test, 500 ml of PFAS-contaminated water was left in the setup for two hours. 4.1-15.3% more PFAS was measured in the sorption test, which is most likely due to analytical uncertainties since no leaching was found.

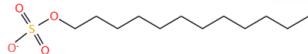
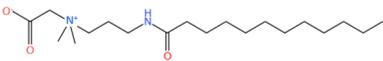
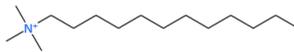
### 3.2.2 Optimization of experimental conditions

As the groundwater did not foam by itself, co-foaming agent had to be added to the sample during the experiments. In this study, anionic, zwitterionic and cationic surfactants were added to the groundwater samples and their performances were assessed. While selecting the surfactants, it was important that they are commercially available and have low toxicity. After consideration, dodecyl trimethyl ammonium chloride (DTAC), sodium dodecyl sulfate (SDS) and cocoamidopropyl betaine (CAPB) were selected as cationic, anionic and zwitterionic surfactants, respectively. DTAC belongs to the group of quaternary ammonium salts, which are highly toxic compounds (C. Zhang et al., 2015). However, studies have shown that DTAC is the least toxic to marine organisms compared to

other cationic surfactants (Quiroga et al., 2021) and biodegradable in seawater (Kaczewska et al., 2020), giving the reason why selected. DTAC was purchased from Sigma Aldrich with >98.0% purity.

SDS is applied in many foam fractionation studies (Buckley et al., 2022a; Buckley et al., 2023; Y. F. Li et al., 2021; Vo et al., 2023) and is a commercially available anionic surfactant. It was purchased from Sigma Aldrich with >90% purity. CAPB is a non-toxic, rapidly biodegradable zwitterionic surfactant (Merkova et al., 2018; Wu et al., 2019). It is used in many cosmetic and household products due to its excellent foaming properties and non-irritability (Madunić-Čačić et al., 2012). It was purchased in a 40% solution from Sapolita, Lithuania. Table 3.2 summarizes the type, CMC, and chemical structure of the selected cosurfactants.

Table 3.2: Parameters of applied surfactants, including type, CMC and structure.

Name	Type	CMC	Molecular structure
Sodium Dodecyl Sulfate (SDS)	anionic	7 mM (Beyaz et al., 2004)	
Cocamidopropyl betaine (CAPB)	zwitterionic	0.09 mM (Haug et al., 2021)	
Dodecyl Trimethyl Ammonium Chloride (DTAC)	cationic	20 mM (Warsi et al., 2022)	

A series of batch experiments were carried out on the groundwater to determine the optimal co-foaming agent addition. The optimal concentration was determined based on when foam production started (~10 min) and when the produced foam reached the foam extraction point (~20 min). During the optimization, SDS was continuously added with a peristaltic pump to the experimental setup to secure the constant formation of bubbles throughout the experiments (Vo et al., 2023).

Buckley et al. (2023) applied 2.5 mg/min SDS addition to 8 L of sample, which resulted in 0.31 mg/L\*min concentration in the treated water. This concentration was tested in this project as well, however, no foaming was obtained under 20 minutes. Therefore, 0.6, 1.8, 3.6, and 6 g/L SDS solutions were experimented with 1 mL/min surfactant flow, which resulted in 1, 3, 6, and 10 mg/L\*min liquid pool concentrations, respectively. It was observed that at 3 mg/L\*min liquid pool concentration foam production started at 13-15 minutes and reached the extraction point in 20-25 minutes, which was considered optimal. Regarding the cationic surfactant, 10 mg/L\*min DTAC liquid pool concentration (6 g/L solution added with a 1 mL/min flow) did not induce sufficient foaming. The height of the produced foam barely increased compared to SDS and the foam was observed to be unstable showing continuous collapsing. DTAC also has the highest CMC among the selected surfactants (3.2 Therefore it was mixed in 1:1 with the CAPB, which produced proper foaming. When applying CAPB, foaming starts within 2-3 minutes, due to the low CMC.

During trial experiments, gas flows up until 2 L/min were tested, and 0.2 L/min flow was determined as optimal. This flow rate ensured the proper foam residence time in the setup for foam drainage and induced suitable volume reduction. For 0.6 L water volume Meng et al. (2018) applied 0.05-0.125 L/min as gas flow, moreover, Vo et al. (2023) applied 0.3 L/min for 0.5 L water further supporting the reason for the application of 0.2 L/min airflow. Applied air flows from previous studies are presented in Tabel 2.2. As the air applied for the foam fractionation came from the laboratory tap in the fume hood and the flowmeter was quite unstable and constant flow was challenging to maintain. To ensure

the proper dewatering of the foam, adequate column headspace was designed, however, this led to residual foam in the setup, which could not be harvested nor analysed. All experiments during this project were conducted with the parameters presented in Table 3.3. To ensure a proper base for comparison between the different surfactant types, stock solutions with the same concentrations were prepared and dosed with the same flow during the experiments.

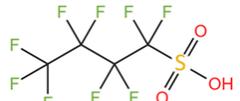
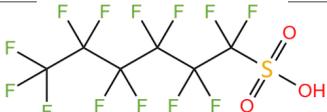
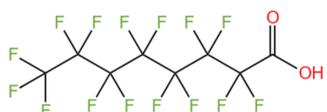
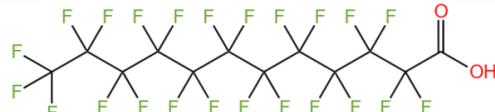
Table 3.3: Experimental parameters applied during the laboratory experiments.

<b>Parameter</b>	<b>Value</b>
Gas flow [L/min]	0.2
Treated volume [L]	0.6
Cosurfactant stock concentration [g/l]	1.8
Cosurfactant addition flow [ml/min]	0.94
Experiment duration [min]	60

### Groundwater spiking experiments

As the groundwater from Vandel -apart from PFOS- did not contain high enough PFAS concentration ( $>1 \mu\text{g/L}$ ) to measure it directly with the HPLC-MS/MS (and the addition of zwitterionic surfactant hindered the SPE method), it was decided to proceed with higher PFAS concentrations to be able to investigate the effect of the applied cosurfactant type. PFBS (potassium salt, 98%), PFHpA (99%), PFHxS (potassium salt,  $>98\%$ ), PFOA (95%), PFDA (98%), PFDoDA (95%) were purchased from Sigma Aldrich and a methanol-based spike solution was prepared with around 100 mg/L concentration of each PFAS. Table 3.4 shows the chain length and structure of the selected PFAS present in the spiking solution. Apart from PFDA and PFDoDA, the compounds are present in the water from the site as shown in Table 3.1. As a result, three sulfonic acids (PFBS, PFHxS, PFOS) and four carboxylic acids (PFHpA, PFOA, PFDA, PFDoDA) are present in quantifiable concentrations in the spiked groundwater representing from C4 to C12. This allows the assessment of the removal of compounds with varying chain-length.

Table 3.4: Composition of spiking solution.

Abbreviation	Compound	Chain length	Molecular structure
PFBS	Perfluorobutanesulfonic acid	C4	
PFHxS	Perfluorohexanesulfonic acid	C6	
PFHpA	Perfluoroheptanoic acid	C7	
PFOA	Perfluorooctanoic acid	C8	
PFDA	Perfluorodecanoic acid	C10	
PFDoDA	Perfluorododecanoic acid	C12	

To perform the experiments, 0.6 L groundwater was spiked with 60  $\mu\text{L}$  spiking solution, which resulted in the following concentrations (performed with duplicates) summarized in Table 3.5. PFOS was not spiked but was present in the water in high enough concentration to be measured without SPE, therefore it is included in the table.

### 3.2.3 Finalized experimental method

The setup was filled with 0.6 L of spiked contaminated groundwater (9.9°C). Before the experiments, the surfactant solution was prepared. Afterwards, the airflow was started and the flowmeter was set to 0.2 L/min. The co-foaming agent was added continuously with the flow rate of 0.93 mL/min (5.5 rpm) from a 1.8 g/L solution, providing 1.674 mg/min surfactant inflow to support foaming. During the 60 minutes long experiments, samples

Table 3.5: Concentrations of PFAS spiked groundwater from Vandel Airport measured in duplicates and standard deviations (SD) included.

Compound	Mean concentration [ $\mu\text{g/L}$ ]
PFBS	4.53 $\pm$ 0.19
PFHpA	12.93 $\pm$ 0.58
PFHxS	12.01 $\pm$ 0.18
PFOA	14.46 $\pm$ 0.49
PFOS	1.02 $\pm$ 0.07
PFDA	3.38 $\pm$ 1.19
PFDoDA	14.95 $\pm$ 4.04
Total PFAS	63.28 $\pm$ 2.33

were taken out every 10 minutes to obtain the time profile of the PFAS removal. The 1-5 ml sample was retrieved and filtered with a 0.22  $\mu\text{m}$  filter, then transferred to a polypropylene tube. The sample at 60 minutes was collected from the discharged water. The treated water was transferred to a PET bottle after an experiment. The foam was harvested in a polypropylene bucket. After an experiment, the collected foam was set aside to collapse and covered with aluminium foil to avoid contamination. The volume of the collapsed foam was measured and the foam was sampled. As the foam was very stable, when needed, a few ml of Acetonitrile was added to fasten the collapse. The setup was washed two times with distilled water and two times with MilliQ water after each experiment. For the HPLC-MS/MS analysis, 1 ml sample was transferred to a polypropylene HPLC vial and 10  $\mu\text{L}$  PFOS and PFOA internal standard (1 g/L solution) was added.

During the laboratory batch experiments, three main types were performed including surfactant experiments, where different surfactant types and ratios were employed, and salt experiments, where the groundwater was spiked separately with four different cations. Lastly, a preozonation experiment was carried out. Each experiment was carried out in duplicates, all performed experiments are presented in Table 3.6.

Table 3.6: Overview of performed experiments.

Experiment type	Applied cofoaming agent	Added reagent
Surfactant	SDS	-
Surfactant	1:1 SDS and CAPB	-
Surfactant	1:1 CAPB and DTAC	-
Surfactant	9:1 CAPB and DTAC	-
Salt	1:1 SDS and CAPB	10 mM Na <sup>+</sup>
Salt	1:1 SDS and CAPB	10 mM K <sup>+</sup>
Salt	1:1 SDS and CAPB	10 mM Mg <sup>2+</sup>
Salt	1:1 SDS and CAPB	10 mM Ca <sup>2+</sup>
Ozone	1:1 SDS and CAPB	2.62 mg/L O <sub>3</sub>

### Surfactant experiments

Experiments were carried out using different surfactants in the same concentrations: SDS, 1:1 SDS+CAPB mixture, 1:1 DTAC+CAPB mixture, 1:9 DTAC+CAPB mixture were ap-

plied according to the method discussed in Section 3.2.3.

### Salt experiments

Different salts were added to the groundwater to investigate the effect of increased ionic strength on the PFAS removal efficiency. Four cations have been selected based on Buckley et al. (2022a), including  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ . Salts were purchased from Sigma Aldrich with chloride as a counter ion. The cation concentrations were adjusted to 10 mM considering their background concentration in the water. The salt experiments were performed separately with each cation type and the experiments were run in duplicates. The 1:1 ratio of SDS-CAPB solution is constantly added to each of the experiments, which results in sodium addition from the SDS. Furthermore, the spiking solution also contained a minimal amount of potassium from PFBS and PFHxS salt. As the elevated sodium and potassium background is present in each experiment regardless of the cation type, the results are considered comparable. Table 3.7 provides an overview of the background cation concentration and salt mass addition to reach 10 mM.

Table 3.7: Background data for salt addition experiments.

Cation type	Background concentration [mg/L]	Salt	Mass addition [mg] to 0.6L
$K^+$	0.83	KCl	446.35
$Na^+$	5.30	NaCl	342.55
$Ca^{2+}$	6.17	$CaCl_2 \cdot 2H_2O$	868.48
$Mg^{2+}$	0.99	$MgCl_2$	568.93

### Ozone experiments

For the ozonation experiments, ozone was dissolved in MilliQ water for an hour. The water bottle was set in an ice bath to accelerate the dissolution. For ozone production, a high-efficiency ozone generator with air cooling (Atlas model, Absolute Ozone®) was employed. The concentration of the stock solution was measured with the indigo method (Bader & Hoigné, 1981), and ozone was added according to the groundwater's DOC content. Afterwards, the gas inlet was started and as no foaming was observed, a 1:1 ratio of CAPB and SDS was added to start foaming. Afterwards, the experiment was carried out as described earlier. Additionally, an experiment was conducted to assess if the water foams with ozonated oxygen as gas flow, where the ozone generator was set to 10. Ozone stock concentration and added stock volumes to the groundwater are presented in Table A.1 in the Appendix.

## 3.3 Sample preparation and analysis

### 3.3.1 Sample preparation with Solid Phase Extraction (SPE)

The sample preparation was carried out based on the PFOS and PFAS sample preparation guidelines from Agilent Technologies (Yang et al., 2018). The samples were prepared with a blank and quality control. C13 isotope-labelled PFOS and PFOA were added to each sample as internal standards. Anion exchange WAX cartridges were used for the solid phase extraction, targeted to the negatively charged PFAS. The used 0.5% ammonia methanol solution and the 0.01 M acetic acid buffer (pH=4) were prepared fresh before each extraction batch. First, the cartridges (SampliQ WAX, Agilent Technologies) were conditioned with 4 mL of 0.5% ammonia methanol solution, followed by 4 mL methanol and 4 mL MilliQ water, respectively. Afterwards, the samples were continuously added to the cartridges followed by 5 mL MilliQ water, and 5 mL acetic acid buffer, respectively.

After the passing through of the liquids, the cartridges were dried under vacuum for one hour. For the PFAS elution, 3 mL methanol and 4 ml 0.5% ammonia methanol were applied, respectively. The samples were collected in a 10 mL polypropylene tube, which was placed under nitrogen drying until almost all the ammonia methanol was evaporated. The residue was redissolved in acetic acid buffer and was transferred to a polypropylene HPLC vial with an aluminium septum.

### 3.3.2 PFAS analysis with an HPLC-MS/MS

The PFAS analysis was carried out with a high-pressure liquid chromatograph (HPLC) from Agilent (1290 Infinity II Model) with double mass spectrometry (MS/MS). The separation was conducted on a ZORBAX Eclipse Plus column (Agilent Technologies) with a C18 alkane stationary phase. The inner diameter and the column length were 2.1 mm and 1.8  $\mu\text{m}$ , respectively. The column pressure was set to 380-385 bar. The instrument was calibrated with 12 points (0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 40, 60, 80, 100  $\mu\text{g/L}$ ), Figure 3.3 visualises the selected PFAS peaks obtained from the calibration. The eluent mixture consisted of 10% Methanol (pH=4) and 90% Acetic acid buffer (pH=4), which altered to 100% Methanol by the end of a measurement. 2  $\mu\text{L}$  sample was injected with an autosampler, and ran for 18 minutes, followed by 5.5 minutes post-run to set the eluent ratio back to 90% Acetic acid buffer and 10% Methanol. The HPLC-MS/MS was equipped with a delay column, which retained the potential PFAS contamination coming from the Teflon septums in the pumps. This step ensured the application of PFAS-free eluent during the analysis. The analysis was carried out with multiple reaction monitoring (MRM) method and negative ion electrospray mode.

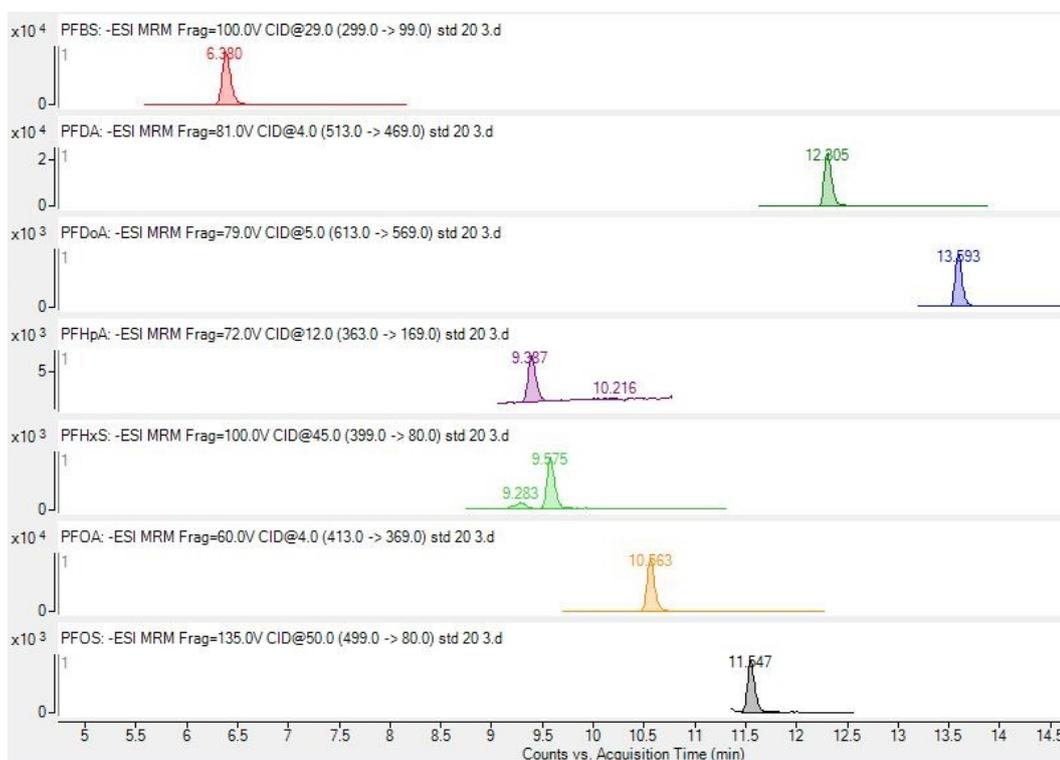


Figure 3.3: Chromatograms of selected PFAS.

## 3.4 Calculations and data treatment

### 3.4.1 HPLC Data treatment

The HPLC data treatment was carried out in Agilent MassHunter Workstation Software (Agilent, 2017). After establishing the calibration, the acquired MRM data was integrated. The quantification limit (QL) was evaluated based on Equation 3.1 below. The samples were measured in two separate batches and therefore different QLs were determined. However, the higher one was selected for the calculations to have unified QLs.

$$QL = \bar{x}_{Blank} + 10 \cdot SD_{Blank} \quad (3.1)$$

where:  $\bar{x}_{Blank}$  is the average response in blanks

$SD_{Blank}$  is the standard deviation between the blank's response

The exported concentration of each sample was dilution corrected due to the cosurfactant addition. The dilution factor was estimated from the initial sample volume (0.6 L), retrieved sample volume in time intervals and volume loss due to foam production and the continuous addition of the cofoaming agent. To estimate the volume depletion due to foam production, the collapsed foam volume was divided by the number of samplings performed after the foam production started. Preozonated samples and foam samples with Acetonitrile addition were also dilution corrected.

### 3.4.2 Foam fractionation performance

PFAS removal (R%) from the treated water was calculated according to Equation 3.2. The removal was computed from the mean spiked concentration presented in Table 3.5. Values below the QL were considered to be the QL to avoid the overestimation of the removal. As the values were dilution corrected, this resulted in a minimal removal decrease due to increased concentration after correction, which can be observed from the graphs in Section 4.

$$R\% = \left(1 - \frac{C_x}{C_0}\right) * 100 \quad (3.2)$$

The foam enrichment factor (E) was calculated according to Equation 3.3.

$$E = \frac{C_{foam}}{C_0} \quad (3.3)$$

The contaminated volume reduction was calculated according to Equation 3.4

$$V\% = 100 - \left(\frac{V_{foam}}{V_0} * 100\right) \quad (3.4)$$

where:

$C_{foam}$  is the foam PFAS concentration [ $\mu\text{g/L}$ ]

$C_0$  is the initial PFAS concentration [ $\mu\text{g/L}$ ]

$C_x$  is the PFAS concentration at x (10-60) minutes [ $\mu\text{g/L}$ ]

$V_{foam}$  is the collapsed foam volume [mL]

$V_0$  is the initial water volume [mL]

### 3.4.3 Preliminary surfactant cost analysis

To assess the economic aspect of the applied surfactants, a cost analysis was carried out. Prior to the analysis, a few assumptions were made:

- The removal is linearly proportional to the applied surfactant dose
- All target species are removed regardless of the surfactant type
- CAPB is sold in a 40% (Sapolita) and 30% (Alibaba) water solution. It was assumed that water does not contribute to the cost, furthermore, prices were converted to Danish kroner [kr] using 7.5 times conversion from Euro and using 6.8 times conversion from US Dollar.
- When a price range was given, a middle price was used for the calculation
- Transportation costs were not considered
- Only surfactant costs are included in the cost analysis disregarding other capital and operation expenses of the FF treatment

The surfactant demand was calculated for the time when the highest removal was achieved using the pump flow and surfactant stock concentration. Then the surfactant demand was calculated for 100% theoretical removal, which was multiplied by the cost of a milligram surfactant, which was applied for 0.6 L treated water. Afterwards, the surfactant cost was calculated for 1000 L. Approximated costs of surfactants from different manufacturers are presented in Table 3.8.

Table 3.8: Approximated cost for applied surfactants from different suppliers.

Applied surfactant	CAS number	Manufacturer	Cost [kr/kg]	Manufacturer	Cost [kr/kg]
SDS	151-21-3	Sigma-Aldrich	758	Alibaba.com (2023b)	51
CAPB	61789-40-0	Sapolita	94	Alibaba.com (2023a)	23
DTAC	112-00-5	Sigma-Aldrich	2720	Alibaba.com (2023c)	136

## 4 Results and discussion

In the present study, the effect of co-foaming agent type, salt addition and preozonation are assessed on the target and total PFAS removal. Target compounds are presented in Table 3.4. Additionally, enrichment factors and volume reductions are calculated to represent the contaminated volume reduction and a preliminary surfactant cost analysis is conducted to compare the different approaches from an economical point of view.

As the raw water was not able to be measured even with spiking without SPE due to the great matrix effect, the removals were therefore calculated from the spiked water SPE results. However, it can not be omitted that the samples retrieved during treatment do not have the same matrix effect, which introduces uncertainty in the results with the risk of overestimating the removal.

The maximum achievable removals with any applied treatment were calculated and are presented in Table 4.1. The QL was considered the lowest obtainable concentration and for the removal, mean values of duplicate measurements were employed from Table 3.5.

Table 4.1: Overview of maximum achievable removals.

Compound	Mean raw GW concentration [ $\mu\text{g/L}$ ]	QL [ $\mu\text{g/L}$ ]	Maximum removal [%]
PFBS	4.5	0.1	97.79
PFHpA	12.9	0.1	99.23
PFHxS	12.0	0.1	99.17
PFOA	14.5	0.2	98.62
PFOS	1.0	0.5	50.82
PFDA	3.4	0.2	94.09
PFDODA	14.9	0.5	96.65
Total	63.3	-	-

Additionally, a notable removal decrease is present at 60 minutes (last time step) in many graphs, which is possibly caused by contamination from the residual foam in the column while discharging the treated water, from where the final sample is taken from.

Regarding the SDS results, there is removal in the first 10 minutes, however, foam production started only after 10 minutes. Therefore, the removal can be the result of the combination of aerosol production, analytical uncertainties and PFAS upconcentration in the upper part of the liquid above the sampling port.

### 4.1 Evaluation of PFAS removal with different co-surfactants

Four experiments were carried out with different co-foaming agents and their mixtures (presented in Table 3.6) and the results are presented in Figure 4.1 and Figure 4.2 below. Figure 4.1 shows that the total PFAS removal is in the following decreasing order: cationic-zwitterionic mixtures, zwitterionic and anionic mixtures and anionic, respectively. This observation is in line with studies evaluating the performance of different cosurfactants (Buckley et al., 2023; McCleaf et al., 2023; Vo et al., 2023). Considering the negative removals in results obtained with SDS, possibly contamination was present in the setup, likely from a previous experiment, where higher concentrations were employed. However, it only appears to affect the PFBS, therefore another explanation could be analytical uncertainties as the surfactant experiments samples were analysed in a separate batch before the salt, ozone and raw samples.

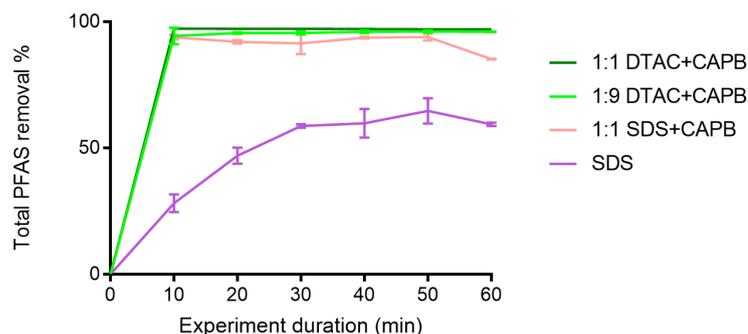


Figure 4.1: Total removals of PFAS with SDS (anionic), 1:1 SDS+CAPB (anionic-zwitterionic), 1:1 and 1:9 mixture of DATC+CAPB (cationic-zwitterionic).

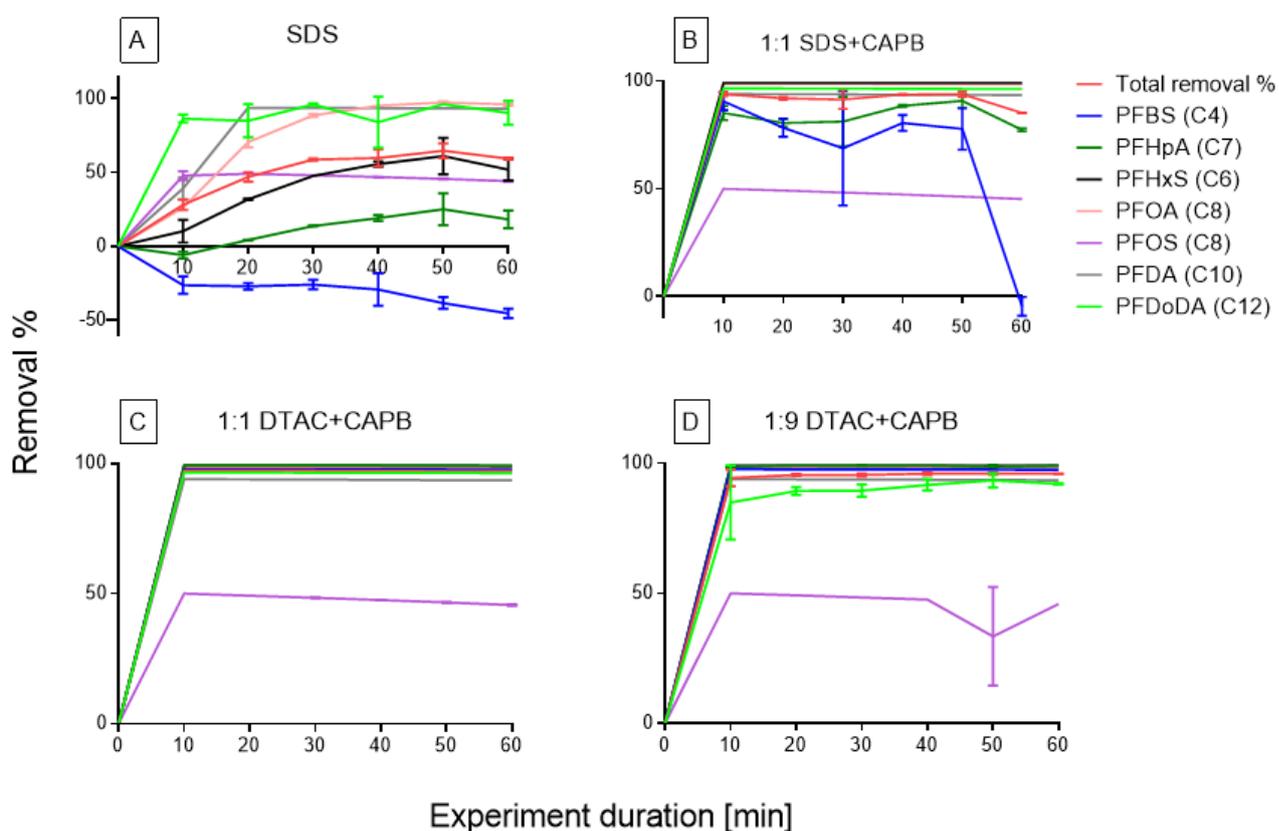


Figure 4.2: Individual PFAS removals from duplicate experiments with (A) SDS (anionic), (B) 1:1 SDS+CAPB (anionic-zwitterionic), (C) 1:1 and 1:9 mixture of DTAC+CAPB (cationic-zwitterionic). The slight decrease in the functions over time is a result of the dilution correction with the fixed QL, as all values below the QL were assigned the QL to avoid the overestimation of the removal.

Regardless of the negative removal of PFBS, it is apparent that the lowest removal was obtained when using an anionic surfactant (SDS), which is in accordance with results from other studies (Buckley et al., 2023; Y. F. Li et al., 2021; Vo et al., 2023). Y. F. Li et al. (2021) achieved 40% of PFOA removal with SDS after 60 minutes, however, in this project, PFOA is well removed (~ 96%) with the same surfactant. This is potentially due to the notably lower initial concentration (14.46  $\mu\text{g/L}$ ) compared to 0.1 g/L applied in Y. F.

Li et al. (2021). Additionally, the initial concentration-dependent PFAS removal has been noted in McCleaf et al. (2021) and Meng et al. (2018) as well. The weak removal achieved by the application of anionic surfactant (SDS) is most likely due to the repulsion forces between the negatively charged PFAS and surfactant heads, which is represented in Figure 2.3. The removal considerably increased when mixing SDS in a 1:1 ratio with zwitterionic surfactant (CAPB) due to the attraction between differently charged headgroups. In addition, two ratios of zwitterionic and cationic mixtures were tested, however, the results do not show striking differences (<3% in 10 minutes). Therefore there is a further optimization potential to reduce the amount of cationic surfactant in the mixture, which is particularly important from an economical and environmental point of view, as cationic surfactants are toxic and expensive. Considering the individual removal of target PFAS species, it can be observed from Figure 4.2 that PFOS, PFOA, PFDA and PFDoDA are completely removed with all four surfactant types/mixtures. The removal of shorter-chain PFAS improved with the mixture of SDS and CAPB, where even ~ 75% PFBS is removed at 50 minutes. With 1:1 and 1:9 cationic mixtures, all PFAS is efficiently removed in 10 minutes with 97.0% and 94.4%, respectively which suggests that a lower surfactant dose would be still sufficient.

## 4.2 Assessing the effect of salt addition

Total PFAS removals with and without cation addition are depicted in Figure 4.3 using 1:1 mixture of SDS and CAPB cosurfactants. It can be observed, that there are minimal variations between the applied cations and cation addition appears to yield a slight decrease in total PFAS removal. This phenomenon has also been reported in the literature, when it was observed that when using a cationic surfactant the elevation in ionic strength does not further improve the removal (Vo et al., 2023). It is most likely due to the competitive sorption of anions with PFAS, which causes the removal decrease (Vo et al., 2023). Additionally, Staszak et al. (2015) observed a decreased performance of CAPB with elevated NaCl concentration, which can be the reason for the removal decrease in the present study, where chloride is employed as well as the counterion. However, more research is needed to obtain an in-detail understanding of the process.

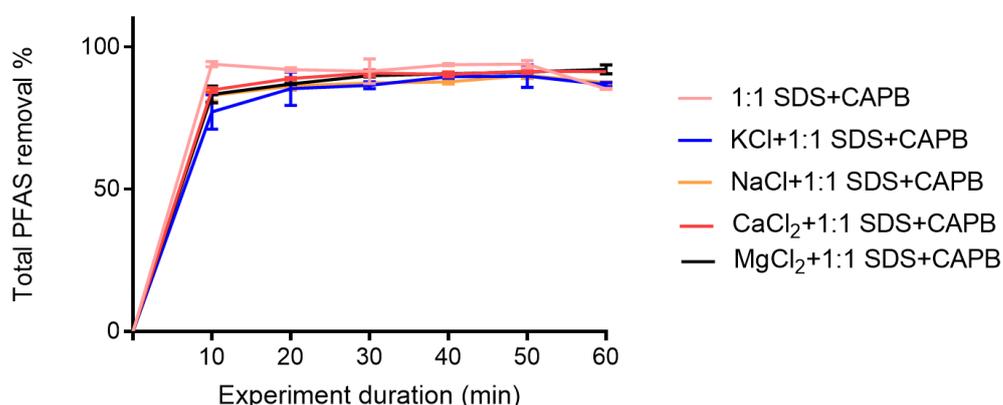


Figure 4.3: Removals of the total PFAS with 10 mM K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> concentration, using 1:1 SDS+CAPB (anionic-zwitterionic) mixture as cosurfactant and total removal with 1:1 SDS+CAPB (without salt addition).

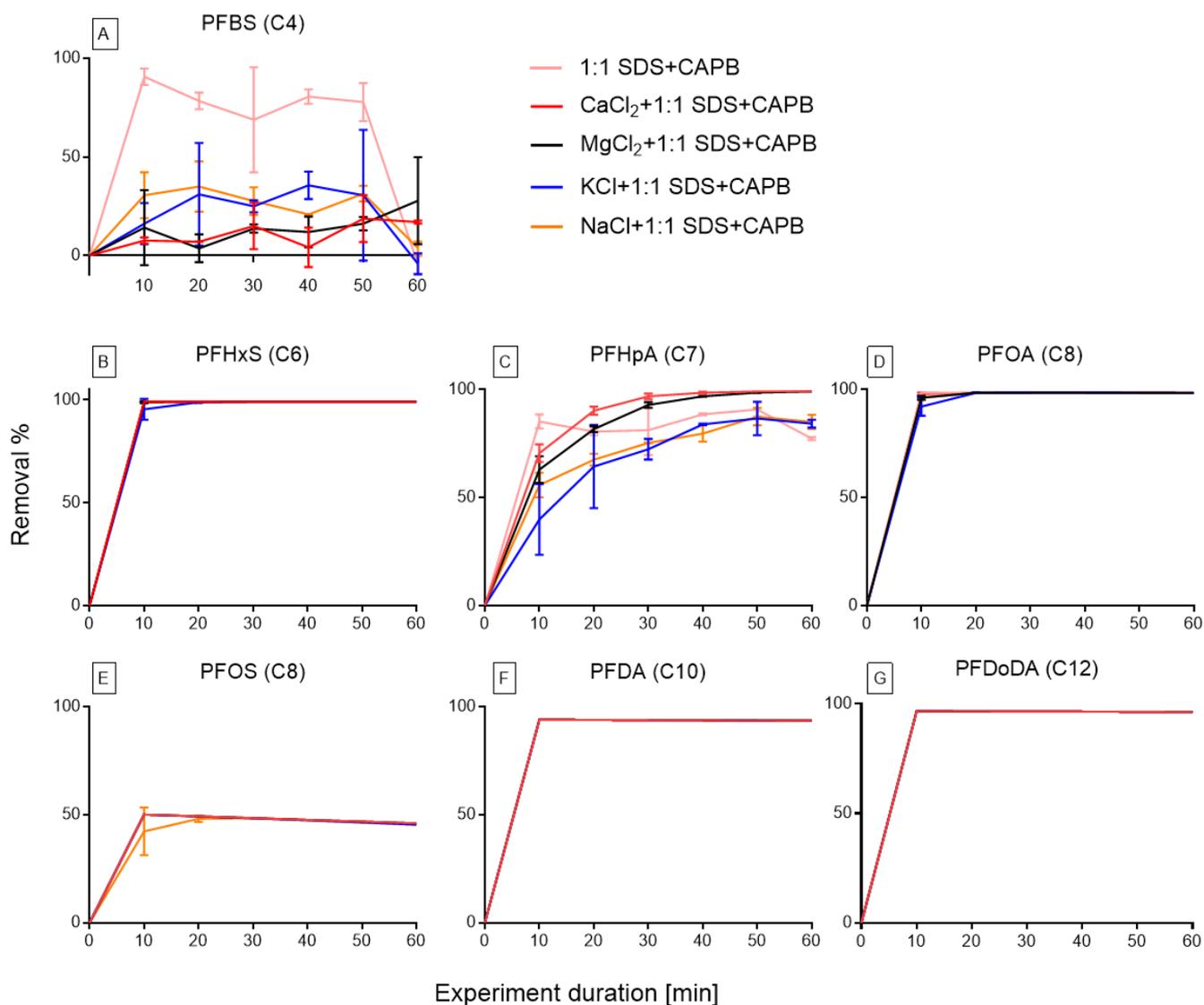


Figure 4.4: Removals of individual PFAS (A-G) with 10 mM  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  concentration, using 1:1 SDS+CAPB (anionic-zwitterionic) mixture as cosurfactant.

Time profile removals from the salt experiments are presented in Figure 4.4. Long-chain compounds, such as PFOA and PFOS are almost, and PFDA and PFDoDA are completely removed in 10 minutes. Considering a shorter-chain compound, PFHxS (C6) is fully removed in the first 10 minutes. However, PFHpA (C7) is removed slower than PFHxS despite having the same alkyl chain length. This can be the result of structural differences, as the sulfonate group increases the hydrophobicity of the molecule which enables better incorporation in the air-water interface and consequently results in better removal (Dai et al., 2019; Smith et al., 2022; Y. Wang et al., 2023).

The outnumbering removal of PFSA over PFCA is reported in many studies (Dai et al., 2019; Smith et al., 2022; Y. Wang et al., 2023). It can be observed that the removal rate of PFHpA increases between 10 and 30 minutes with the addition of divalent cations and by 20 minutes it outperforms the removal without cation addition (1:1 SDS+CAPB). Regarding the effect of monovalent salt addition on the removal of PFHpA, it can be seen that the removal is better when the ionic strength is unchanged. The better removal of PFHpA can be the result of higher ionic strength with divalent ( $Ca^{2+}$ ,  $Mg^{2+}$ ) cation appli-

cation compared to monovalent ions ( $K^+$ ,  $Na^+$ ). At higher ionic strength the solubility of PFAS is decreased (Meng et al., 2018), which can be the reason for the elevated removal of PFHpA. However, it appears that the effect of  $Ca^{2+}$  is greater than  $Mg^{2+}$ , which is not proportional to their charge density (Rayner-Canham & Overton, 2009). This is the opposite of what was observed in Buckley et al. (2022a), where the removal improvement was proportional to the applied cation's charge density.

Moreover, no SDS- $Ca^{2+}$  complexation is observed, which was reported in Buckley et al. (2022a). Potentially due to applying a surfactant mixture thus a lower SDS concentration is present, while for the complexation a higher concentration is required.

Regarding the removal of PFBS it is visible that the removal is higher when adding monovalent cations and diminishes with divalent addition. This can be the result of twice as high chloride concentration present (20 mM) for divalent cations compared to monovalent cation addition (10 mM), which proportionally increases the competition of the negatively charged species with PFAS. However, when comparing PFBS removal with monovalent salt addition to the baseline case with no salt added, it is noted that the removal is substantially lower, most likely due to elevated anion concentration-induced competition. In summary, an increase in ionic strength, when using a SDS+CAPB mixture, does not have a substantial effect on the total PFAS removal. With divalent cations, a slight removal elevation is observed in the case of PFHpA, however, the removal of PFBS is about halved with divalent salts. This suggests, that PFBS might be more sensitive to competitive sorption, while this effect does not apply for the longer chain molecules, where cation addition shows improvement (PFHpA) or where the removal is efficient regardless of the possible effect (PFHxS, PFOS, PFOA, PFDA, PFDoDA). Another reason could be that elevated salt concentration alters the behaviour of zwitterionic surfactants, which was reported by Staszak et al. (2015) with elevated NaCl concentration, although it cannot be concluded without additional investigations. Further research is needed to understand the removal mechanism of PFAS with the application of anionic-zwitterionic mixtures in a high-salt concentration media.

### 4.3 The effect of ozone - visual evaluation

Figure 4.5 depicts foaming with airflow (A), preozonated groundwater with airflow (B) and groundwater with ozonated oxygen as the gas flow (C). It can be concluded that neither water preozonation or ozonated oxygen gas flow improved the foaming properties of the groundwater. Most probably as a result of low DOC content (2.62 mg/L), which is in the drinking water range of 1.5–11.2 mg/L (Golea et al., 2020; Hu et al., 2016). In contrast to RAS water DOC, which is ~ 7-30 (Aguilar-Alarcón et al., 2020; Hambly et al., 2015). In RAS water more organic molecules are present, which can be transformed by ozone to more hydrophilic ones and improve foaming, as reported in a study investigating ozonation-skimming combined systems (Park et al., 2011). This suggests, that the foaming property of originally non-foaming waters might not be able to improve with ozonation. However, there is a potential positive effect of preozonation on waters which already produce foam and the advantages of the ozonated air as gas flow could also be utilized as described in Dai et al. (2019).

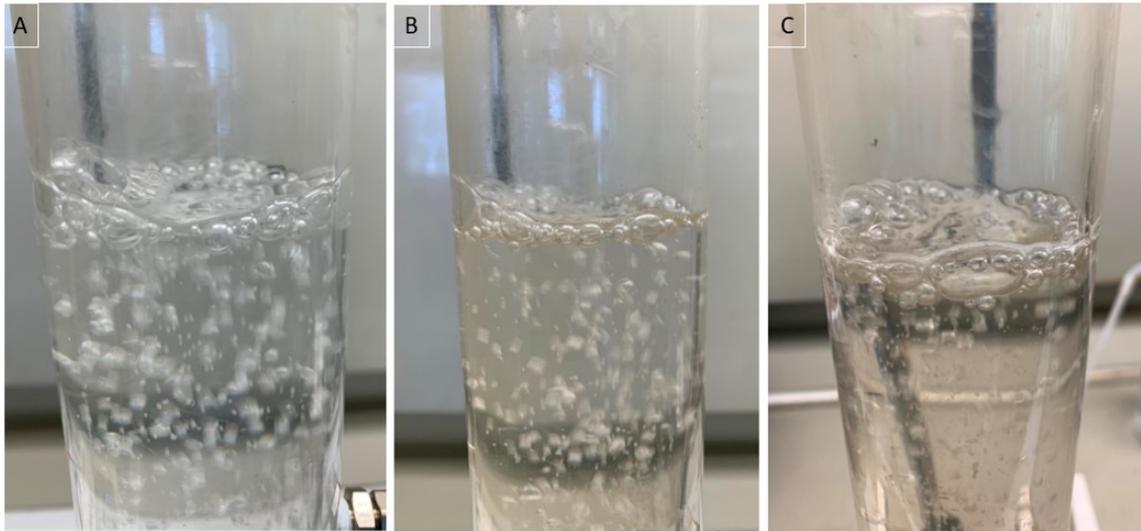


Figure 4.5: (A) Groundwater bubbling with air, (B) ozonated groundwater bubbling with air and (C) groundwater bubbling with ozonated oxygen.

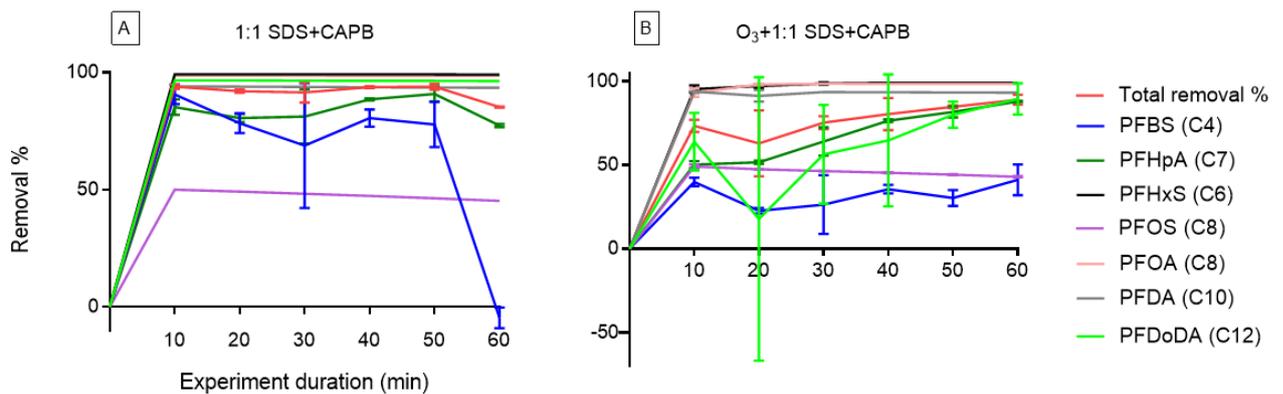


Figure 4.6: PFAS removal with (B) and without (A) preozonation from spiked groundwater using 1:1 SDS+CAPB surfactant mixture.

Figure 4.6 shows the removal of target PFAS with and without preozonation of the spiked groundwater. It can be seen that PFBS, PFHpA and PFDoDA are removed slower. It can possibly be the result of elevated concentrations due to PFAA precursor transformation by ozone (Kaiser et al., 2021), as the removal depends on the initial concentration noted in McCleaf et al. (2021) and Meng et al. (2018). The transformation of precursors has been observed after ozonation in water treatment systems, where negative removal of PFBS (Kim et al., 2022), PFHpA and PFDoDA (Cao et al., 2023) were reported. The ozone-induced precursor transformation could be confirmed by performing a precursor analysis on the water prior to and after ozonation, to assess which compounds are formed.

Elevated foam volume was observed with preozonation as without ozonation the foam volume was ~90 ml and with preozonation ~130 ml. Possibly, it is caused by the increased water height (+~ 8 cm) in the setup - as a result of the ozone stock addition- decreased the drainage height of the foam, which lead to increased foam volume.

## 4.4 Comparison of target PFAS removal between the nine approaches

Figure 4.7 presents the removal of individual PFAS obtained from the nine experiments in the present study. It is apparent that the removal of PFBS varies the most between the performed approaches. PFBS removal above 50% was only achieved with the application of SDS+CAPB, while both cationic mixtures removed 97.76% PFBS in 10 minutes. Salt addition experiments appear to hinder the PFBS removal and there was contamination/uncertainty present when applying the SDS. Furthermore, PFBS appeared to be produced after ozonation. Regarding the removal of PFHxS and PFHpA, sulfonic acids are removed better due to their increased hydrophobicity, as addressed in Section 4.2 (Dai et al., 2019; Smith et al., 2022; Y. Wang et al., 2023). Long-chain PFAS such as PFOA, PFDA, PFDoDA and PFOS, are completely removed within 60 minutes with all experiment types.

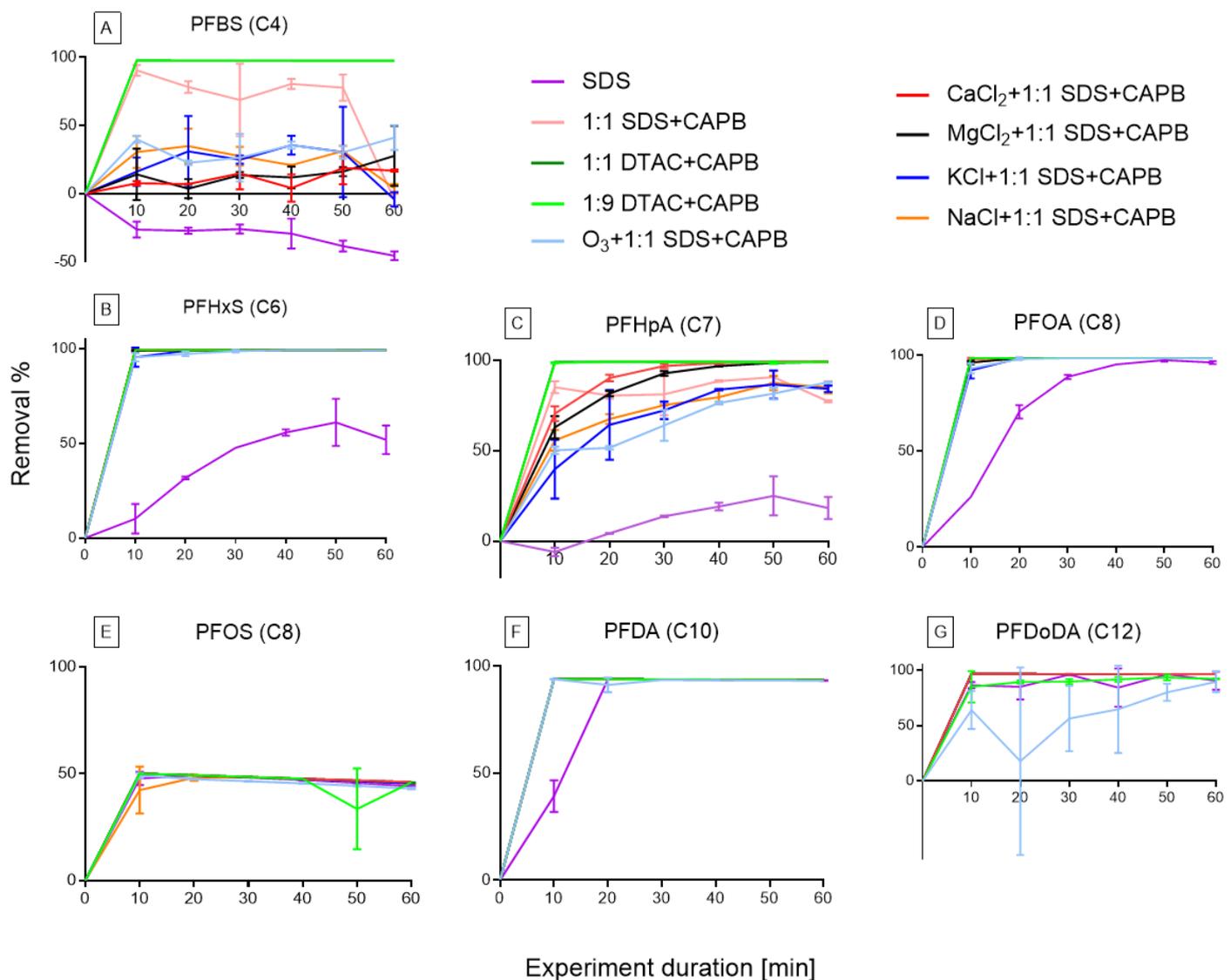


Figure 4.7: Removal of target PFAS (A-G) from the surfactant, salt addition and pre-ozonation experiments, performed in duplicates

## 4.5 Assessment of enrichment factors and volume reduction

Total PFAS enrichment factors were calculated for all experiment types and presented in Figure 4.8. The enrichment factor is the ratio of the initial raw water and the foam PFAS concentrations. The results showed that the highest enrichment factor was achieved with the 1:9 ratio of the cationic and zwitterionic (DTAC+CAPB) mixture followed by divalent cation (magnesium and calcium) spiked experiments with the application of SDS+CAPB mixture. Regarding the DTAC-CAPB mixtures, the reduction of the cationic fraction in the mixture improved the enrichment factor more than 3 times, while the removal did not show a notable decrease (<3%). The highest foam volumes and consequently lowest enrichment factors were obtained from experiments with SDS application and preozonation with SDS+CAPB surfactant mixtures. It was observed during the laboratory experiments, that the addition of CAPB greatly improved the foam stability and significantly reduced the collapsed foam volume, resulting in higher enrichment factors compared to SDS.

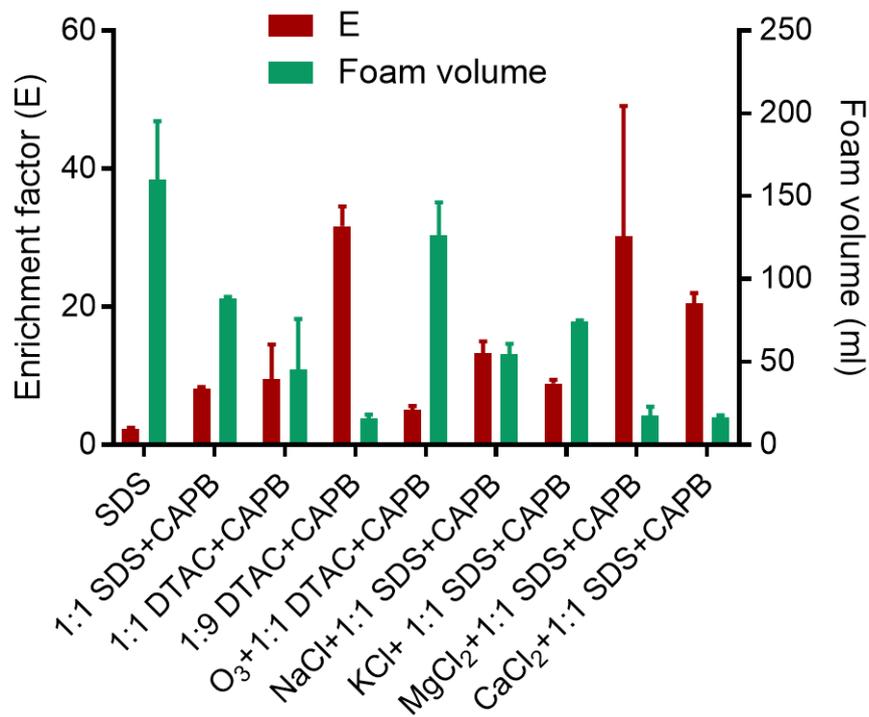


Figure 4.8: Calculated Enrichment factors and foam volumes of the performed experiments.

Enrichment factors calculated for total PFAS concentrations are collected in Table 4.2 and range from 2.1 (SDS) to 33.7 (1:9 DTAC+CAPB).

Table 4.2: Calculated enrichment factors from the present study and from literature. (The mean enrichment factor of 4.96 from Burns et al. (2021) was estimated by the mean of PFOS, PFOA and PFHxS enrichment factors. In addition, the mean 2.5 enrichment was estimated for PFBS, PFHxs, PFHpA, PFOA, PFOS and PFDA from Figure 3. presented in the work of (Y. Wang et al., 2023), both enrichment factors are from a first stage of a multiple stage FF).

Experiment	Reagent	Mean enrichment factor
This study	SDS	2.3
This study	1:1 SDS+CAPB	8.1
This study	1:1 DTAC+CAPB	9.5
This study	1:9 DTAC+CAPB	31.7
This study	O <sub>3</sub> +1:1 SDS+CAPB	5.1
This study	1:1 SDS+CAPB+ NaCl	13.3
This study	1:1 SDS+CAPB+ KCl	8.9
This study	1:1 SDS+CAPB+ MgCl <sub>2</sub>	30.2
This study	1:1 SDS+CAPB+ CaCl <sub>2</sub>	20.5
McCleaf et al. (2023)	Batch experiment, no reagent	2.5
McCleaf et al. (2023)	Continuous experiment, no reagent	7.7
McCleaf et al. (2021)	Batch experiment, no reagent	2.9
Burns et al. (2021)	First stage FF, no reagent	5.0
Z. Wang et al. (2017)	First stage FF, no reagent	2.5
Robey et al. (2020) quoted from McCleaf et al. (2021) and McCleaf et al. (2023)	Batch experiment, no reagent	3.7

The enrichment factors found in the literature are from studies where no surfactants were applied and the studied PFAS species also vary, therefore the factors can only give an indication and are not suitable for direct comparison. Factors from the literature are similar to the low-performance experiments in this study, such as the application of SDS and preozonation, where the foam volumes are the highest, which caused low enrichment. Other enrichment factors obtained from this project are higher due to the application of surfactants, which have an effect on foam stability. Salt addition had a positive effect on foam production by surfactants, as the foam volumes were lower with salt addition in all four cases. The opposite is reported in the literature, when with no surfactant application, the higher ionic strength results in elevated foam volume due to increased bubble stability (Meng et al., 2018). In the present case, salt addition possibly altered the behaviour of the surfactants, which resulted in improved drainage. Furthermore, the gas flow applied in this project is relatively low and the headspace in the setup is high. These two factors resulted in the foam staying longer in the setup, thus having adequate time to dewater, which increased the enrichment factors.

Contaminant volume reductions were calculated as the ratio of the treated water and produced collapsed foam volume (Equation 3.4) and are shown in Table 4.3. The highest reductions were achieved by 1:9 DTAC+CAPB and divalent cation additions, furthermore, the addition of monovalent salts also improved the volume reduction, therefore higher enrichment is achieved. It suggests that cations alter the behaviour of the surfactant mixture which improves dewatering, this phenomenon was reported by Behera et al. (2014), where decreased foam volume was observed in the presence of salts. Robey et al. (2020) reported 78% contaminated volume reduction, which is exceeded with all nine approaches in this study, potentially due to the application of surfactants.

Table 4.3: Calculated volume reductions

Experiment	Volume reduction [%]
SDS	73.3
1:1 SDS+CAPB	85.8
1:1 DTAC+CAPB	92.7
1:9 DTAC+CAPB	97.4
O <sub>3</sub> +1:1 SDS+CAPB	79.5
1:1 SDS+CAPB+ NaCl	91.3
1:1 SDS+CAPB+ KCl	87.9
1:1 SDS+CAPB+ MgCl <sub>2</sub>	97.4
1:1 SDS+CAPB+ CaCl <sub>2</sub>	97.6

## 4.6 Preliminary surfactant cost analysis

Cost analysis was performed to uncover the most cost-efficient surfactant type. The calculation was carried out for the applied laboratory reagents and also commercially available market prices, which are more relevant for field applications. From both approaches, the results show that the 1:9 DTAC+CAPB mixture is the most cost-efficient, shown in Tables 4.4 and 4.5. As seen from the enrichment factor, this mixture induces the highest contaminant volume reduction, which further supports its efficacy. Lastly, it is shown in Figure 4.2 that the 1:9 DTAC+CAPB mixture can efficiently remove all target PFAS, even though it was only an assumption while performing the cost analysis.

Table 4.4: Cost analysis performed for laboratory reagents.

Surfactant type	Maximum removal %	Maximum removal [min]	Surfactant demand [mg]	Surfactant cost [kr]	Cost of 100% removal [kr] (0.6 L treated volume)	Cost of 100% removal [kr] (1000 L)
SDS	64.70	50	84.60	0.06	0.10	165.19
1:1 SDS+CAPB	93.89	10	16.92	0.01	0.01	12.79
1:1 DTAC+CAPB	97.27	10	16.92	0.02	0.02	40.79
1:9 DTAC+CAPB	94.41	10	16.92	0.01	0.01	10.64

Table 4.5: Cost analysis performed for surfactant prices from Alibaba.com (conducted based on the same calculation as Table 4.4)

Surfactant type	Surfactant cost [kr]	Cost of 100% removal [kr] (0.6 L treated volume)	Cost of 100% removal [kr] (1000 L)
SDS	0.00431	0.00667	11.11
1:1 SDS+CAPB	0.00062	0.00066	1.11
1:1 DTAC+CAPB	0.00134	0.00138	2.30
1:9 DTAC+CAPB	0.00058	0.00061	1.02

As the results show, the 1:9 ratio of the cationic-zwitterionic mixture induces the highest enrichment, removes short-chain PFAS efficiently and is the most cost-effective. Additionally, 97.4% contaminated volume reduction was achieved, which suggests that this mixture is the most efficient among the tested ones. These findings can be important for future technologies. CAPB produces a stable foam with high volume, which takes more than a day to collapse, hence adequate space needs to be designed if applied. In addition, cationic surfactants can be toxic to aquatic environments, therefore an additional treatment step is needed before discharging the treated water to the environment, such as secondary foam fractionation or biotreatment.

## 5 Conclusions

In the present study, a laboratory-scale foam fractionation setup was built and a corresponding experimental method was developed and optimized. A series of batch experiments were carried out on PFAS-spiked groundwater and the effect of surfactant types, mixtures, ionic strength and preozonation were evaluated. Based on the obtained results, it can be concluded that:

- The type of the applied cofoaming agent greatly influences the PFAS removal, especially the short-chain compounds, which are difficult to remove otherwise. Long- and short-chain compounds are efficiently removed with the anionic-zwitterionic and zwitterionic-cationic surfactant mixtures used in this study.
- There is a further optimization potential to decrease the cationic fraction in the DTAC and CAPB mixture, as there is a minor (<3%) removal difference obtained from the two different ratios (1:1 and 1:9).
- Increasing the ionic strength only had a positive effect on PFHpA removal with divalent cations and decreased PFBS removal with both mono- and divalent salts. Total removal was higher with no salt addition, which suggests that the effect of the electrostatic attractive forces between the zwitterionic surfactant and PFAS headgroups outweighed the effect of elevated ionic strength.
- Neither preozonation nor ozonated air improved foaming, potentially due to the low organic content of the groundwater.
- Preozonation resulted in lower removal of PFBS, PFHpA and PFDoDA likely due to precursor transformation. In addition, the foam volume also increased, potentially due to an increase in the water column height, hence less foam drainage, which decreased enrichment
- 97.4% volume reduction, the highest enrichment factor and the lowest cost were calculated for the 1:9 ratio of DTAC+CAPB, which confirms that this surfactant is the most effective among the tested ones. This suggests that the mixture can carry a potential for future applications.
- Regarding the employment of cationic surfactants during foam fractionation, it must be noted that they can be toxic to aquatic environments, therefore biotreatment or secondary foam fractionation is needed before the water is discharged into the environment.

## 6 Recommendations and future perspectives

Findings from the current thesis can potentially contribute to the development of future pump and treat technologies for PFAS-contaminated water remediation. However, the results should be handled with precautions due to analytical uncertainties and only duplicate data points from the experiments. Future projects should consider the following recommendations:

- Regarding the laboratory experiments, the constant gas flow was challenging to maintain. Therefore, establishing a more stable gas flow would enable better repeatability of the experiments as the gas flow drives the PFAS removal.
- Including more replicate experiments and more sampling points between 0 and 10 minutes would give a closer estimate of the removal curve.
- Additionally, SPE method development is needed for matrixes containing zwitterions and cations. Performing SPE on all retrieved samples during the experiments would lower the analytical uncertainties.
- The cosurfactant's residual concentration after treatment was not measured during this project, although is essential to include it in the scope of future projects. Acquiring information on how much surfactant is left in the treated water would indicate the potential toxicity and the extent of the needed post-treatment could be designed accordingly. Spectrophotometric methods from literature such as Gholami et al. (2018), Sar et al. (2008), and Scott (1968) could be applied for the analysis of SDS, CAPB and DTAC, respectively.
- Further optimization of the surfactant ratio of DTAC and CAPB would result in an even more cost-effective and less toxic surfactant mixture application.
- Even with cationic surfactants McCleaf et al. (2023) and Vo et al. (2023) report less efficient removal of some short-chain PFAS (PFBA, PFPeA), therefore it is essential to research if it depends on the surfactant type and how the removal of these compounds can be improved.
- In addition, including more PFAS compounds and precursors in the analysis and evaluation of their removal is essential to uncover whether the DTAC-CAPB mixture is effective for a wide range of PFAS.
- Additional research is needed to investigate the effect of increased ionic strength on zwitterionic and anionic surfactant mixtures and precursor transformation by ozone.

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<https://doi.org/10.1016/j.envres.2022.115188>

# A Appendix

## A.1 Pump calibration

The pump was calibrated using MilliQ water.

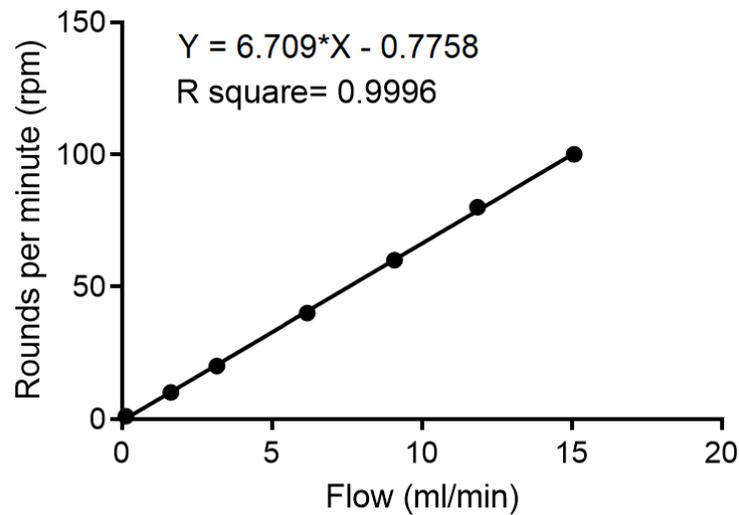


Figure A.1: Pump calibration

## A.2 Ozonation experiments

Table A.1 summarizes the ozone stock concentration and added volumes to the ground-water.

Table A.1: Ozone stock concentration and stock spiking volume

$O_3$ stock concentration [mg/L]	Added stock volume to 0.6 L [mL]
73.91	21.27
80.76	19.47

## A.3 Data and calculations

An Excel file with all data and calculations is handed in along with the thesis.

