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Treatment of per- and polyfluoroalkylsubstance (PFAS)-contaminated water using aeration foam collection

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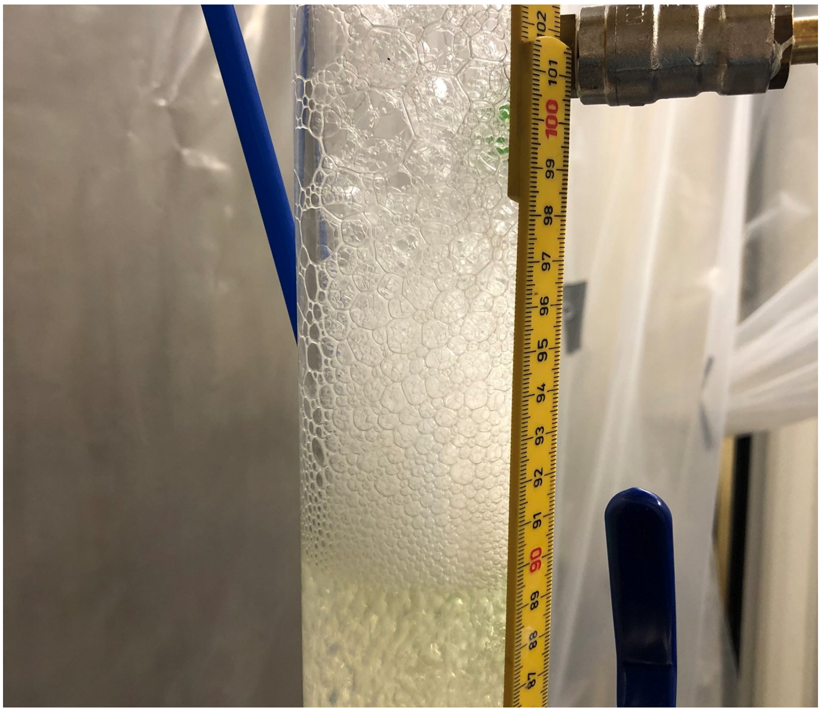

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Abstract

Landfills are potential sources for PFASs and treatment techniques for landfill leachate are urgently needed. Foam fractionation is an aeration technique which utilizes the tendency of PFASs to escape the liquid phase and build foam. The foam is harvested and with it the contamination. Landfill leachate from Hovgården, Uppsala Sweden contained PFASs of higher concentration than desired and investigations into whether foam fractionation could reduce PFASs amounts were initiated.

Landfill leachate containing sum PFASs of 5500 ng/L on average were aerated in two different aeration foam collection pilot set-ups for the research. The pilot set-ups were divided into two models: a batch pilot and a continuous pilot. The batch pilot was run for 60 minutes testing parameters such as column volume, air flow rate, dilution and using additives as NaCl, $FeCl_3$ and dish soap. The continuous pilot used contact times of 5, 10 and 20 minutes with constant air flow rate and column volume and no additives.

All batch experiments showed reduced concentrations of PFASs, from 62 up to 91%, with an average $\sum$PFASs removal efficiency of 77%. Air flow rates of 4 and 6 L/min were more effective than 2 L/min to reduce the amount of PFASs. Smaller volumes got higher removal efficiency. The dilution experiments showed mixed and somewhat contradictory results, where the non-diluted experiment had removal efficiency of $\sum$PFASs of average 77% while the 50% diluted had an average $\sum$PFASs removal efficiency of 84%. The experiment with the greatest dilution (75%) had the lowest average $\sum$PFASs removal efficiency as suspected, at 68%. Regarding additives, the experiments with added 0.155 and 0.313% NaCl in the leachate were most effective at removing PFASs. The dish soap and $FeCl_3$ additives also contributed to higher PFASs reduction. The experiment with the addition of dish soap had an average $\sum$PFASs removal efficiency of 88% compared to 77% without additives, and the highest concentration of $FeCl_3$ (0,09% of the leachate) had an average $\sum$PFASs removal efficiency of 85%.

All continuous experiments showed reduced reduced PFASs concentrations with $\sum$PFASs removal efficiencies ranging from 72 up to 94%, with an average of 86%. The majority of the PFASs were reduced within the first time steps for all experiments, but for the last amount to be removed the contact time needed to be longer. The column contact time of 20 min had the highest average $\sum$PFASs removal efficiency.

The conclusion is that PFASs are reduced during the treatment in the pilots and that the reduction is dependent on the chain length and functional groups of the substances, and increased with additives and increased air flow rate. The volume treated and the concentration of raw water also influenced the removal efficiency.

Keywords: PFAS, aeration foam collection, landfill leachate treatment, WWTP

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Referat

Deponianläggningar är potentiella källor av PFAS och teknik för att behandla lakvattnet behövs omgående. Skumfraktionering är en luftningsteknik som utnyttjar egenskapen hos PFAS att den uppgår i en skumfas istället för att vara kvar i vattnet. Skummet samlas in och med det även PFAS-kontamineringen. Lakvatten från Hovgårdens deponianläggning i Uppsala Sverige innehöll PFAS med högre koncentrationer än vad som eftersträvades. Frågan om luftning kunde vara ett framgångsrikt verktyg för att minska PFAS-kontaminering började undersökas.

Lakvatten innehållande en total PFAS koncentration på 5500 ng/L i genomsnitt luftades i två olika pilotuppsättningar, en satsvis och en kontinuerlig. Den satsvisa kördes under 60 minuter med testparametrar såsom kolonnvolym, luftflöde, utspädning och tillsatser som NaCl, $FeCl_3$ och diskmedel. Den kontinuerliga piloten använde kontakttider i kolonnen på 5, 10 och 20 minuter med konstant luftflöde och kolonnvolym.

Alla satsvisa experiment visade reducerade halter av PFAS, från 62 till 91%, med en genomsnittlig reducering av$\sum$PFAS på 77%. Luftflödeshastigheter på 4 och 6 L/min var effektivare än 2 L/min med att minska mängden PFAS. Mindre volymer lakvatten behandlat fick högre reduceringseffektivitet. Utspädningsexperimenten visade något motstridiga resultat, där experimentet utan utspädning hade en reduceringseffektivitet på $\sum$PFAS-medel 77% medan experimentet med 50% utspätt lakvatten hade en genomsnittlig reduceringseffektivitet av $\sum$PFASs på 84%. Experimentet med störst utspädning (75%) hade den lägsta genomsnittliga reduceringseffektivitet av $\sum$PFASs som misstänkt, på 68%. Gällande tillsatser var experimenten med 0,155 och 0,313% tillsatt NaCl i lakvatten mest effektiva med att avlägsna PFAS. Diskmedel och $FeCl_3$-tillsatser bidrog också till högre PFAS-reducering. Experimentet med tillsats av diskmedel hade en genomsnittlig reduceringseffektivitet av $\sum$PFAS på 88% jämfört med 77% utan tillsatser, och den högsta koncentrationen av $FeCl_3$ (0,09% av lakvattnet) hade en genomsnittlig reduceringseffektivitet av $\sum$PFASs på 85%.

Alla kontinuerliga experiment visade reducerade halter av $\sum$PFASs, med reduceringseffektivitet från 72 till 94%, med ett genomsnitt på 86%. Majoriteten av PFAS-innehållet reducerades inom det första tidssteget för alla experiment, men för att den sista mängden skulle reduceras behövde kontakttiden vara längre. Kolonnens kontakttid på 20 min hade den högsta genomsnittliga reduceringseffektiviteten av $\sum$PFASs.

Slutsatsen är att PFAS minskar under behandlingen i pilotanläggningarna och att minskningen beror på kedjelängden och den funktionella gruppen hos ämnet samt att reducering är störst med tillsatser och ökat luftflöde. Den behandlade volymen och koncentrationen av råvattnet påverkade också effektiviteten av behandlingen.

Nyckelord: PFAS, luftning, lakvatten från deponi, reningsverk

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Populärvetenskaplig sammanfattning

Vattnets väg genom samhället börjar med en vattenkälla, t.ex. grund- eller ytvatten. Vattnet renas och dricks, används i matlagning, tvätt, städning, disk och hygien och i slutändan hamnar det i avloppet. I alla användningsområden av dricksvattnet finns risk för kontaminering och avloppsvattnet kan komma att innehålla ämnen som inte går att rena bort med hjälp av konventionella metoder. När slammet som återstår efter avloppsreningen senare läggs på deponi finns föroreningarna kvar. På deponin tillkommer regnvatten som rinner genom deponimassorna och lakvatten bildas. Lakvattnet kan komma att innehålla just de föroreningar som användes i hemmen och industrin, och efter enklare rening rinner lakvattnet ut tillbaka till kretsloppets början: till grund- eller ytvattnet.

Kontamineringar som hamnar i avloppet är allt från tungmetaller till näringsämnen, och en ny grupp ämnen kallade PFAS, Per- och polyFluorerade AlkylSubstanser, förekommer numera allt oftare. PFAS är ytaktiva och mycket motståndskraftiga ämnen. De är både fett- och vattenavstötande och har därför använts i många hushållsprodukter som beläggningar till exempel i stekpannor, på kläder, i smink och i industrikemikalier så som brandskum. PFAS renas inte bort med traditionella metoder, bryts inte ner i naturen och ansamlas i levande organismer. PFAS tros vara tumörbildande, hormonstörande och farliga för alla levande organismer.

Denna studie syftar på att undersöka om PFAS kan reduceras i lakvatten genom att utnyttja att PFAS binder till ytor på vatten och gärna inte stannar i vatten. En kolonn med lakvatten luftades underifrån för att bilda bubblor där PFAS kunde fästa. Skummet som bildades skummades av med vakuumsug och målet var att fästa PFASen till skummet.

Två olika experimentuppställningar genomfördes: en i omgångar och en med kontinuerligt in- och utflöde. Experimenten i omgångar testade olika luftinflöde, kolonnvolymer, utspädning av lakvattnet samt om tillsatser av salt, järnklorid eller diskmedel kunde öka skumbildningen och reduceringen av PFAS. De kontinuerliga experimenten undersökte den kontakttid lakvattnet behövde i kolonnen för maximal PFAS-reducering.

Resultaten visade att alla försöken i omgångar hade en reduceringsförmåga på i genomsnitt 77%. Resultaten visade att högre luftflöden skapade större ytor för PFAS att fästa på. Det visades också att mindre volymer åt gången fick högre reducering av PFAS. Utspädningsförsöken visade motstridigt att en utspädning på 50% var bättre för reduceringen än outspätt lakvatten, men att en utspädning på 75% var klart värre. Tillsatserna hade en positiv effekt på reduceringen, där saltet med båda koncentrationerna testade var klart bättre än utan tillsatser. En reducering av 90-91% åstadkoms. Diskmedlet bidrog till en reducering med 88% jämfört med experimentet utan som hade 77%. Den högsta koncentrationen av $FeCl_3$ testad (0,09% av lakvattnet) hade en reduceringsförmåga på 85%.

De kontinuerliga försöken hade en reduceringsförmåga på i genomsnitt 86%. Majoriteten av föroreningen reducerades inom 25% av experimenttiden, men den sista andelen PFAS reducerades något senare. Kontakttiden i kolonnen som var bäst i genomsnitt var 20 minuter.

Slutsatsen landar i att PFAS reduceras i försöken och att reduceringen är beroende av kolkedjelängden samt den funktionella gruppen, att tillsatser och ökad luftning ökar reduceringen och att volym och startkoncentration också har inverkad på resultaten.

Abbreviations

- Ct - (Column) Contact time
- EPA - The United States Environmental Protection Agency
- EtFOSA - N-ethyl perfluorooctane sulfonamide
- EtFOSAA - N-ethylperfluorooctanesulfonamido acid
- EtFOSE - N-ethyl perfluorooctane sulfonamidoethanol
- EU - European Union
- FOSA - Perfluorooctanesulfonamide 1
- FOSAA - Perfluorooctane sulfonamidoacetic acid
- HPFHpA7 - H-perflouroheptanic acid
- ibid. - Latin: ibīdem, meaning: in the same place. Used when the same reference is used in two consecutive sentences.
- MeFOSA - N-methyl perfluorooctane sulfonamide
- MeFOSAA - N-methylperfluorooctanesulfonamido acid
- MeFOSE - N-methyl perfluorooctane sulfonamidoethanol
- PFAS - Per- and polyfluoroalkyl substance
- PFBA - Perfluoro-n-butanoic acid
- PFBS - Perfluorobutanesulfonic acid
- PFDA - Perfluoro-n-decanoic acid
- PFDoDA - Perfluoro-n-dodecanoic acid
- PFDoDS - Perfluorodecane sulfonic acid
- PFDS - Perfluorodecanesulfonic acid
- PFHpA - Perfluoro-n-heptanoic acid
- PFHpS - Perfluoroheptanesulfonic acid

- PFHxA - Perfluoro-n-hexanoic acid
- PFHxS - Perfluorohexanesulfonic acid
- PFNA - Perfluoro-n-nonanoic acid
- PFNS - Perfluorononane sulfonic acid
- PFOA - Perfluoro-n-octanoic acid
- PFOS - Perfluorooctanesulfonic acid
- PFPeA - Perfluoro-n-pentanoic acid
- PFPeS - Perfluoropentane sulfonic acid
- PFTeDA - Perfluoro-n-tetradecanoic acid
- PFTrDA - Perfluoro-n-tridecanoic acid
- PFUnDA - Perfluoro-n-undecanoic acid
- PF37DMOA - Perfluoro-3,7-dimethyloctanic acid
- SLV - The Swedish National Food Agency, Livsmedelsverket
- 4:2 FTSA - Fluorotelomer sulfonic acid
- 6:2 FTSA - Fluorotelomer sulfonate
- 8:2 FTSA - Fluorotelomer sulfonate

Preface

This thesis was written as the conclusive part of the master program Environmental and Water Engineering at Uppsala University and the Swedish University of Agricultural Sciences (SLU), holding 30 credits. The research was supported by Uppsala Vatten och Avfall AB, providing the PFAS treatment technology, equipment, water analyses, and access to Bäcklösa drinking water treatment plant. Supervisor was Philip McCleaf from Uppsala Vatten och Avfall AB and subject reader was Lutz Ahrens from the Department of Aquatic Sciences and Assessment.

I would like to take the chance to wholeheartedly thank my supervisor and subject reader Philip McCleaf and Lutz Ahrens for mentoring and guiding me through the entire project. Their dedication to the research is evident by their perseverance and goodwill as well as their dedication to answer questions and contribute with thoughts and knowledge in the entire process. Thank you for always being there.

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Uppsala, September 2020

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Contents

1 Introduction

Landfills are potential sources for PFASs and treatment techniques for landfill leachate are urgently needed. Foam fractionation is an aeration technique which utilizes the tendency of PFASs to escape the liquid phase and build foam (Meng, Deng, Maimaiti, et al. 2018). The foam is harvested with a vacuum, and with it the contamination is captured.

The PFASs spread through the everyday life of people through clothes, make-up, kitchen utensils, drinking water or sewage and are found almost everywhere (US EPA 2016). PFASs are difficult to control and they accumulate in sewage sludge and later in landfills (ibid.). The effluent of affected landfills contains high concentrations of PFASs that cannot be removed in the traditional effluent treatment (Thompson et al. 2011). This contributes to the pollution spreading further into the ecosystem. Cutting off the inflow of the substances in to the system is crucial, but since the substances are widely spread, new treatment techniques of lechate are also needed immediately.

At Hovgården landfill, in Uppsala Sweden, high concentrations of PFASs have been observed in the effluent lechate from the site. Foam in the on-site aeration biological treatment step has been suspected of containing PFASs, but no targeted treatment of the PFASs exists on site at present time.

1.1 Aims and research questions

The aim of the thesis work is to find out if aeration foam collection can be a successful method of removing PFASs and decrease volumes of PFAS-contaminated water. The aim is also to aerate a one meter column of contaminated water and to see if the PFASs will enter into a foam phase. The foam phase that may contain PFASs is easier to remove than when PFASs are bound in the liquid, and the foam removed collects the PFASs for separate treatment of a smaller volume.

1. Does aeration foam collection reduce PFASs concentrations in the specific leachate from Hovgården?
2. Do the perfluoroalkyl chain length and functional group have an influence on the removal efficiency?
3. Is the PFAS removal influenced by additives such as salt, iron chloride or dish soap or other parameters such as air flow rate, column volume and raw water concentration?

1.2 Hypothesis

The hypothesis is that the air flow rate into the column is a crucial factor of how much PFASs that will enter a foam phase. Adding coagulants and other surfactants might increase foam build-up, and the presence of foam may be dependent on salt levels (ionic strength), column water volume, concentrations of leachate and column contact time.

After setting up the column, it is clear that some foam samples can be taken.

2 Background and theory

2.1 Introduction to PFASs

According to the U.S Environmental Protection Agency (EPA)(2016) per- and polyfluoroalkyl substances (PFASs) are a large group of synthetic chemicals that includes perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), GenX (trade name), and many other chemicals. The manufacturing of the PFAS substances began in the mid 1900s, and PFASs are now found everywhere on the globe (US EPA 2016). Often when referring to PFAS, it is really the PFOA or PFOS substances that are intended. The two substances are very well researched and distributed in the environment as well as in households (ibid.). PFASs can be found in household items such as food packaging, stain- and water-repellent fabrics, non-stick products, cleaning products and fire-fighting foams (ibid.). A study made with the perspective of nordic environment concluded that sewage sludge and landfills had high concentrations of PFASs and residues. PFOS and PFOA dominated in the sewage sludge, and the highest levels of PFAS contaminants were found in landfill effluent (Kallenborn, Berger, & Järnberg 2004).

The Swedish national food agency, Livsmedelsverket(SLV)(2020), states that the European Union (EU) have since 2008 banned the usage of PFOS and substances that can be degraded to PFOS. The PFOA will be banned from year 2020 and onward (SLV 2018). Some exceptions have been made, and other types of PFASs have replaced PFOS and PFOA (SLV 2020).

The U.S. EPA (2016) claims that the question if PFASs affect human health is still unanswered, however there is evidence that shows health impacts on animals exposed to PFOA and PFOS. PFOA and PFOS are the most studied substances within the PFAS group and animals exposed to them while tested in laboratories showed effects on reproductivity, development, cholesterol levels and the frequency of tumors (US EPA 2016).

(a) *PFOS*

(b) *PFOA*

Figure 1: *Structural formulas of two PFASs (SLV 2020)*

According to the Swedish SLV (2020) PFOS is a substance that is persistent, bio accumulative, toxic and is not degraded in the environment. The molecular structure of PFOS is seen in Figure 1a. Since the substance is prohibited since 2008, some of the usage of PFOS has been replaced with the other, well researched form PFOA. Some other forms that replace PFOS will later degrade into PFOA (SLV 2020). PFOA is not degraded in nature. The structure of it can be seen in Figure 1b. With the exception of PFOA, the health effects of the perfluorinated carboxylic acid (PFCAs) group that PFOA belongs to is not clear (ibid.). The EU have a list of potentially harmful substances, where PFCAs are listed (ibid.). The length of the carbon chain in the chemicals determines how persistent and biodegradable the substances are, where the long chains are considered very persistent and bio-accumulative (ibid.).

According to SLV's guidelines (2018) drinking water containing 0-90 ng/liter PFASs is completely safe to drink. If the water contains over 90 ng/L it is not directly harmful and is potable but the levels need to be lowered to under 90 ng/L as soon as possible (SLV 2018). If the water contained dosages of over 900 ng/L it should not be used for drinking or preparing food, but it can still be used for washing dishes, taking baths and showers (ibid.).

2.2 Chemistry behind PFASs

The carbon fluorine bond (C-F bond) is a large part of the molecular structure behind the PFAS, as seen in Figure 1. One reason why the molecule is very persistent is its bond between carbon and fluorine atoms. Because of the electronegativity difference between carbon and fluorine (2.5 vs 4.0), C-F bonds are highly polar, which contributes to a bond strength (Lemal 2004).

In a summary report Franke et al. (2017) summarizes characteristics of PFAS. They state that the chain of the PFAS molecule is based on a partly (per-) or fully (poly-) florinated carbon chain. The chain is attached to a head of a polar functional group which is hydrophilic, whilst the chain is hydrophobic and non-polar (ibid.). This configuration is the base of any surfactants, for example used in dish soap. PFASs alike the dish soap surfactants are also surface active substances. A micelle that emulgates fat and water uses the same principle, shown in Figure 2 (SuperManu 2007).

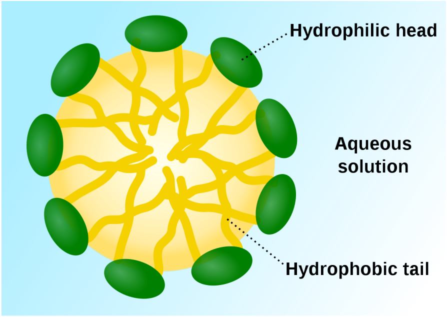


Figure 2: *Scheme of a micelle formed by phospholipids in an aqueous solution(ibid.).*

Regarding the length of the chains, PFCAs with chains longer than eight (the length of PFOA) are considered having longer chains. The PFOS is also considered a long chained substance among the PFSAs. The longer chained PFASs can be reduced to shorter chained PFASs, and thus the shorter chained PFASs are considered harder to eliminate, since they can not degrade and the C-F bond still is very strong.

PFAS is not easy to detect or to work with and the substance causes trouble on several levels, according to Kallenborg et.al (2004). Technology of liquid chromatography is needed to detect the group of substances, therefore it is hard to monitor levels on a long time scale. The PFAS residuals are both lipophobic and hydrophobic and usually adsorb strongly on natural surfaces. The strong C-F bond in the molecule also makes the substance almost indestructible. All previously mentioned traits make it hard to use already existing risk assessment tools used for conventional persistent organic pollutants (ibid.).

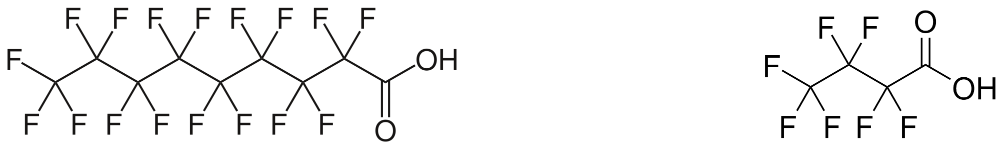
Table 1 lists the eleven most important substances to monitor according to Swedish drinking water guidelines (SLV 2018).

Table 1: *11 most important PFASs and precursors according to Swedish drinking water guidelines. Gray illustrates PFCAs, red symbolizes PFSAs and blue PFASs precursors. The length of the carbon chain that the functional groups are attached on (chain length) is shown in the third column.*

Substance analyzed	**Full name**	**Carbon chain length**
PFBA	Perfluoro-n-butanoic acid	C3
PFPeA	Perfluoro-n-pentanoic acid	C4
PFHxA	Perfluoro-n-hexanoic acid	C5
PFHpA	Perfluoro-n-heptanoic acid	C6
PFOA	Perfluoro-n-octanoic acid	C7
PFNA	Perfluoro-n-nonanoic acid	C8
PFDA	Perfluoro-n-decanoic acid	C9
PFBS	Perfluorobutanesulfonic acid	C4
PFHxS	Perfluorohexanesulfonic acid	C6
PFOS	Perfluorooctanesulfonic acid	C8
6:2 FTSA	Fluorotelomer sulfonate	C6

2.2.1 PFCAs

The carbon chains of PFASs have different lengths and can be divided into groups based upon their length property. Perfluorinated carboxylic acids (PFCAs), or perfluorocarboxylic acids are compounds of the formula CnF(2n+1)CO2H. One of the most common PFCAs is PFOA, and is considered a long chained PFCA. Figure 3 shows two other structures of PFCAs.



(a) *PFNA* ***(b)*** *PFBA*

Figure 3: *Structural formulas of two PFCAs.*

2.2.2 PFSAs

Perfluorosulfonic acids (PFSAs) are chemical compounds of the formula CnF(2n+1)SO3H. The substance PFOS is the most common example of this group. Figure 4 shows the structure of two examples of PFSAs.

(a) *PFSA* ***(b)*** *PFHxS*

Figure 4: *Structural formulas of two PFSAs.*

2.2.3 PFAS precursors

The last main group discussed in this thesis is the group of all precursors. The precursors are substances that will degrade into a PFAS classified substance through a reaction. Two examples of precursors that break down into PFOS is shown in Figure 5.

(a) 6:2 FTS

(b) FOSA

Figure 5: *Structural formulas of two precursors that break down to PFOS.*

2.3 Coagulation, flocculation and flotation techniques

Coagulation and flocculation are well used and traditional methods in water treatment, where the techniques reduce the amount of particles present in the water. Coagulation is when a chemical is added to the water to neutralize the charge of individual organic particles present. Usually a metal salt like ferric chloride ($FeCl_3$) or aluminum sulphate ($Al_2(SO_4)_3$) is added to the water. Polymers can also be used for the same purpose. The chemicals reduces the repulsive forces between particles and the attractive forces can dominate so that the particles can attach to each other to form larger groups of particles (called flocs). As the flocs become larger they can sink, or if air bubbles are enmeshed in the floc they can rise to the surface. Coagulation is the process of adding a neutralizing substance to the water and mixing it, and flocculation is the process to make the particles lump together and form larger particles. Together they work as a treatment method. (IWA publishing n.d.)

Dissolved air flotation (DAF) is a technique that transfers the flocs to the surface by attaching air bubbles to the floc (Ratnayaka, Brandt, & Johnson 2009). The floc surfaces and floats until it is skimmed off to become sludge (ibid.).

Studies have shown that traditional waste water treatment methods are unable to remove PFASs to a sufficient level (Thompson et al. 2011). A study in Queensland Australia showed PFASs levels through two types of treatments. The first treatment plant utilized adsorption and filtration methods with ozonation, whilst the second used membrane processes and advanced oxidation. Neither of the plats managed to remove PFASs to a sufficient level, although some levels of PFOS were reduced following coagulation and dissolved air flotation/sand filtration (DAFF) (ibid.). According to reviewers of the original report, the lack of effectiveness of DAF was generally ascribed to the low volatility of PFAS. However, the surfactant nature of the compounds suggests that polyelectrolytes (PEs), especially of the hydrophobic variety, would assist in aggregating PFAS on the air/water interface, and thus improve performance (Bolto & Xie 2019).

Meng et al. (2018) speculates whether aeration could be a promising treatment step for PFASs, partly due to the strong surface activity of PFOS. Aeration is considered a traditional waste water treatment method. According to Meng et al. (2018) adsorption of PFOS on some adsorbents, with the assistance of air bubbles, exploits the tendency of strong surfactants to accumulate at air-water interfaces (Meng, Deng, Lu, et al. 2014),(Meng, Deng, Wang, et al. 2017).

2.4 Previous scientific attempts at recovery of PFASs

2.4.1 Aided foam flotation for PFOS and PFOA

Lee et. al (2017) successfully recovered and separated PFOS and PFOA surfactants using foam flotation, aided by metallic activators. The metallic activators used were Al(III), Fe(III), La(III), Ca(II), Fe(II) and K(I). The removal efficiency of PFOS were highest using Fe(III) followed by the other trivalent compounds. High levels of Fe(III) and PFASs enhanced surfactant removal. An efficiency as high as >99% removal was achived when 11.4 mM Fe(III) was added to the contaminated water and exposed to flotation for 5 min. The removal was also pH dependent, and experiments with low pH were more successful at removing PFASs. At pH 6 or higher, no significant removal was observed. The maximum removal occurred at the lowest observed pH: 2.3. Higher concentrations of PFOS or PFOA led to higher reduction because of higher surface activity (Lee et al. 2017).

The reason that experiments with high pH were less effective at removing the surfactants was that the hydroxide ion (OH^-) started to bind to the Fe(III), instead of the PFOS and PFOA (ibid.). The OH^- and Fe(III) formed ferric hydroxo species that lowered the removal (ibid.). Although it seemed low pH was better for recovery, a higher pH at the level 7 in the separated scum could recover as much as 84-91% of the PFASs (ibid.).

Experiments were conducted with a batch-type foam flotation in a 30 cm long and 4 cm wide column (volume of 502 cm^3). A diffuser with a pore size of 25-50 micrometer. The air flow rate was 7.5 L/min, and was purified with glass wool, ascarite and distilled water (removing particles, carbon dioxide and controlling humidity). Regarding the surface tension, Lee et.al. states that the surface tension of the solution was determined by a du Nouy interfacial tensiometer using the standard ring method (ASTMD1331-89. All test were repeated three times (ibid.).

2.4.2 Areation foam collection of PFAS

A study where aeration and foam collection was combined was conducted by Meng et. al (2018). The study used a water column with PFAS contaminated water. The PFOS removal reached 96% after 2 hours duration with an air flow rate of 75 mL/min. Meng et al. (2018) state that increased aeration flow rate, ionic strength concentration of co-existing surfactant, as well as decreasing the initial PFOS concentration, increased the removal percentage of PFOS by increasing the foam volume, but reduced the enrichment of PFOS in the foam. When using other hydrocarbon surfactants in the test, the reduction of PFOS was over 99.9% when conducting the aeration foam collection principle for two hours. The enrichment factor calculated exceeded 8400 under the same conditions (Meng, Deng, Maimaiti, et al. 2018).

The study also shows that the technique was less effective on PFASs consisting of shorter chains, because of their lower surface acitivity (Meng, Deng, Maimaiti, et al. 2018). Meng et al. (ibid.) also state that the technique of aeration foam collection was effective when treating PFAS contaminated wastewater, even with high concentrations.

The study was conducted using a column with a total volume of 600 mL, that was 750 mm high. The air diffuser on the bottom of the column had a diameter of 10 micrometer. Some parameters were held constant during the experiments. PFOS concentration, pH and aeration flow rate were set at 0.378 mmol/L, 6 and 75 mL/min, respectively (ibid.).

The influence of the following parameters were tested: pH (adding NaOH and HCl), air flow rate, ionic strength (using NaCl), initial PFOS-concentration, co-existing hydrocarbon surfactant (adding alkyl polyglycosides (APGs)) and foam depth.

2.5 Process at and samples from municipal landfill

The municipal landfill Hovgården is run by Uppsala Vatten och Avfall AB and is a waste facility with both active and final landfill, intermediate storage of sludge and sorting of waste. A map of the facility can be found in Appendix 8.1.

Drainage pipes at the bottom of the landfill collects all leachate formed on site and forward it to the treatment plant. The leachate that comes from the sludge storage is passed through septic treatment, then transferred to sedimentation basins and later transferred to the treatment plant.

The treatment plant was last renovated in 2007 and the leachate is mechanically treated, then passed through a purification step, a biological step and a polishing step. The mechanical treatment step consists of aeration of the leachate that oxidizes iron, manganese and some of the organic substances. After the oxidation, the water passes through lamella where particles sediment, and is after that taken to the bio step. The biological treatment consists of two parallel lines, both lines consisting of two basins. One of the basins contains large surface area carriers for the microbes to grow on, and the other one does not contain carriers. The amount of organic substances is reduced and an oxidation of ammonium nitrogen to nitrate nitrogen occurs in the biological treatment step. The biological step is followed by a sedimentation basin and two large parallel polishing basins. The last step of the entire treatment process is a large aerated basin to increase oxygen levels, and after this the waste water is let out to the recipient lake Funbosjön, via streams Hovgårdsbäcken, Lissån och Tomtaån. The total retention time for the leachate through the plant is 16 hours and in the ponds about nine days.

Observations regarding foam building at the aerated biological step were made by employees at Uppsala Vatten. Tests of the foam were conducted and the results showed that the foam contained PFASs. Several tests of the leachate and treatment process water have been made by Uppsala Vatten, and material and results of the testing are shown in Appendix 8.2.

The municipal landfill Hovgården outside Uppsala Sweden, had the lechate water sampled for PFASs contamination. The procedure was done by the owning company Uppsala Vatten och

Avfall AB in the years 2014-2019. Samples were taken with different frequency, intervals and quantity at seven locations at the site. Samples were also taken during all different seasons of the year. To get some kind of PFAS representation of the landfill, yearly mean values were calculated for each sampling point. Below is a list of the sampling points and all data of PFASs detected.

- D0 - Untreated leachate from the landfill
- S0 - Water from sludge cell, septic basins and sedimentation ponds
- R1 - Inlet to treatment plant
- R2 - Inlet to bio reactor
- R3 - Outlet of bio reactor line 1
- R4 - Outlet of bio reactor line 2
- A1 - Treated water from outlet of the ponds after the treatment plant

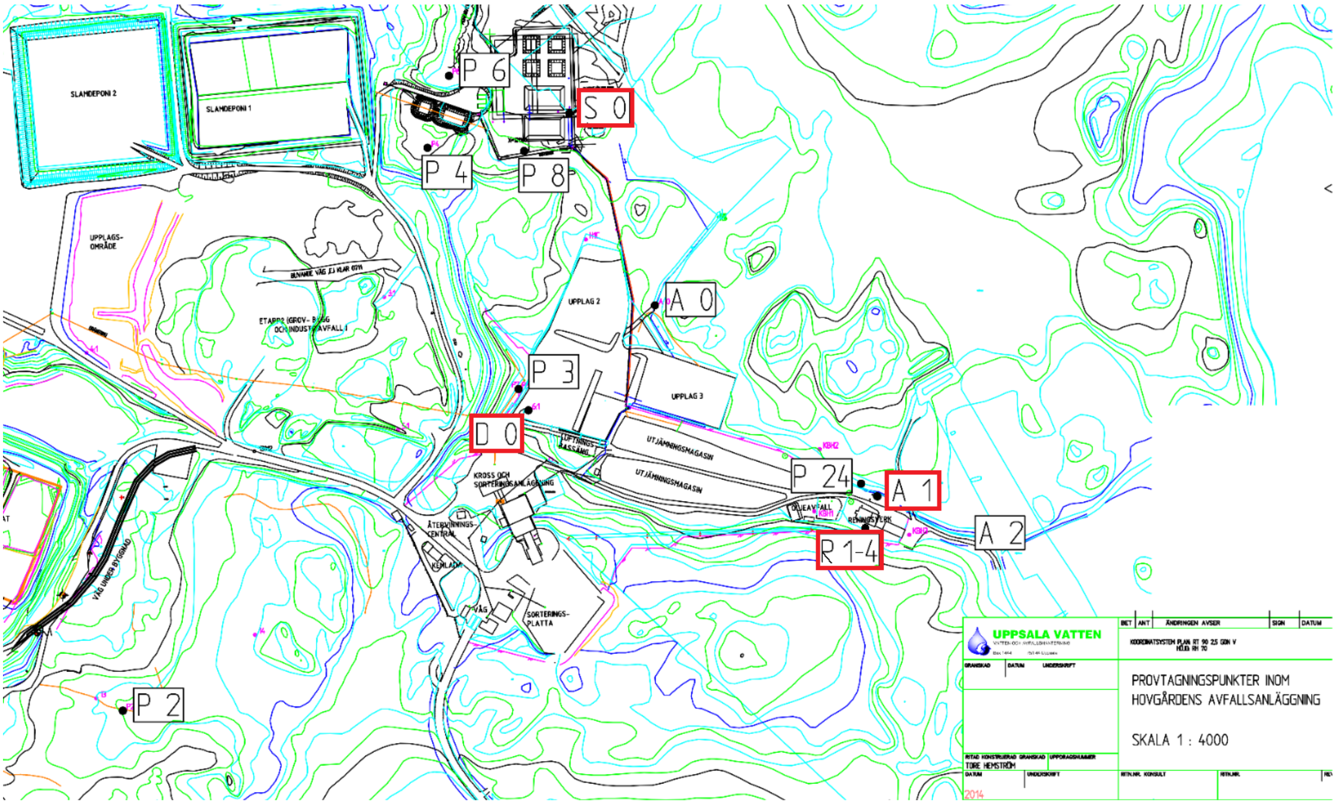
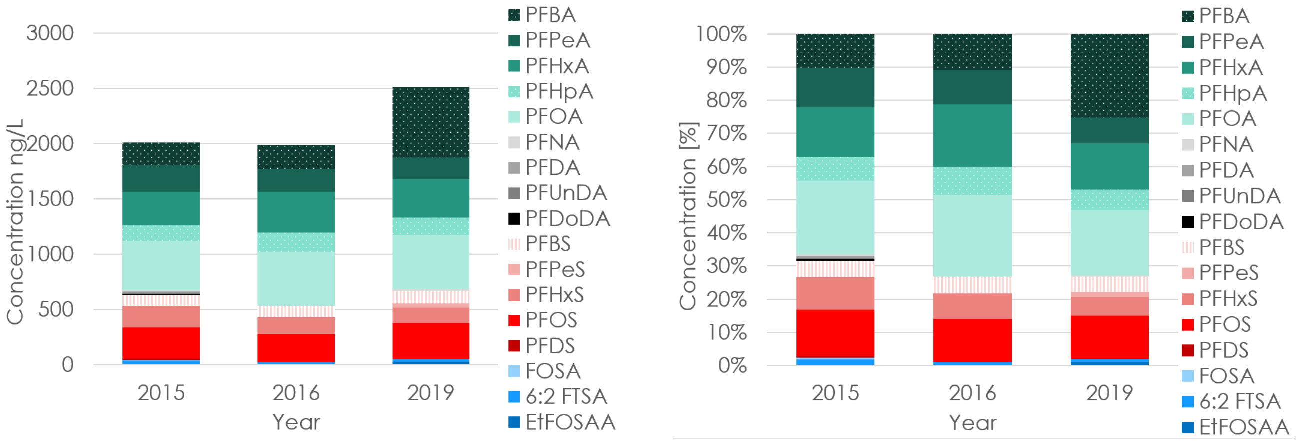


Figure 6: *Sample points at landfill site. Cropped and highlighted map. The original map was made by the owning municipal company Uppsala Vatten och Avfall AB in 2014.*

17 different PFASs and precursors are shown in Figures 7 and 48. The same color code is used for all figures of the sampling site. The green and gray tones that colors PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFUnDA and PFDoDA belong to the group PFCAs. The red tones that colors PFBS, PEPeS PFHxS, PFOS and PFDS belong to the group PFSAs. The blue color coded substances FOSA, 6:2 FTSA and EtFOSAA represent precursors.

The raw water used in all experiments is taken at sampling point R1. Data from previous sampling points S0 and D0 as well as following steps R2-R4 can be found in Appendix 8.2. R1 is equivalent to the incoming water of the treatment plant. Shown in Figure 7 are yearly mean levels from the years 2015, 2016 and 2019. Concentration of total PFASs varies between 2000-2500 ng/L, the majority of which are PFCAs.



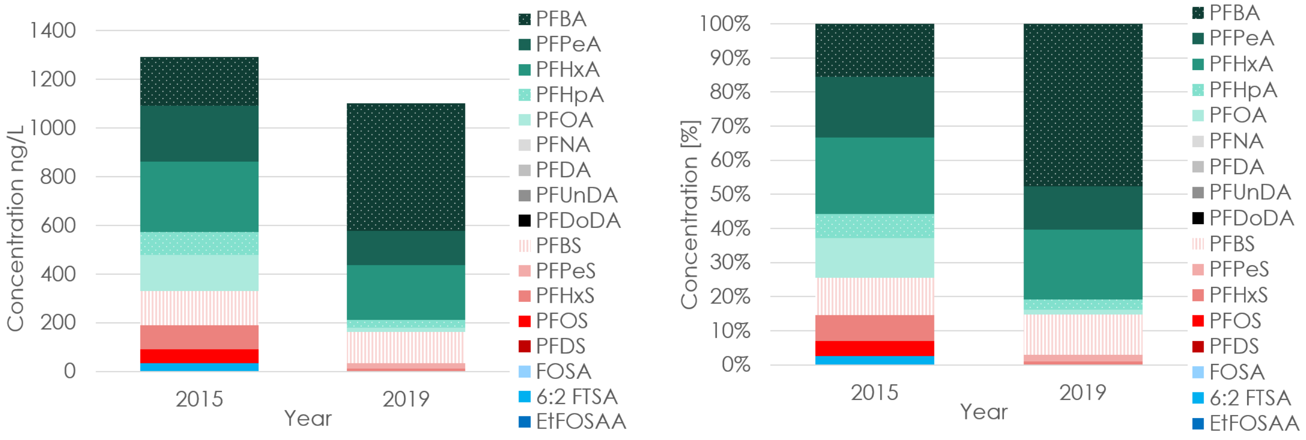
(a) *Concentration distribution [ng/L]*

(b) *Percent distribution [%]*

Figure 7: *Distribution of PFASs from sample point R1 at the inlet of the treatment plant.*

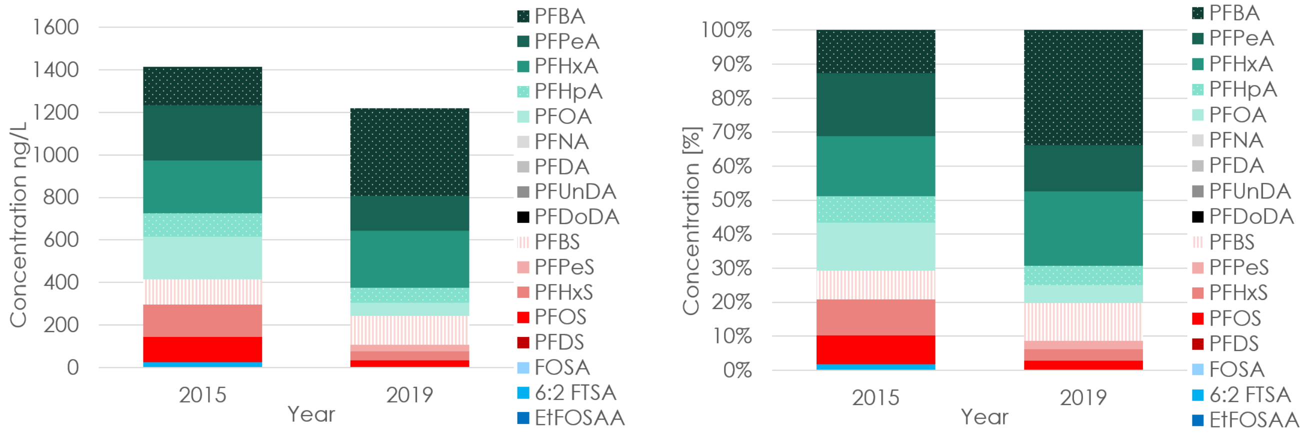
The water later transfers to the biological aerated basins of step R2 and R3. The figure of data collected in the inlet of the bio reactors R2 is inserted into Appendix 8.2.

The water at sampling point R3 and R4 has been passed through the aerated biological step. One out of the two basins in each steps has added bio carriers for greater surface area. From the look of the results in Figures 8 and 9 the both basins contain a very similar amount of PFASs. It seems as R3 has higher reduction of PFASs, 1100-1300 ng/L instead of 1200-1400 ng/L. Looking at the graphs, R3 have a smaller amount of PFOS and PFBS, but have higher levels of PFBA and 6:2FTSA than R4. When looking at the two diagrams, one can get a sense of the measuring errors that occurs, the variations of treatment efficiency and other factors that also impact the other samples but are harder to spot, since in theory they should be the same.



(a) Concentration distribution [ng/l] *(b) Percent distribution [%]*

Figure 8: *Distribution of PFASs from sample point R3, found at the outlet of the bio reactor line 1.*



(a) Concentration distribution [ng/l] *(b) Percent distribution [%]*

Figure 9: *Distribution of PFASs from sample point R4, found at the outlet of the bio reactor line 2.*

When roughly comparing sampling points R1 to R3 and R4 the removal of PFASs inside the treatment plant is shown. At R1 mean concentration levels were at 2000-2500 ng/l, and at R3 and R4 they were approximately 1100-1400 ng/l. That is translated roughly into a removal efficiency of about 44-45%.

The question of where in the process the contamination is removed and where the substances end up is unfortunately not answered and is out of the boundaries of this project. Further testing on sludge, vegetation and ponds would be necessary to answer that question.

3 Material and methods

3.1 PFAS target analysis

Below in Table 2 are all PFASs tested in accredited laboratory (company ALS). The substances focused on in the study is highlighted with bold font.

Table 2: *Table of all PFASs and precursors tested in ALS's laboratory. Gray illustrates substances of PFCAs, blue illustrates PFASs precursors and red symbolizes PFSAs. In the column to the left the report limit is shown, which represents the lowest level the lab will report.*

Substance analyzed	**Full name**	**Report limit [µg/L]**
PFBA	**Perfluoro-n-butanoic acid**	0.01
PFPeA	**Perfluoro-n-pentanoic acid**	0.01
PFHxA	**Perfluoro-n-hexanoic acid**	0.01
PFHpA	**Perfluoro-n-heptanoic acid**	0.01
PFOA	**Perfluoro-n-octanoic acid**	0.01
PFNA	**Perfluoro-n-nonanoic acid**	0.01
PFDA	**Perfluoro-n-decanoic acid**	0.01
PFBS	**Perfluorobutanesulfonic acid**	0.01
PFHxS	**Perfluorohexanesulfonic acid**	0.01
PFOS	**Perfluorooctanesulfonic acid**	0.01
6:2 FTSA	**Fluorotelomer sulfonate**	0.01
PFAS sum 11	-	-
PFUnDA	Perfluoro-n-undecanoic acid	0.01
PFDoDA	Perfluoro-n-dodecanoic acid	0.01
PFTrDA	Perfluoro-n-tridecanoic acid	0.025
PFTeDA	Perfluoro-n-tetradecanoic acid	0.025
PFPeS	**Perfluoropentane sulfonic acid**	0.01
PFHpS	**Perfluoroheptanesulfonic acid**	0.01
PFNS	Perfluorononane sulfonic acid	0.01
PFDS	Perfluorodecanesulfonic acid	0.01
PFDoDS	Perfluorodecane sulfonic acid	0.025
4:2 FTSA	Fluorotelomer sulfonic acid	0.01
8:2 FTSA	Fluorotelomer sulfonate	0.01
FOSA	**Perfluorooctanesulfonamide 1**	0.01
MeFOSA	N-methyl perfluorooctane sulfonamide	0.050
EtFOSA	N-ethyl perfluorooctane sulfonamide	0.050
MeFOSE	N-methyl perfluorooctane sulfonamidoethanol	0.025
EtFOSE	N-ethyl perfluorooctane sulfonamidoethanol	0.025
FOSAA	Perfluorooctane sulfonamidoacetic acid	0.01
MeFOSAA	**N-methylperfluorooctanesulfonamido acid**	0.01
EtFOSAA	**N-ethylperfluorooctanesulfonamido acid**	0.01
HPFHpA	7H-perflouroheptanic acid	0.01
PF37DMOA	Perfluoro-3,7-dimethyloctanic acid	0.01

3.2 Chemicals and materials

Ultra pure water (Milli-Q-water) was used for dilutions during the experiments, it was obtained at Uppsala Vatten's and SLU's laboratories. Regular tap water was used to rinse bottles and hoses and to disinfect pH and conductivity electrodes a chlorine solution of 1% was used.

Dish soap was used for batch experiments testing surfactants. The dish soap with marketing name Yes contained 15-30% anionic surfactants, 5-15% nonionic surfactants, methylisothiazolinone, phenoxythanol and perfume. A more detailed list of ingredients can be found on the manufacturer's website and is inserted in Appendix 8.3.

Table salt with iodine, NaCl, was used for batch experiments testing ionic strength. The ingredient list was NaCl, iodine (5mg/100g, 0,005%) and lump preventants (E535).

For batch experiments adding coagulants, Iron chloride ($FeCl_3$) was used. The sales name of the product is Kemira Pix 311, and it contains 35-45% $FeCl_3$.

The materials used was a scale of model PB602-S/FACT of brand Mettler Toledo. The scale measured maximum 610g with error 0.1 g and minimum 0.5 g with error 0.01g. An air diffusing membrane of model Xylem Silver Series II aeration membrane was inserted at the bottom of the column. Oil free compressed air was fed to the aeration membrane. A peristaltic pump of brand Watson Marlow, a vacuum pump, a pH-meter, a conductivity instrument, magnetic sterrers, plastic sampling bottles, silicone hoses, pressure vents and other lab material such as safety material and laboratory glass were used in the experiments. The pilot column itself was made by employees as Uppsala Vatten AB and consisted of a clear acrylic plastic pipe with metal outlet valves.

3.3 Leachate collection

Leachate water was collected for the experiment at sampling point R1 at the treatment plant of landfill Hovgården using a manual action suction pump. The landfill leachate was transferred to 25 liter plastic containers that were were transported to the room containing the pilot column and kept at room temperature, approximately 18 C°. The containers were shaken before the start of each experiment. In Appendix 8.4 there is a table displaying the different containers used, as well as harvesting date and times.

3.4 Experimental design

3.4.1 Aeration foam collection batch pilot

The column volume content was regulated by measuring the water level from a mounted measuring scale on the column. The initial measurement was wrong, and this lead to the water column level being 1.04 m instead of exactly 1.00 m. The column water level is rounded to 1 m in the rest of the report. When the column water level was at 1.04 m (1m), the volume of the column was 2.38 L. The design of the column for the batch experiment is showed in Figure 10.

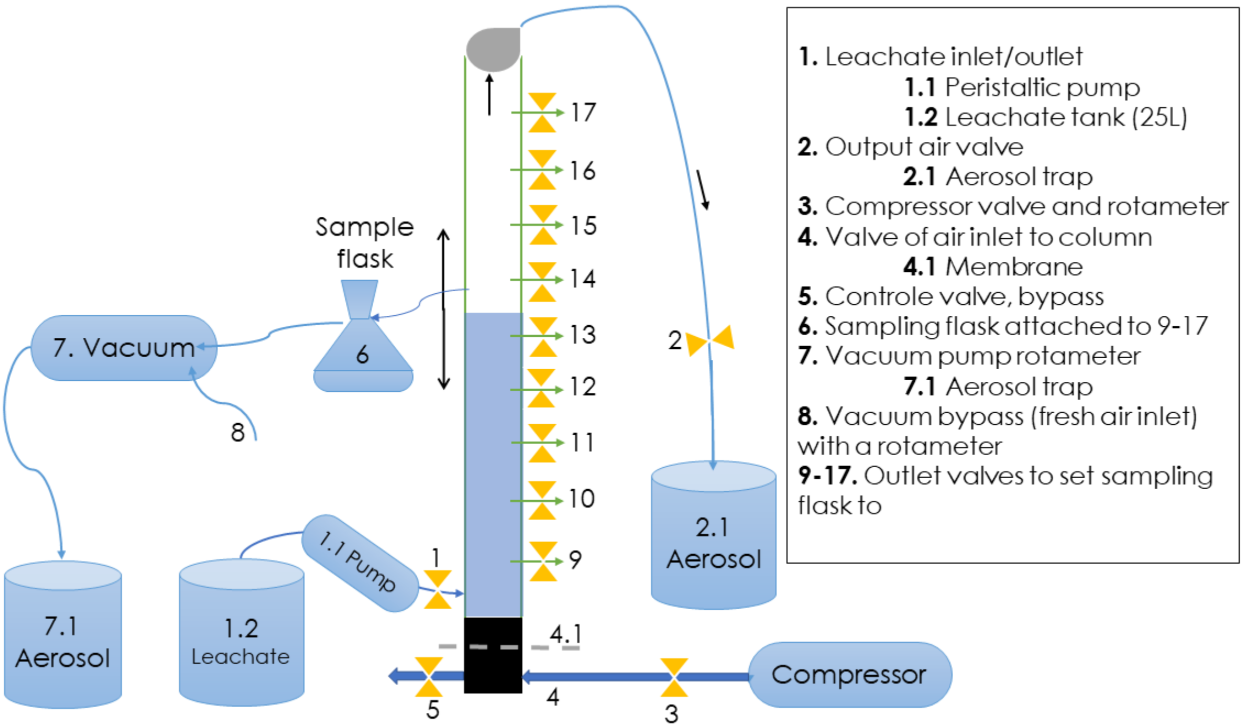


Figure 10: *Pilot schematics showing batch model's functions.*

The procedure of how each batch experiment was conducted is explained as the following:

- A protocol of all data that had to be collected was prepared. Date of water harvesting and place as well as date when equipment was cleaned was noted. This protocol later gives information about all samples, volumes, weights, times and foam measurements.
- Aerosol traps [2.1] and [7.1] were filled with tap water. Previous testing showed that no aerosols from the pilot escaped into the traps, but they were left as a safety measure.
- The column was filled with test water (leachate) to a specific level using the peristaltic pump. The water level was elevated above wished level in the column and then water for raw water sample and pH, temperature and conductivity sample was taken from vent [9] so that the water level was lowered to the correct level. The samples taken in this way were considered more representative of the content of the column.
- The sampling flask [6] with vacuum tube was attached to adequate vent above water level.
- All vents necessary to aerate the column were opened and the experiment timer was started. The compressor was started and rotameter [3] was set to a fix air flow rate and rotameter [7] for the same vacuum. This step had a time efficiency factor to consider, since the experiment timer and the aeration of the column should start at the same time.
- Samples of both foam and column water were taken at 5, 10, 20, 40 and 60 minutes from start.
  - The column water samples were taken from vent [9] at the sampling time.

  - First 5 ml was taken and washed out to rinse the vent, and then another 5 ml was taken as the sample.
  - The 5 ml were transferred to a 250 ml bottle of known weight and then diluted.
  - The weights of the undiluted sample and then the diluted samples were noted in the laboratory protocol.
  - All samples were immediately diluted with MilliQ-water.

  - The foam was harvested continuously with vacuum since the last sampling time. Each sample represents a longer time period, from start to given time step. For example F5 equals all foam harvested between 0-5 min.
  - At the sampling time the flask was weighed with the sample and then emptied into a 250 ml sample bottle of known weight.
  - Before the foam flask was reattached it was rinsed with tap water.
  - The foam samples represent a longer time interval in between the sampling times, while the column water was taken precisely at the certain time.

- When time was at 60 minutes, one last column water sample was taken as previously, the air flow and vacuum were shut off and water level without air was noted. When emptying the column, an undiluted sample of 250ml was taken from the column and water for pH, conductivity and temperature measurements was saved.

- The column was after this filled with tap water to get a rinsing effect and to prevent precipitation on the inside of the column to harden.

- Samples of the water trap [7.1] and sometimes also [2.1] was taken.

3.4.2 Aeration foam collection continuous pilot

The continuous pilot set-up was similar to the batch set up, seen in Figure 10, but used the principle of continuous flow through with counter-current air flow. How the pilot continuous model was set up is shown in Figure 11 and 12.

The inflow into the column was determined with a peristaltic pump. The outflow was a direct response to the inflow through a valve at the very bottom of the column attached to an elevated silicone hose. The hose was elevated to a level so that a water column of approximate 1 m was achieved. The hose was directed so air could enter the opening to achieve a laminar flow. The direction, elevation and amount of air let in to the hose determined the flow during the experiment, and parameters could be altered to improve flow. Another important part of the experiment setup was a bubble trap placed on the exit water valve inside the column. The bubble trap is illustrated in Figure 12. When laminar flow is achieved due to the bubble trap, the flow of the input and output can be measured by volume over time. When volume over time has been measured a measurement of column contact time is also available.

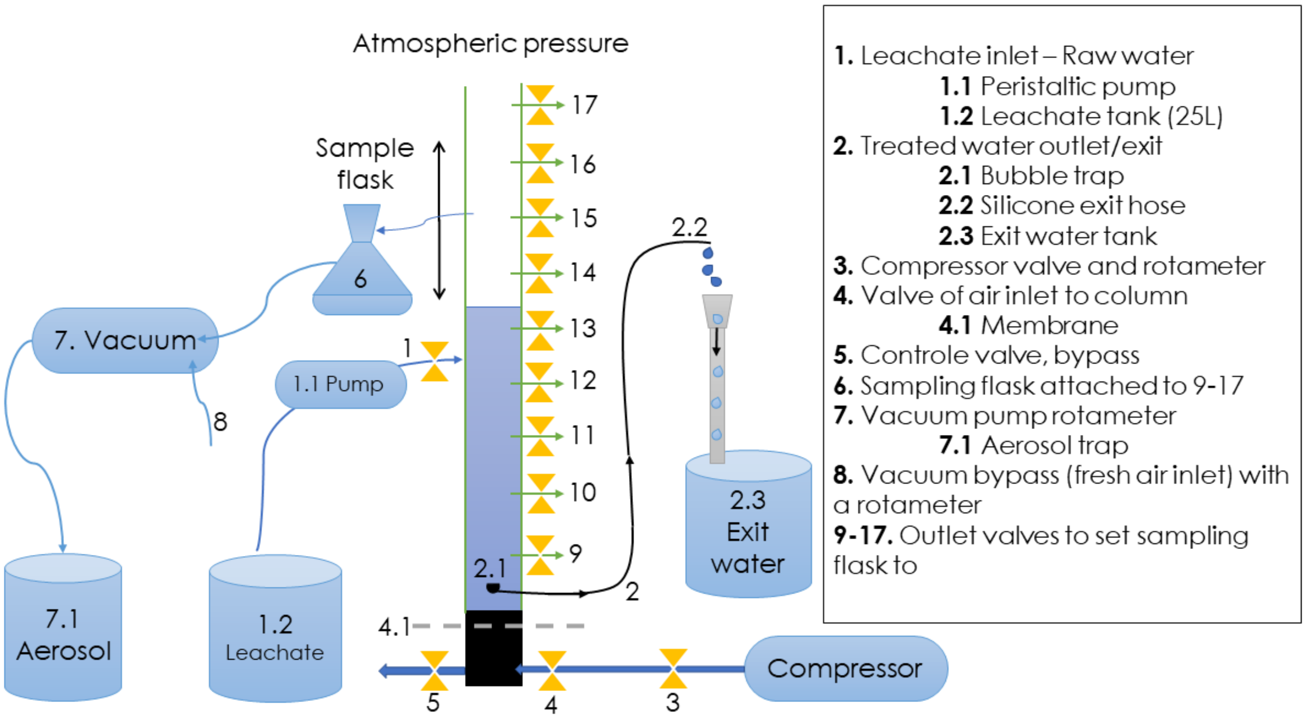


Figure 11: *Continuous schematic model of pilot showing functions.*

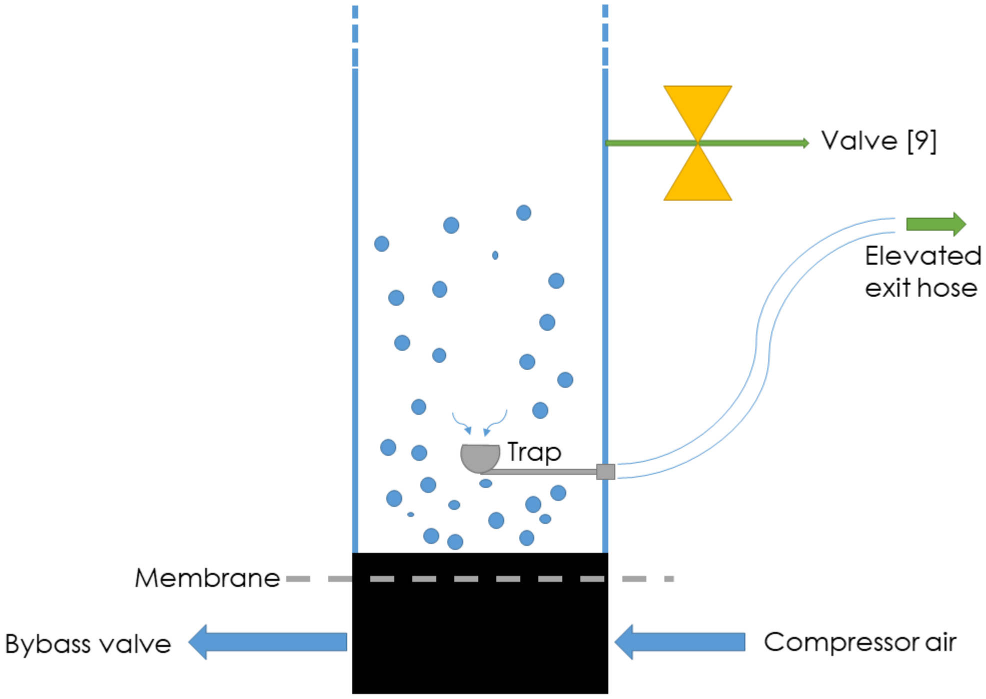


Figure 12: *Schematic image of bubble trap.*

The procedure of the continuous model of the experiment was the following:

- Date of water harvesting and place as well as date when equipment was cleaned was noted in the lab protocol.
- Top valves were opened to obtain atmospheric pressure. Bubble trap valve to elevated exit hose was opened.
- The peristaltic pump was set to a pace that corresponds to the desired column contact time. The total length of the experiment was double the column contact time. The sampling times were selected according to the length of the experiment.
- The column was filled with test water (leachate) to a certain level using a peristaltic pump and the elevation of the exit hose was corrected so that a 1 meter column was achieved. Raw water sample and pH, temperature and conductivity samples were taken from the exit hose. For continuous experiment 5-7, the raw water tank was under magnetic mixing during this part and rest of the experiment.
- The vacuumed sampling flask [6] was attached to an adequate vent above water level.
- The compressor was started and rotameter [3] was set to a fix air flow rate and rotameter [7] for the same vacuum. At approximately the same time a new exit water container was attached so that only the water of the experiment was kept.
- At chosen time intervals from start, samples of both exit water and column water were taken into small 10 ml tubes. Approximately 10 ml of exit water was collected at the exit point. The column water samples were taken from vent [9] at the sampling time. First 5 ml were taken and washed out to rinse the vent, and then another 5 ml were taken for the sample. The samples of column water and exit water were transferred to a 250 ml bottle, weighed and then diluted. All samples were immediately diluted with MilliQ-water, and weights of undiluted samples and diluted samples were noted in the lab protocol.
- The foam was harvested continuously with vacuum since the previous sampling time. For example the F20 sample contains foam from the previous time step to 20 min. The flask was emptied into a separate sample bottle at suitable time step and the foam flask was rinsed with tap water. The foam samples represent a longer time interval in between the sampling times. For shorter experiments, the foam flask was only emptied into a sample bottle at the end of the experiment.
- At the time where the experiment was finished, the last column water sample and exit water sample were taken as previously. The air flow and vacuum were then shut off and water level without air was noted. When emptying the column, an undiluted sample of 250ml was taken and water for pH, conductivity and temperature levels was saved.
- The level of the exit water tank was noted. This functioned as an evidence of total volume during the entire experiment. The tank was then carefully mixed. A 250 ml mixed sample was taken and represents the "real" treated water from the entire experiment.
- The column was after this filled with tap water to get a rinsing effect and to prevent precipitation on the inside of the column to harden.

3.5 Chemical analysis

3.5.1 PFASs

PFASs tests were executed by an accredited laboratory (ALS) according to a standard PFAS test named "OV-34a Perflourinated substances, PFAS (32) in water". The testing method consisted of Liquid chromatography - Tandem mass spectrometry (LC-MS/MS) and each sample had to be 250 ml of water contained in a 250 ml PE-HD plastic bottle. The lowest concentration possible to get reported was between 0.01 µg/L and 0.05 µg/L and varies between the substances. Table 2 in previous chapter shows all PFAS substances tested for each water sample and their report limit.

3.5.2 Dissolved ion and organic carbon analysis

Limited all-round analysis of chemical parameters such as TOC, chloride, manganese and sodium content were taken for chosen experiments. The testing was executed by accredited laboratory at Uppsala Vatten AB.

3.6 Data analysis and formulas

Volume of leachate content in the column is calculated as shown in Equation 1. In this calculation and for all experiments a 1 m column is used. That corresponds to a water level of 87 cm on the mounted measuring tape on the column. The measuring tape was mounted 17 cm from the bottom of the column. This lead to a real water level of 104 cm, when during the experiments the goal was to use a 100 cm water level.

$$V = \pi * r^2 * h = \pi * 27^2 mm * (870mm + 170mm) = 2.38 * 10^3 mL = 2.38L \tag{1}$$

The dilution factors for the samples were calculated according to Equation 2. The flask was 250 ml and weighed with its cap on. The term sample refers to the undiluted sample. All calculated dilution factors can be found in Appendix 8.5.

$$Dilution.Factor = \frac{Diluted.sample[g] - Flask.weight[g]}{Sample[g] - Flask.weight[g]} \tag{2}$$

To calculate column contact time (Ct) the volume of the column was used along with the outlet flow, according to Equation 3.

$$Flow = \frac{Volume}{Time} \tag{3}$$

$$Ct[min] = \frac{Volume[L]}{Flow[L/min]} \tag{4}$$

The volume of a sphere relates to its radius r. The volume can be useful when calculating bubble volumes.

$$V_{Sphere} = \frac{4}{3} * \pi * r^3 \tag{5}$$

Removal efficiency (RE) is calculated using the levels at each time point of the experiment related to the levels of raw water. In Equation 6 the [RW] is the concentration level of the raw water and the [CW$_x$] is the column water concentration at a certain time step x.

$$RE = \frac{[RW] - [CW_x]}{[RW]} * 100 \tag{6}$$

3.7 Experiments conducted

In total 16 batch experiments and 7 continuous experiments were made. Each experiment was named after its type, order in time and the date of the experiment. The batch experiments start with B, and the continuous ones start with C.

Table 3 shows a simple table of the different parameters that were tested. Table 4 shows in more detail what the experiments looked like.

Table 3: *Parameters tested in all conducted experiments.*

Experiment	**Parameter tested**
B1-B3	Air flow rate
B4-B6	Height of water column
B7-B9	Dilution of leachate
B10-B12	Adding iron chloride
B13-B14	Adding dish soap (surfactants)
B15-16	Adding salt
C1	Ct 10 min (experiment removed)
C2 and C6	Ct 20 min
C3	Ct 20 min (experiment removed)
C4 and C5	Ct 10 min
C7	Ct 5 min

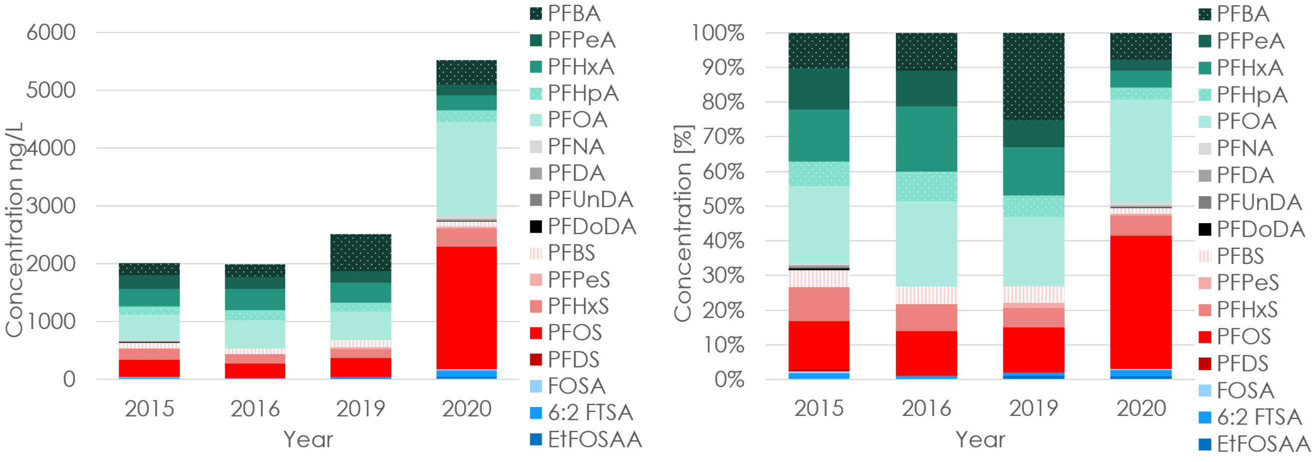
Table 4: *Executed experiments with parameters and when improvements were introduced.*

Experiment ID	Air flow rate [L/min]	Water column height [m]	Time [min]	Other parameter tested	New procedure step introduced
B1-200429	2	1	60		
B2-200430-200504	4	1	1+90 h		Diluting samples right away
B3-200504	6	1	60		pH and conductivity measurements.
B4-200505	2	0.5	60		Rinsing of column inbetween batches
B5-200505	4	0.5	60		
B6-200505	6	0.5	30		
B7-200505	4	1	60	Conc.=100% leachate	Vent 9 rinsed w. 5 ml then 5 ml sample taken.
B8-200507	4	1	60	Conce.=50% leachate, 50% milliq	
B9-200527	4	1	60	Conc.=25% leachate, 75% milliq	
B10-200508	4	1	60	Conc. FeCl3= 0.89 g +4 L leachate	
B11-200508	4	1	60	Conc. FeCl3=1.78 g + 4 L leachate	
B12-200508	4	1	60	Conc. FeCl3=3.60 g + 4 L leachate	
B13-200513	2	1	60	Conc. dish soap =0.10 g +4 L leachate	
B14-200513	2	1	60	Conc. dish soap =0.20 g +4 L leachate	
B15-200514	2	1	60	6.20 g NaCl+4L Ionic strength+50%	
B16-200514	2	1	60	12.55 g NaCl+4L Ionic strength +100%	
C1-200518	2	1	20	Flow not measured. Ct unknown	
C2-200519	2	1	40	ct≈20 min	Measuring water exit flow continously.
C3-200519	2	1	40	ct≈20 min. Non-consistant flow	
C4-200520	2	1	20	ct≈10 min	
C5-200604	2	1	20	ct≈10 min	Larger exit hose. Mixing of leachate.
C6-200605	2	1	40	ct≈20 min	
C7-200605	2	1	15	ct≈5 min	3 x contact time.

4 Results

4.1 Raw water

A compilation of all samples taken during all experiments was made to get information of the raw water quality. The results of all raw water samples were then compared to the previous testing results from the sampling place (R1), see Figure 13. The figure displays concentration levels of approximately 200-2500 ng/L of total PFASs, and a higher concentration of about 5500 ng/L of total PFASs. The more common PFASs for the entire time period are PFBA, PFOA and PFOS. The PFCAs contributes to about 70-80% of the concentration in 2015, 2016 and 2019, and about 50% in 2020.



(a) *Concentration distribution [ng/l]*

(b) *Percent distribution [%]*

Figure 13: *Yearly mean distribution of PFASs from sample point R1. Mean value calculated from 2 samples taken 2015, 1 sample taken 2016 and 2019 and 23 samples taken 2020.*

It is important to keep in mind that the mean values from previous years are calculated based on one to two values, where the mean value from the experiments conducted in 2020 is based on 23 values from 2020-04-28 to 2020-06-03.

Gathered in Table 5 are dispersion measurements from all tested raw water from B1-C7. The table is divided into categories PFCA, PFSA and Precursors and total sums.

The substances summarized in the ”sum-11”-value are the substances with a deeper color, and the ones with a lighter tone (PFPeS, PFHps, FOSA, MeFOSAA and EtFOSAA) are excluded from that sum. All PFASs in Table 5 are added in the total sum: $\sum$ PFASs. One thing to take from Table 5 was that all different raw water samples were very separated regarding concentration levels of different type of PFASs. The same conclusion of large differences stands out when looking at min and max values and when comparing the mean and median value.

Table 5: *Dispersion measurements of the 23 raw water samples analyzed from point R1 in 2020. The grey substances are PFCAs, the red are PFSAs, the blue are FTSAs and precursors and the green at the bottom are accumulative sums of sum 11 and sum of all previously mentioned. Sum 11 substances are shown in a deeper color.*

	PFBA	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**
Chain length	C3	C4	C5	C6	C7	C8	C9
Mean	430	180	260	200	1600	61	27
Std	220	46	75	100	1400	79	40
Median	360	190	290	160	800	24	11
Min	100	63	60	46	370	11	5.0
Max	900	2300	320	400	5700	360	180

	PFBS	**PFPeS**	**PFHxS**	**PFHpS**	**PFOS**
Chain length	C4	C5	C6	C7	C8
Mean	92	28	320	43	2100
Std	30	11	260	57	3300
Median	100	27	200	18	700
Min	24	5.0	74	5.0	260
Max	130	50	990	250	16000

	6:2 FTS	**FOSA**	**MeFOSAA**	**EtFOSAA**	**Sum 11 PFAS**	**$\sum$ PFASs**
Chain length	C6	C8	C8	C8		
Mean	100	230	110	510	5300	5600
Std	64	40	13	52	5300	5400
Median	92	5.0	5.0	29	2900	3000
Min	21	5.0	5.0	13	930	1100
Max	250	170	51	210	24000	25000

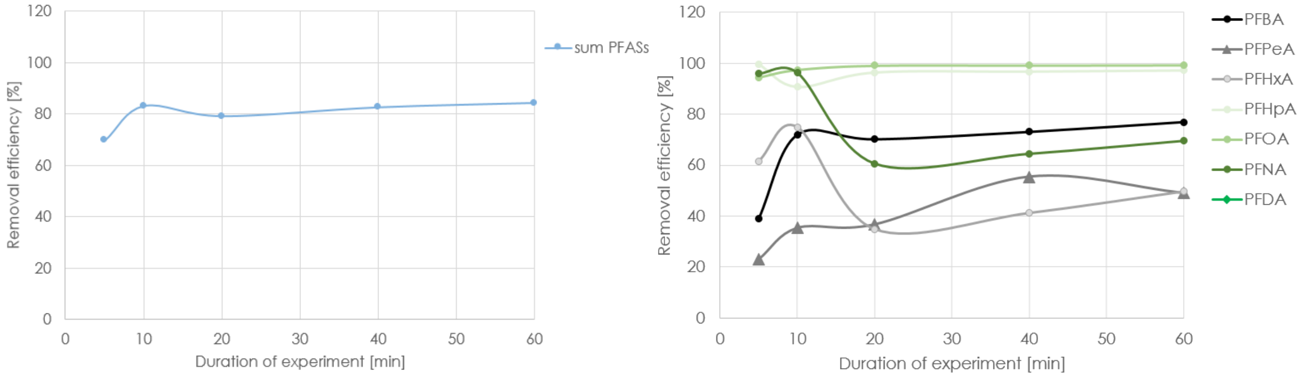
4.2 Batch experiments

4.2.1 Removal efficiency

The removal efficiency is a measurement that was plotted for all experiments. It is a comparison between raw water levels and the column water level at each time step, see Equation 6 in chapter 3.6. The removal efficiency measurement is considered more representative of the ability of the experiments to decrease PFASs content in the column water than just looking at levels over time when comparing different experiments to each other.

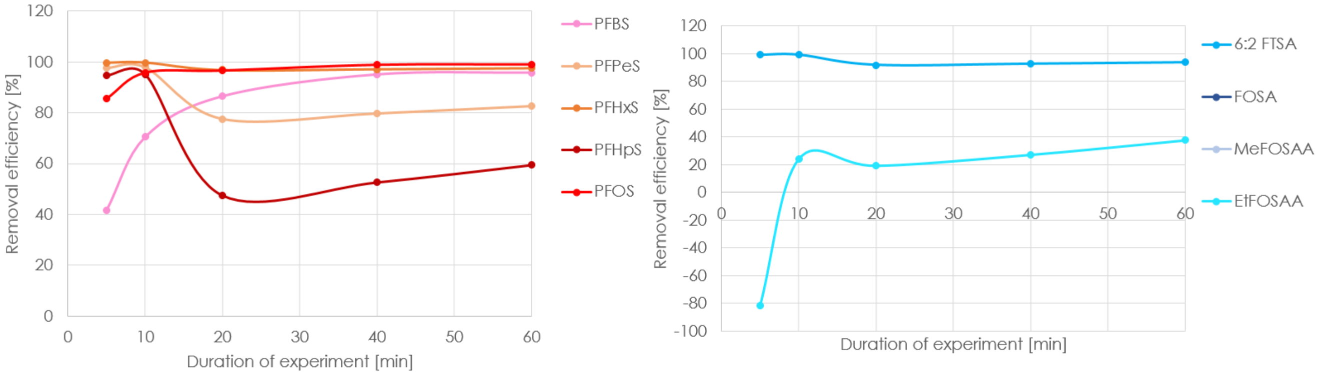
Removal efficiency over time was plotted for all experiments. For experiment B2 all individual PFASs were plotted over time. All different substances and their divisions into subgroups are presented in Figure 14 for batch experiment B2. This experiment was chosen due to the fact that it was one of few tests without any other parameters tested than air flow rate, as well as the fact that that all of the samples from 0-60 min was analyzed.

Figure 14a shows the $\sum$ PFASs, and in Figures 14b, 14c and 14d all substances are divided by color: in grey and green PFCAs, in red and pink PFSAs and in blue are the precursors. The highest obtained removal efficiency is not present just in one group of substances, but is instead spread out in each group. Looking at Figures 14b, 14c and 14d one can see each individual group and the removal efficiency of each substance with detectable levels in the raw water. That means all substances that were not detected in the raw water were not included in the comparison, for example FOSA, MeFOSAA and PFDA. The highest achieved removal of PFCAs is from PFOA and PFHpA. For PFSAs it is PFOS, PFHxS and for longer treatment times also PFBS. The only sufficiently effective removal of precursors was of 6:2 FTSA.



(a) All PFASs detected

(b) PFCA



(c) PFSA

(d) Precursors

Figure 14: *Removal efficiency over time for batch experiment B2 for all analyzed substances. Air flow rate = 4 L/min, Column water level = 1 m.*

Another interesting measure or trait to look at is the chain length of the substances. Looking again at batch experiment B2, the different chain lengths are displayed regarding their subgroup and removal efficiency in Figure 15. The graph was constructed using an average removal efficiency of at all time steps (average of column water sample CW5-CW60) with a standard deviation of the same data points. The PFSAs have a higher removal efficiency than both PFCAs and the precursors, except for chain length 7 where the PFCA have a much higher removal efficiency. The detected precursor with a chain length of 8 has a very low removal efficiency, with whiskers displaying the standard deviation that are on the negative side of the percentage scale. A negative removal efficiency would mean that a higher level of the substance was found at the end of the experiment, than in the beginning.

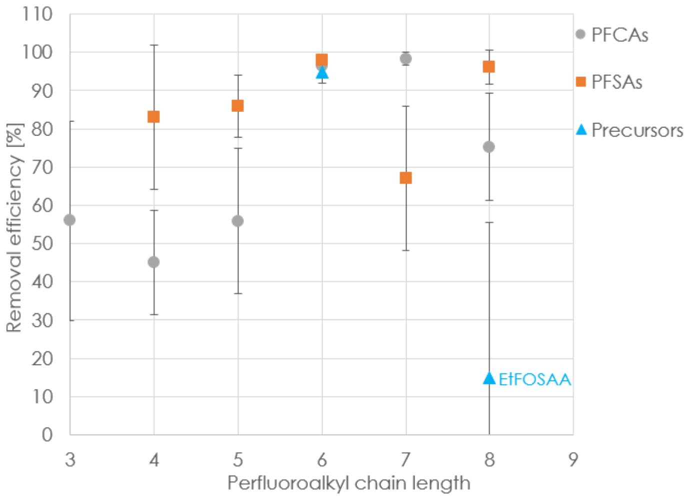


Figure 15: *Removal efficiency for B2 with connection to chain length divided in PFAS subgroups PFCAs, PFSAs and precursors. AFR = 4 L/min, CWL = 1 m.*

An average of the removal efficiency for all PFSAs divided into subgroups and chain lengths are shown in Figure 16. All of the removal efficiency graphs used to make the average is inserted in Appendix 8.6.

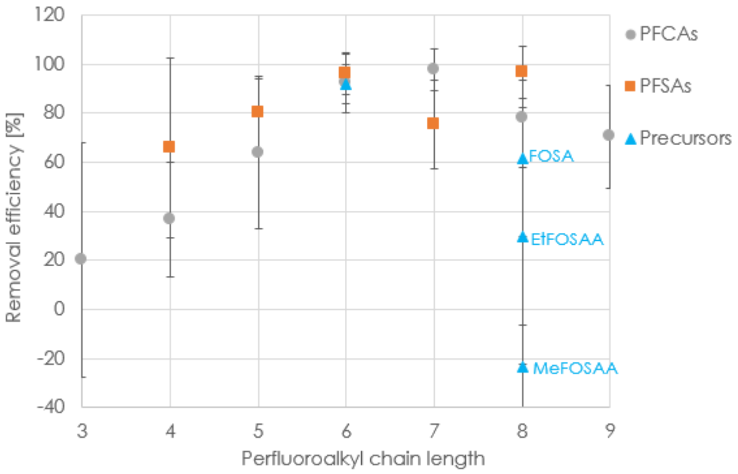


Figure 16: *Removal efficiency for substance specific average of all batch experiments with connection to chain length divided in PFAS subgroups PFCAs, PFSAs and precursors.*

Each experiment will be presented in the following chapters with their specific removal efficiency graphs in said chapters.

4.2.2 Altering air flow rate and column water level

The parameter that may have the biggest impact on the result is the amount of air let in to the bottom of the column. The first experiments made B1-B3 altered air flow rate with 2 L/min, 4 L/min and 6 L/min. All of these experiments had a water level at 1 m.

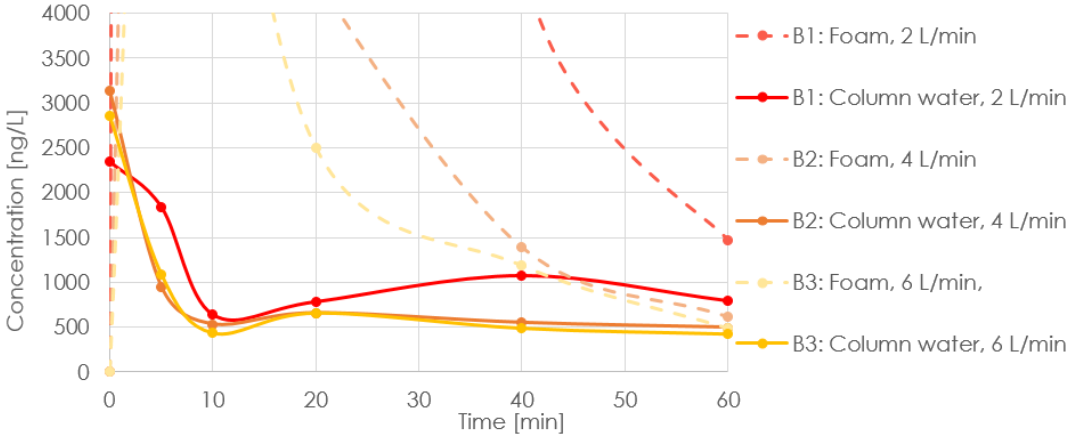


Figure 17: *$\sum$ PFASs concentration over time in foam and column water for experiment B1, B2 and B3. {B1, B2, B3} Air flow rate = {2, 4, 6} L/min. Column water level = 1 m.*

The experiments made for B1-B3 was later made for B4-B6, but with a 0.5 m column water level. The B6 experiment was discontinued due to the amount of foam that was building up and then removed. Some samples were taken, but never analyzed. It was visibly clear that the amount of foam increased with increased air flow rate. The results of concentration over time is presented in Figure 18 below. The concentration level of sample point 20 min from experiment B5 is higher than both before and after. At 60 min the concentration of the column water is almost at the same level as the raw water sample, the sample is removed in following results.

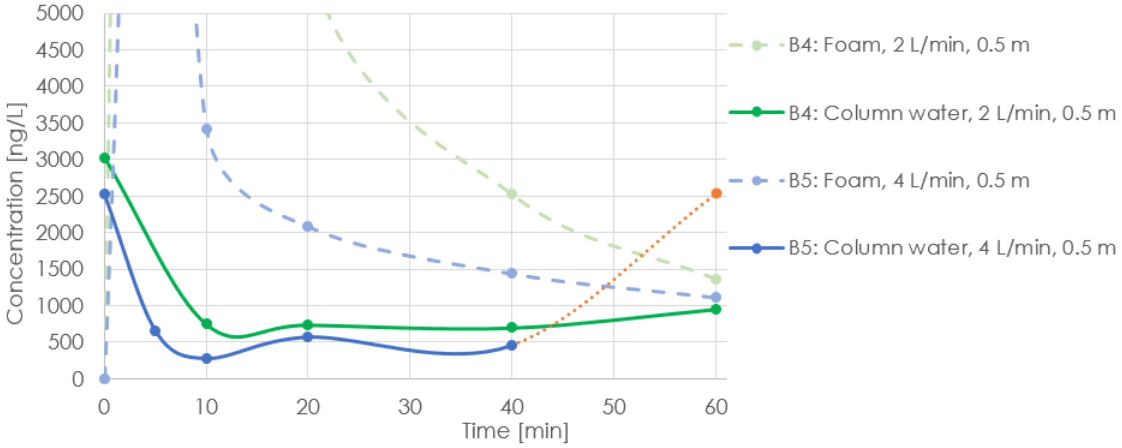


Figure 18: *$\sum$ PFASs concentration over time in foam and column water for experiment B4 and B5. Column water sample at 60 min highlighted for experiment B5 since it was removed. {B4, B5} Air flow rate = {2, 4} L/min. Column water level = 0.5 m.*

The effect of altering column water level (i.e column volume) is shown when looking at concentration levels over time for B1-B5. The last point of B5 is shown in a dotted line, since it is suspected of being faulty. The B1 and B4 experiments, which both had an air flow rate of 2 L/min seem to have the highest concentrations during the entire experiment time. The lowest concentrations seem to be obtained by B2 and B3 which are very similar, as well as B5 up until 40 min. The batches with lowest concentrations had an air flow rate of 4 L/min or 6 L/min.

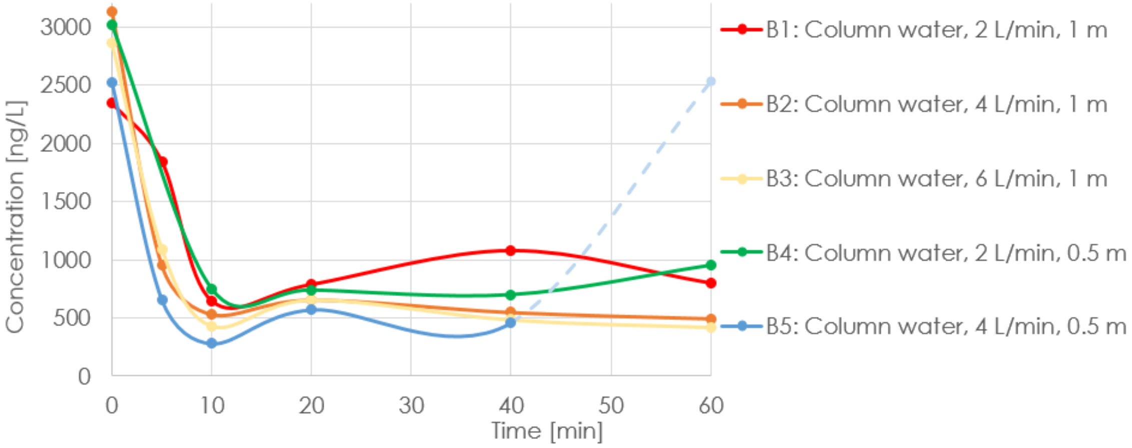


Figure 19: *$\sum$ PFASs concentration in column water for experiment B1-B5. {B1, B2, B3, B4, B5} Air flow rate = {2, 4, 6, 2, 4} L/min. Column water level= {1, 1, 1, 0.5, 0.5}.*

The removal efficiency graph for the same experiments show that the highest reduction during the experiment is for B2 and B3. B1, B2 and B5 are all graphed from the same time step, at 5 min. The look of the curve shows how the reduction early in the experiment is lower than of the next point. The curves of B2 and B3 are very similar, but the same can not be said for B1 that also have the same column water level. For points column water samples CW5-CW40, the B5 has a higher reduction than B4. After 40 min the reduction is very unstable for B5, and as mentioned before the point is removed.

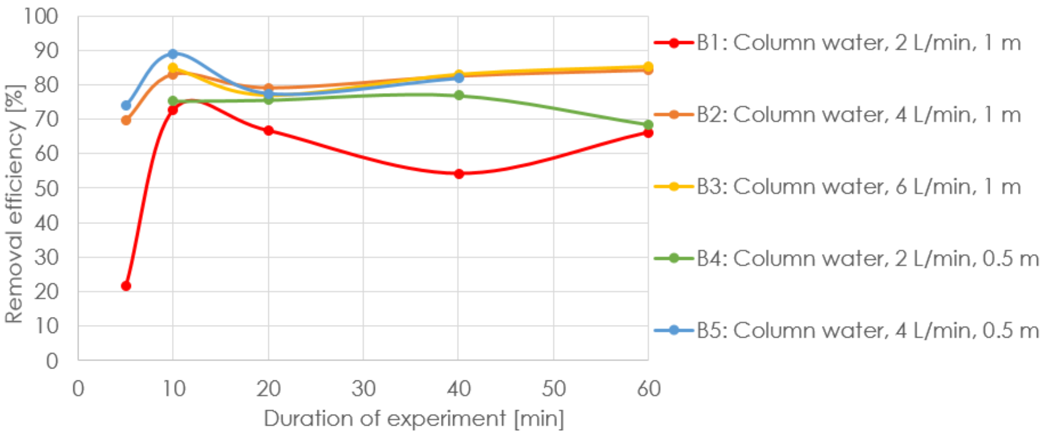


Figure 20: *Removal efficiency of $\sum$ PFASs in column water for experiment {B1, B2, B3, B4, B5}. Air flow rate={2, 4, 6, 2, 4} L/min. Column water level={1, 1, 1, 0.5, 0.5}.*

4.2.3 Altering PFASs levels with dilution

For batch experiments B7, B8 and B9 a dilution was made. B7 was conducted with 100% leachate in the usual way, and is also a duplicate of experiment B2. For experiment B8 the raw water was a mixture of 3L of leachate and 3L of Milli-Q water. For B9 3L of Milli-Q water was mixed with 1L of leachate, resulting in a 25% raw water concentration. In Figure 21 the results from the dilution experiments are plotted. The foam content of the B7 for 5 and 10 min are excluded to show the same point as B8 and B9.

A dispersion in concentration order is shown, although the raw water level of $\sum$PFASs is not 100, 50 and 25% as expected. A $\sum$PFASs raw water concentration of 2890 ng/L for B7, 2570 ng/L for B8 and 1080 ng/L for B9 was obtained. If B7 had a 100% concentration, that corresponds to 89% for B8 and 37% for B9. B9 had a raw water concentration of 42% compared to B8.

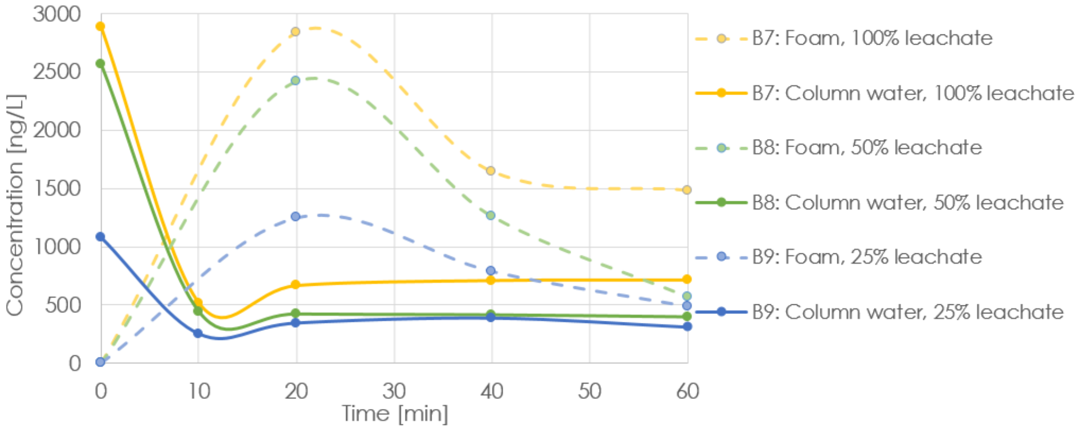


Figure 21: *$\sum$PFASs in foam and column water for experiment B7 and B10-B12. Air flow rate=4 L/min, Column water level=1 m, B7: 100%, B8: 50% and B9: 25% leachate.*

Figure 22 depicts the $\sum$ PFASs removal efficiency over time in the column water for B7-B9. B8 has an even removal efficiency over time and B9 varies more. B8 have higher removal efficiency over all time steps than both B7 and B9.

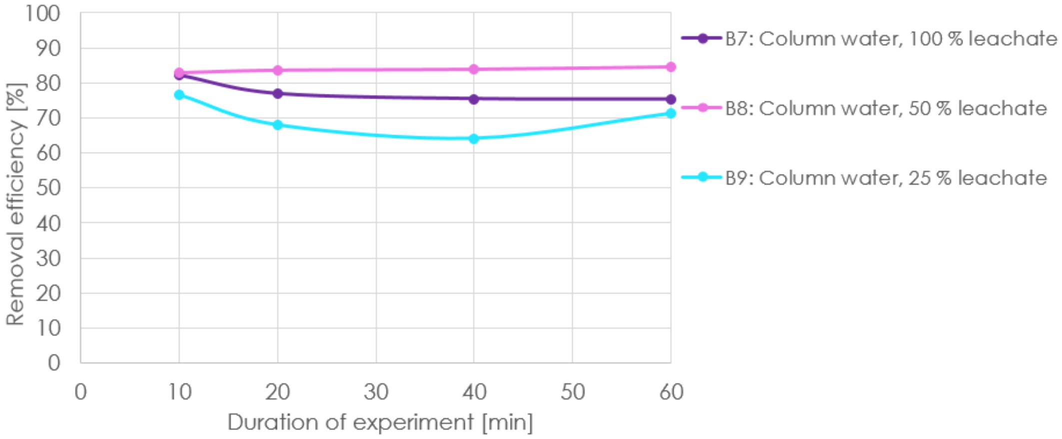


Figure 22: *Removal efficiency of $\sum$ PFASs in column water for B7-B9. Air flow rate=4 L/min, Column water level=1 m, B7: 100%, B8: 50% and B9: 25% leachate.*

4.2.4 Addition of iron chloride

To test whether an addition of coagulants would increase PFASs reduction, experiments B10, B11 and B12 were made. By adding 0.89 g, 1.78 g and 3.60 g iron chloride ($FeCl_3$) into 4L of leachate, a coagulating effect was hoped to be achieved. In the comparison of concentrations in Figure 23 the levels of B10-B12 were very similar. They are dispersed with B10 having the highest raw water and foam concentration and the other following in descending order B11 and B12. The control batch B7 has the lowest levels of $\sum$PFASs at the end of the experiment and then comes B12 followed by B10 and B11.

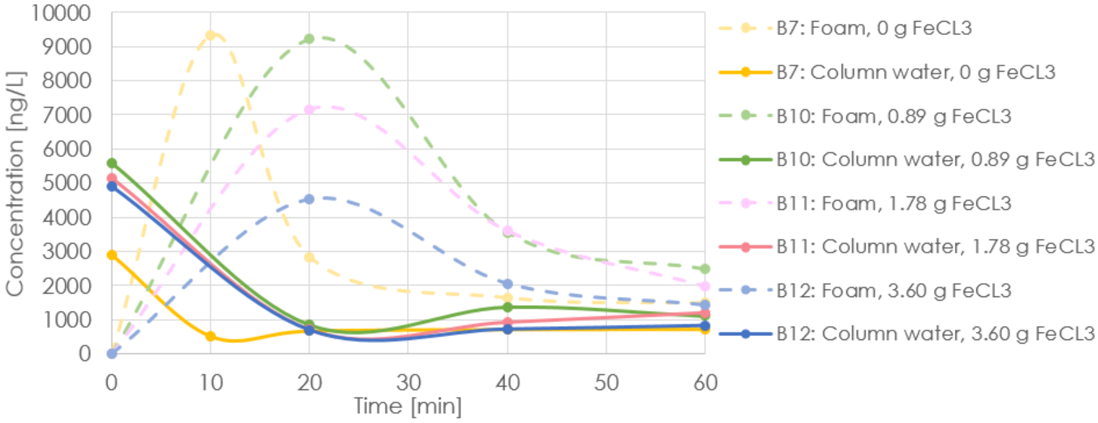


Figure 23: *Concentration of $\sum$ PFASs in foam and column water for experiment B7 and B10-B12. Air flow rate=4 L/min, Column water level=1 m. B7: 0.00g, B10: 0.89g, B11: 1.78g and B12: 3.60g iron chloride*

The removal efficiency graph over time was made to compare the different batches with each other. Figure 24 shows that addition of $FeCl_3$ contributes to higher removal efficiency. A decrease of removal efficiency occurs at 40 min for B20, but returns to original level at 60 min. Aside from B10, all other removal efficiencies for batches shown are decreasing over time. The graph shows that adding $FeCl_3$ contributes to higher removal efficiency, and with higher dosage of $FeCl_3$ the higher the removal efficiency gets. The fact that B10 had the highest raw water levels and B7 had the lowest is notable.

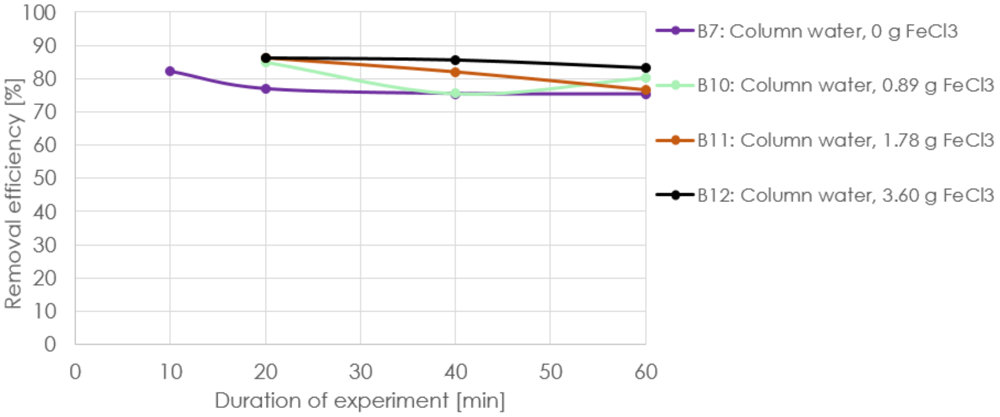


Figure 24: *$\sum$PFASs removal efficiency in column water for B7 & B10-B12. Air flow rate =4 L/min, Column water level=1 m. B7: 0.00g, B10: 0.89g, B11: 1.78g and B12: 3.60g FeCl3.*

4.2.5 Addition of surfactants (dish soap)

Batch experiments B13 and B14 were conducted to test whether addition of surfactants could increase the removal of PFASs. More foam than previous experiments was built up for both experiments. Higher dosages of dish soap increased the foam building greatly. This lead to experiment B14 having excessive volumes of foam. The surface tension in the foam seemed greater than in previous experiments, making the foam stay in the foam phase longer. The foam was harvested into 5L containers at each time step and the containers rested for 21 hours inside the lab. After 21 hours the foam had entered a liquid phase and was possible dilute. The experiment B14 was considered excessive due to foam amounts and no samples were analyzed.

The raw water concentration of B13 is three times higher than for B7, seen in Figure 25. The reduction pattern over time is similar between B7 and B13. The first time step analyzed for B13 is at 20 min, and for B7 it is at 10. The difference in time of first sample analyzed is shown in the figure as a steep drop, and could be even steeper for B13 than shown in the picture.

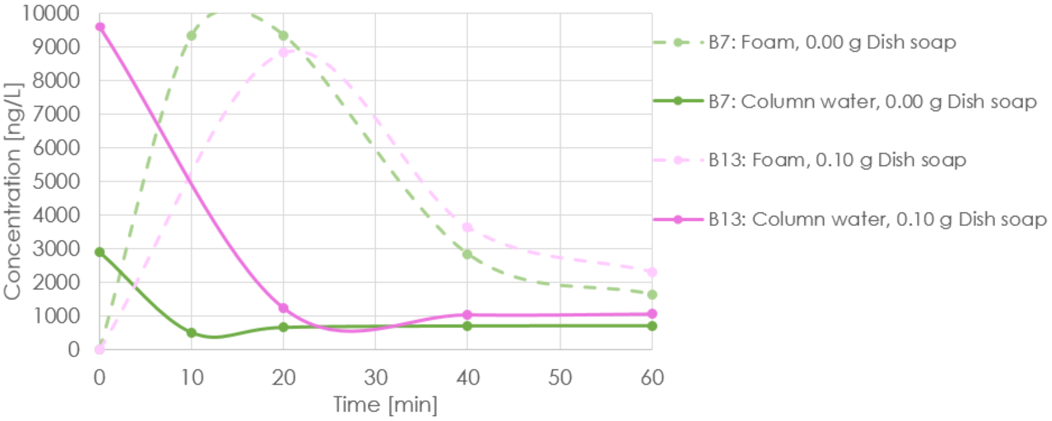


Figure 25: *Levels of PFASs in foam and column water for experiment B7 and B13. Air flow rate=4 L/min, Column water level=1 m, B7: 0.00 g dish soap. B13: 0.10 g dish soap.*

Results of B13 being better at removing $\sum$ PFASs than B7 is seen in Figure 26. The removal efficiency of B13 increases over time and the RE of B7 decreases.

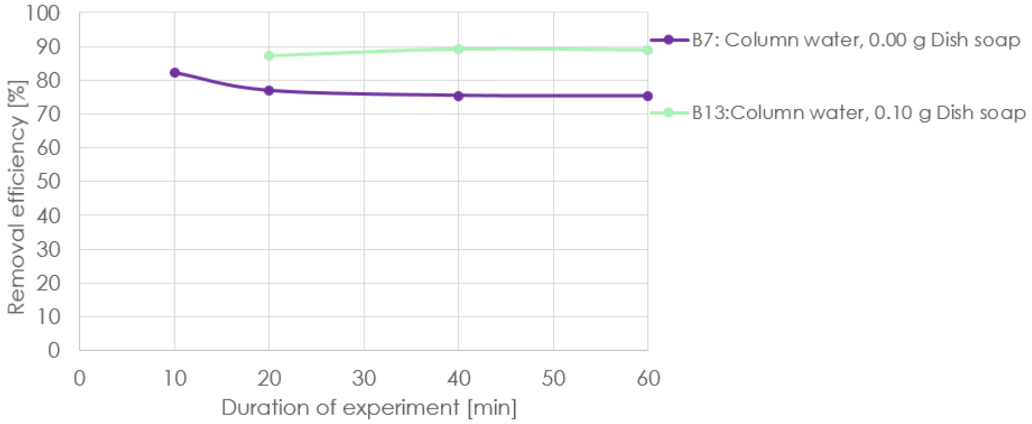


Figure 26: *Removal efficiency of $\sum$ PFASs in column water for experiment B7 and B13. Air flow rate=4 L/min, Column water level=1 m, B7:0.00g dish soap. B13: 0.10g dish soap.*

4.2.6 Addition of salt (NaCl)

A sense of how the reduction of PFASs are impacted by addition of salt are obtained looking at the levels over time in Figure 27. The raw water levels differ a lot between B7 and B15-B16, but are similar between B15-16. The difference in levels at the end of the experiment does not seem to be so large. The lowest obtained level of $\sum$ PFASs is found in B15, then B7 and last B16.

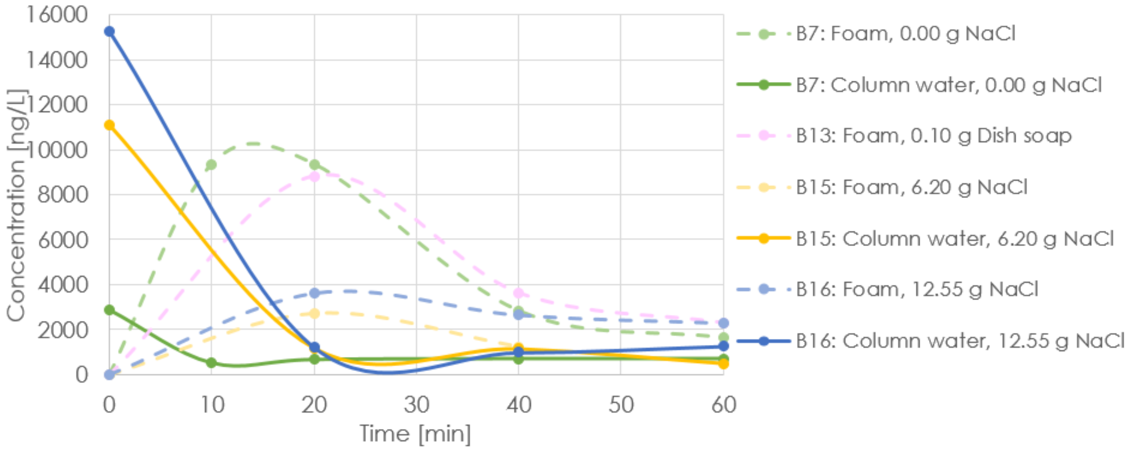


Figure 27: *Levels of PFASs in foam and column water for experiment B7, B15 and B16. Air flow rate = 4 L/min, Column water level = 1 m, B7: 0.00 g NaCl. B15: 6.20g NaCl. B16: 12.55g NaCl.*

Looking instead at the $\sum$ PFASs removal efficiency of the same experiments in Figure 28 one can see that the addition of salt probably helps removal efficiency moving PFASs to a certain level. What happens at time point 60 between B15-B16 is unclear.

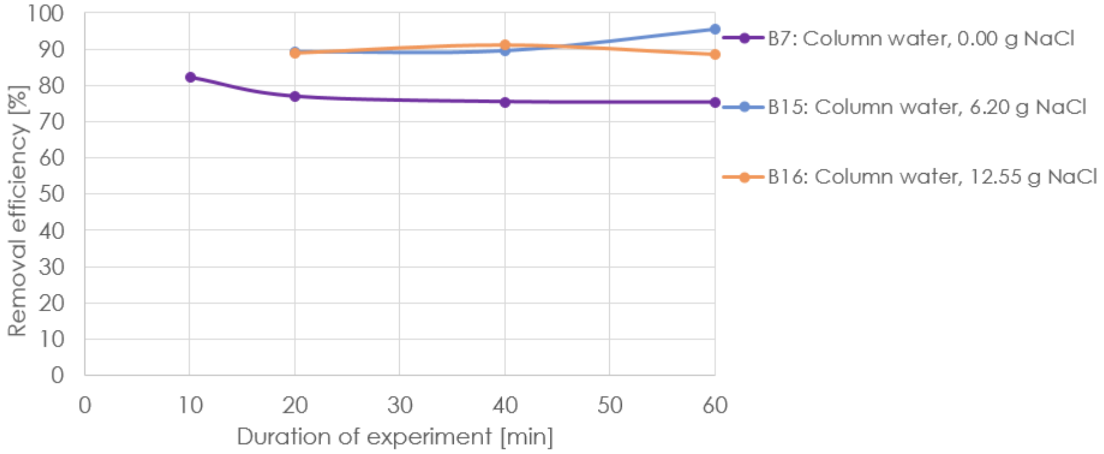
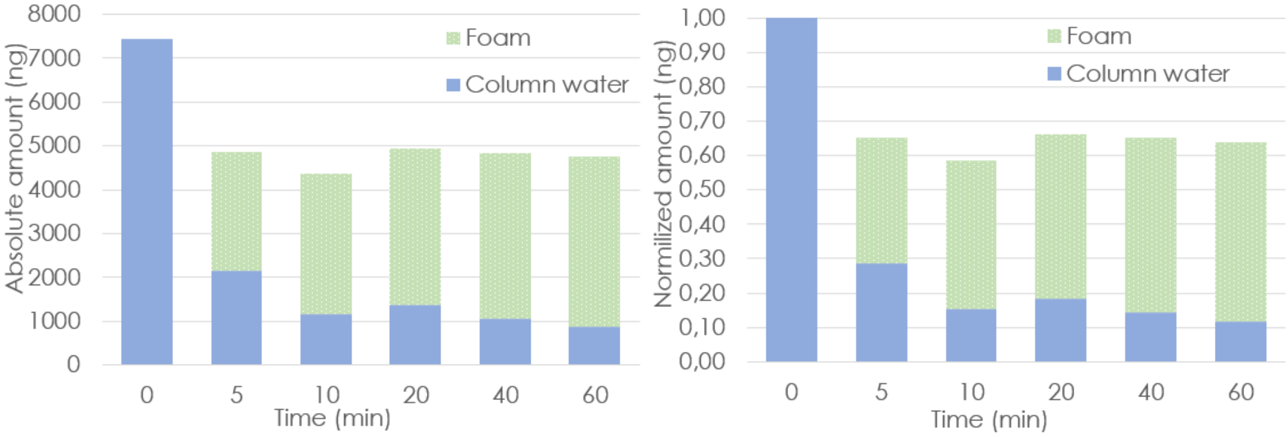


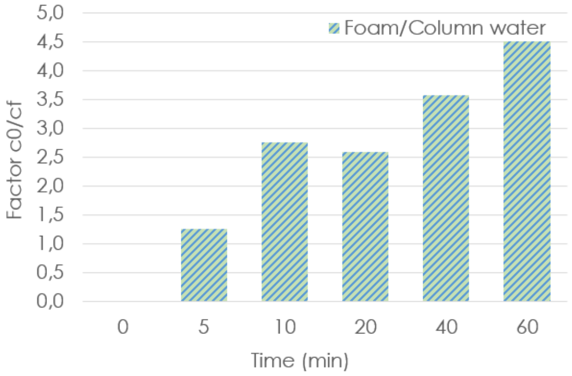
Figure 28: *Removal efficiency over time of $\sum$ PFASs in column water for experiment B7, B15 and B16. Air flow rate = 4 L/min, Column water level=1 m, B7: 0.00 g NaCl. B15: 6.20g NaCl. B16: 12.55g NaCl.*

4.2.7 Mass balance

The mass balance verifies if PFASs removed from the column water was captured in the foam phase. The concentration in ng/L can be recalculated into absolute amount of substance in the sample by multiplying it with the volume of the sample. The absolute amount can then be normalized by dividing the amount of each time step with the raw water content. The absolute amount as well as the normalized amount of experiment B2 can be found in Figure 29. In Figure 29c the factor of the division between foam and column water amount is plotted. The foam values in the figures are accumulative, meaning the amount at 5 min is just the first sample, the amount at 10 min is the 5+10 min amount and so on. The last bar contains the amount of all foam harvested from 0-60 min. The column water sample is just a momentary sample at each time step. Ideally, all total bars in Figure 29a and 29b should be the same height.



(a) *Absolute amount in ng.* ***(b)*** *Normalized amount in ng.*

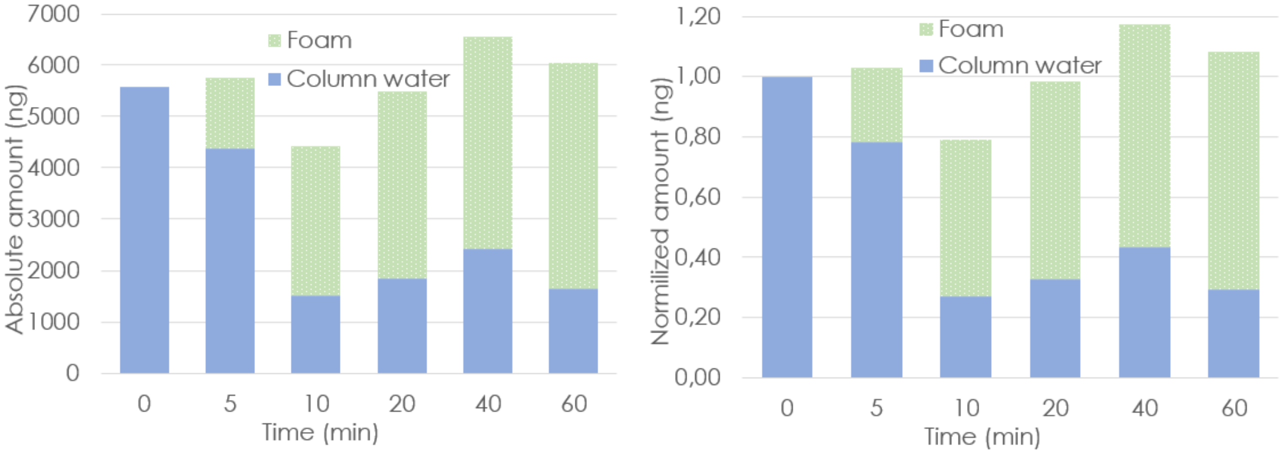


(c) *Factor of initial concentration divided with final concentration.*

Figure 29: *Mass balance of experiment B2.*

All samples withdrawn from the column during experiments needs to be analyzed to be able to do a mass balance. B2 was the first to have all samples analyzed. After this B1, B3 and B5 were also experiments where all samples were analyzed. Below are some more examples of mass balance graphs.

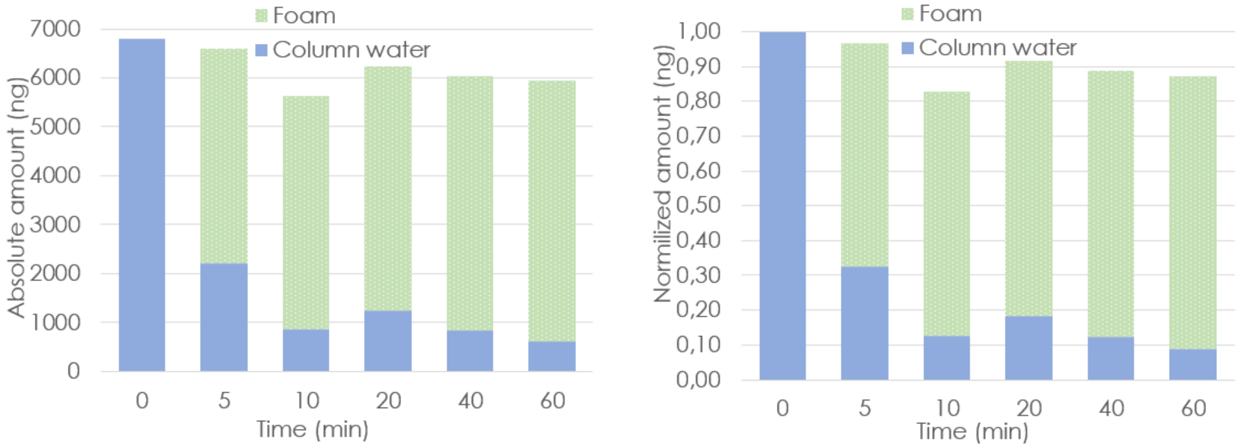
Figure 30 shows the absolute amount and normalized amount for batch experiment B1 over time. The normalized amount is almost equal to the raw water concentration for time points 5, 20 and 60 min, and for 10 and 40 an offset of 20 percentage points.



(a) Absolute amount in ng. *(b) Normalized amount in ng.*

Figure 30: *Mass balance of experiment B1.*

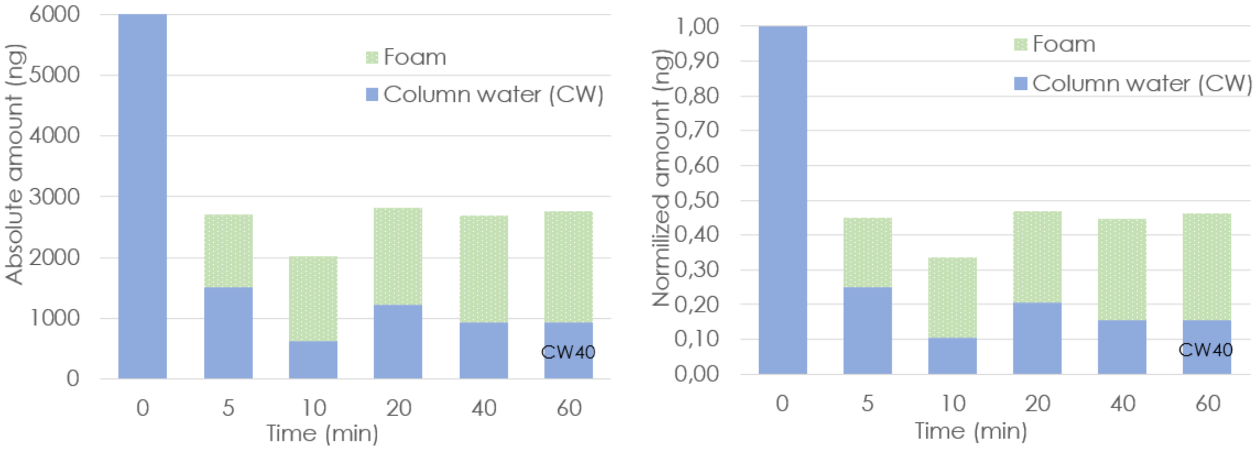
In Figure 31 the absolute amount and normalized amount massbalance of B3 is plotted. The amount is gradually decreased over time with an even pattern in Figure 31b, with an exception of the 10 min point. If that point is excluded, the graph indicates that the amount of PFASs in the column is gradually misplaced, with about the same amount at each time step.



(a) Absolute amount in ng. *(b) Normalized amount in ng.*

Figure 31: *Mass balance of experiment B3.*

In Figure 32 the massbalance of B5 is shown. The column water sample at 60 min is excluded and replaced with the column water value of 40 min to be able to compare the foam sample. The figure depicts a difference from the raw water amount to the other time point which are more similar to each other. More than 50% of the original amount is not shown in the rest of the samples.



(a) Absolute amount in ng. *(b) Normalized amount in ng.*

Figure 32: *Mass balance of experiment B5. CW60 is replaced with CW40 due to exclusion.*

4.2.8 Long-term effects of aeration

To understand the long-term effects of aeration experiment, a regular set-up for B2 was continued over a weekend. Samples were taken for the first 60 minutes as usual, then the next was taken at the 90 minutes time step. The following sample was taken after 49 hours total and finally the experiment was terminated after 91 hours. The concentration level quickly dropped to about 500 ng/L within the first hour, it increased again after 40 hours and ended up at about 500 ng/L in the end. Foam was not harvested continuously between the 60 min and 91 hours samples.

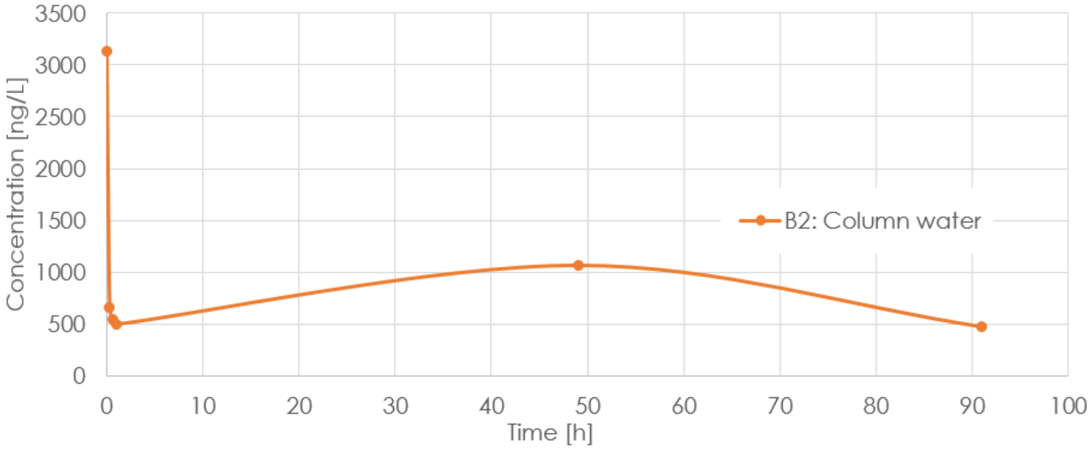


Figure 33: *Levels of PFASs in column water for experiment B2 for long exposure time (91 h). Air flow rate= 4 L/min, Column water level= 1 m.*

4.2.9 Dissolved ion and organic carbon analysis

The all-round analysis was made for chosen experiments. In Table 6 the results of the analysis is shown. Sample identification is written in the top row where RW0 is the raw water sample at 0 min, CW60+ corresponds to the last sample taken at 60 min and Milli-Q is the ultra pure water used for dilutions. All samples for the chemical analysis were undiluted. Table 6 shows that the water used for dilution does not show any substances above report limit. To get a reference, an average value of the drinking water (tap water) from Uppsala city of year 2019 was included.

Table 6: *Results of chemical analysis. Average tap water value from Uppsala city 2019.*

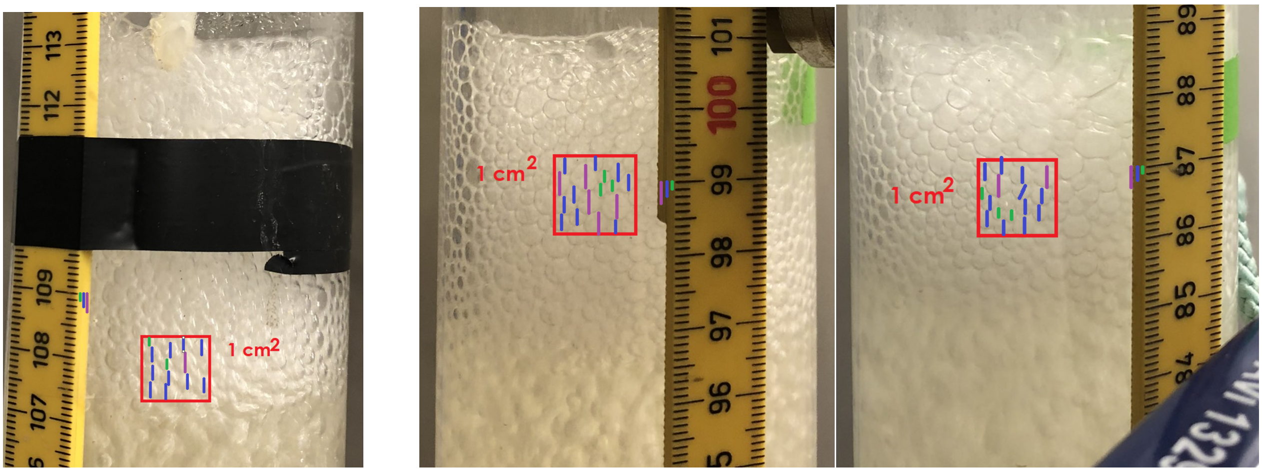
	B3 CW60+	**B4 RW0**	**B7 Milli-Q**	**B10 RW0**	**B10 CW60+**	**B12 CW60+**	**Average tap water -19**
Conductivity [mS/m, 25°C]	569	567	<2.0	574	529	545	390
HCO3 [mg/L]	1130	1080	<5.0	1230	769	638	88
NH4-N [mg/L]	49.9	48.3	<0.02	52.9	53.1	50.4	<0.02
PO4-P [mg/L]	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cl [mg/L]	1500	1400	<5	1500	1500	1700	45
SO4 [mg/L]	170	170	<3	170	170	170	39
Fe [mg/L]	1.53	4.85	<0.010	2.99	-	-	<0.010
Mn [mg/L]	0.285	0.283	<0.005	0.278	0.074	0.332	<0.005
Na [mg/L]	826	831	<5	827	817	825	22
TOC [mg/L]	40.4	41.1	<1	41.8	39.4	40.5	2.8

4.2.10 Bubble size analysis

Photos of the foam on top of the water column were taken for a majority of the batch experiments. For some experiments, multiple photos were taken at different time steps throughout the experiment. To get information of the difference in the leachate content or experiment parameters, bubbles were compared.

The volume of a bubble of diameter 1 mm is calculated using Equation 5 and is 0,00052 mL. If diameter is 2 mm the volume is 0.0042 mL and if the bubble has a diameter of 3 mm the volume is 0.014 mL. The volume of the foam was not calculated, but ocularly estimated.

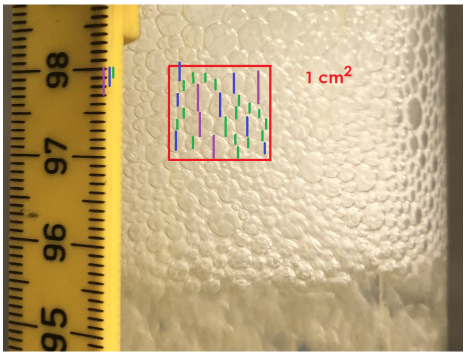
Pictures from B2 was compared to see difference in bubble size over time. The pictures are shown in Figure 34. To see how the bubble size changed, a square of 1 cm^2 was drawn accordingly to the length scale at the side of each picture. The placement of the red square was chosen were the image was most clear closest to the measuring scale. All bubbles inside the square were then categorized by color from their diameter. Bubbles of diameter 1 mm was marked green, bubbles with diameter 2 mm was marked red and the ones with a diameter of 3 mm were marked purple. The results shows that the bubble size of the foam varies between 1-3 mm for most bubbles in the foam throughout the experiment. Although, the amount of bubbles of different sizes varied and was more difficult to measure.



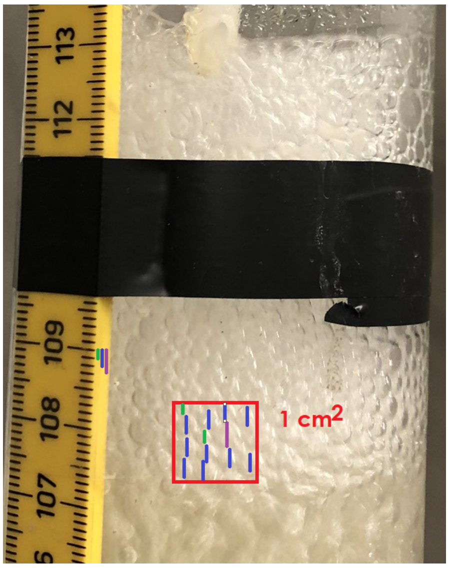
(a) *7 min. {2, 10, 1}* ***(b)*** *24 min. {3, 9, 5}* ***(c)*** *54 min. {3, 11, 2}*

Figure 34: *Photos taken during B2 experiment. Green = 1 mm, blue = 2mm, purple=3mm. The number of different sizes given under the picture in order: {1mm, 2mm, 3mm}*

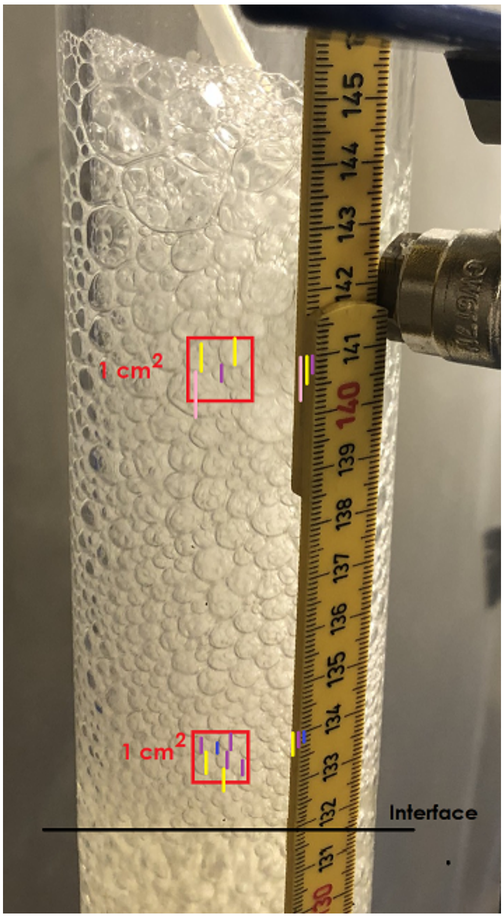
The bubble size in the foam did not change measurable during the experiments duration, see Figure 34. Some larger bubbles were seen early in the experiments, but for most part it was the height of foam that changed during the experiments. The size of the bubbles were different in different experiments, and they seem to get larger with a higher air flow rate. Seen in Figure 35 are the first pictures taken from B1-B3 testing air flow rate. The bubble sizes are marked with green (1 mm), blue (2 mm), purple (3 mm), yellow(5 mm) and pink(8 mm) color in following increasing diameter. Seen in Figure 35c are also the difference in bubble size over the height of the foam. Larger bubbles of sizes 3-8 mm in diameter was seen higher in the foam, and lower were bubbles of sizes 2-5mm in diameter.



(a) B1 9 min



(b) B2 7 min



(c) B3 2 min

Figure 35: *Photos of the foam taken during batch experiments B1-B3. A selected area of 1 cm^2 is highlighted and the diameter of the bubbles contained are marked according to size with the colors green (1 mm), blue (2 mm), purple (3 mm), yellow(5 mm) and pink(8 mm).*

4.2.11 pH, conductivity and temperature measurements

Measurements of the pH, conductivity and temperature were taken at the start and end of each experiment. Seen in Table 7 are the results of all these levels at time 0 and 60 min. The pH increases over time for all experiments and the mean value increases 0.9 pH units during the time of the experiments. The conductivity stays in at a more even level throughout, but conductivity decreases for all experiments except B15 and B16 that had an addition of salt. In B15 the conductivity increases with 30 % and in B16 the conductivity is almost doubled (46%). This was due to the raw water not having any addition of salt, as the salt was added right before the experiment started. This influences the mean value of time point 60 min. The temperature for all experiments was either the same as in the beginning or lowered of between 1-2 degrees. The decrease of temperature is explained by the addition of oxygen.

Table 7: Measurements of pH, conductivity and temperature at the start and end of each experiment.

	pH	**pH**	**Conductivity [mS/cm]**	**Conductivity [mS/cm]**	**Temp [C*]**	**Temp [C*]**
Time [min]	**0**	**60**	**0**	**60**	**0**	**60**
B1						
B2						
B3	7.7	8.8	5.7	5.3	16	16
B4	7.8	8.8	5.7	5.2	19	17
B5	7.9	8.9	5.6	5.2	18	17
B6	7.9	8.7	5.6	5.3	18	17
B7	7.9	8.8	5.5	5.2	19	18
B8	7.7	8.7	3.0	2.8	19	18
B9	7.7	8.6	1.6	1.5	19	18
B10	7.7	8.8	5.7	5.3	19	19
B11	7.7	8.8	5.7	5.4	19	18
B12	7.8	8.6	5.7	5.4	18	18
B13	7.6	8.6	5.5	5.0	18	18
B14	7.7	8.7	5.5	5.0	19	18
B15	7.7	8.8	5.5	7.7	18	18
B16	7.6	8.8	5.4	10	19	18
C1	7.7	8.1	5.5	5.4	17	17
C2	7.6	8.3	5.5	5.4	19	18
C3	7.7	8.2	5.4	5.3	18	18
C4	7.7	8.0	5.4	5.3	18	18
C5	7.8	8.2	5.6	5.5	19	19
C6	7.6	8.2	5.7	5.4	19	19
C7	7.6	8.9	5.6	5.5	20	19
Average	7.7	8.6	5.3	5.3	18	18
Standard deviation	0.10	0.28	0.99	1.5	0.85	0.75

4.2.12 Sample representation

Vent [9], from image in Figure 10, was used each time a sample was taken during the experiments. The procedure was that first 5 mL of sample was taken to rinse out the vent, and then the real 5-10 mL sample was taken and also diluted. The samples that were taken at the last time step of 60 min during the experiments are called CW60, column water 60 min. The step of first rinsing out the vent was first introduced for experiment B7. After an experiment ended and the air was shut off, another sample of the column water was taken of the water that was supposed to be emptied out. This sample was also taken from vent [9], but without the rinsing procedure. This type of sample was named CW60+, column water 60 min contact time and with the plus indicating that it was after the experiment was finished. The CW60+ samples were undiluted.

The concentration levels of CW60 and CW60+ are presented in Table 8, along with a calculation of the difference between the samples and a mean, median and standard deviation for each point for the samples. Ideally, the two samples are equal at all times. Equal values would indicate that samples taken from vent [9] are representative of the content in the entire column. The samples are not similar at all times, but have instead a negative average difference, meaning the undiluted sample have a lower concentration than the diluted one taken previously. In many cases the difference is large between the two types of samples, but the mean and median both are around -260 ng/L. The negative difference indicates that the removal efficiency probably is greater than calculated in previous chapter, but can also be a stratification effect after the aeration had been shut off. In Appendix 8.9 a table, Figure 51, shows all the different substances unlike Table 8 that shows $\sum$ PFASs. In the figures in Appendix 8.9 it shows that the difference between the samples are contributed by the shorter chained PFCAs.

Table 8: *Concentrations of the last column water sample for each experiment and concentrations of the water being emptied after each experiment.*

Exp.	**Level of CW60 [ng/L]**	**Level of CW60+ [ng/L]**	**Difference [ng/L]**
B1	795	534	-261
B2	494	-	
B3	420	700	280
B4	949	-	
B5	2530	-	
B6	-	-	
B7	714	-	
B8	397	412	15.0
B9	309	293	-15.6
B10	1110	559	-548
B11	1210	577	-633
B12	813	551	-262
B13	1070	667	-402
B14	-	-	
B15	504	602	98,3
B16	1270	434	-834
Mean	899	533	-256
Meadian	804	555	-262
STD.p	547	116	336

4.3 Continuous experiments

The second type of experiments were conducted after the batch experiments: the continuous. The peristaltic pump used was able to keep flows corresponding to 5-20 min column contact times. Two of the experiments, C1 and C3, were excluded due to non-consistent flow. Successful experiments was C2 and C4-C7, which are plotted in Figure 36 below. All $\sum$ PFASs concentrations over time are visible in the figure and even though the experiments had different raw water concentrations a similar level at the end of each experiment was achieved. The duration of each experiment was two times the column contact time (Ct), to let the set-up reach steady state. Experiment C7 that had a short Ct of 5 min used three times the Ct as experiment duration. In figures, only two Ct are plotted though.

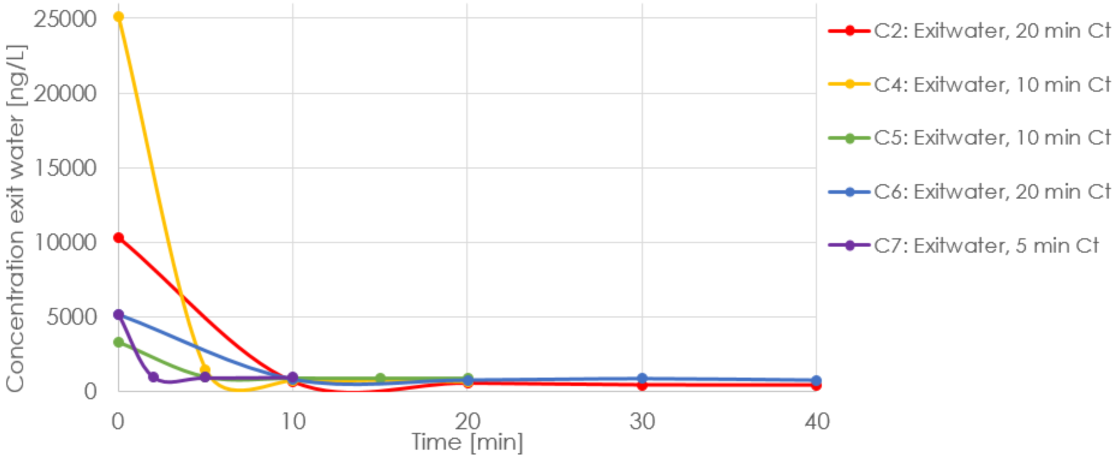


Figure 36: *All continuous experiments exit water $\sum$ PFASs concentrations. C2: Contact time (Ct) = 20 min, C4: Ct= 10 min, C5: Ct = 10 min, C6: Ct= 20 min, C7: Ct= 5 min*

Other results from the continuous experiments, as flow during the experiments and calculated column contact time, are presented in Appendix 8.8. The data shows that experiment C1 and C3 should be excluded, and the experiments that remain are precise enough to be compared.

4.3.1 Removal efficiency

A comparison of raw water concentration and removed amount was made for the continuous experiments as well. The raw water level was compared according to Equation 6 in chapter 3.6, but instead of using column water as for the batch comparison the exit water was used at each time step. Since there also is a sample taken at the end of each experiment that contains the mixed exit water in total, this sample is also compared. In Figure 37 the removal efficiency of $\sum$ PFASs over time for C2 and C4-C7 are plotted, as well as the mixed exit water sample in dotted line for each series. The removal efficiency increases over time for all experiments, except for time step 30 min C6 and 10 min step for C7. The mixed exit water sample have a lower removal efficiency for all experiments, except for C7 where the mixed and total exit water sample have a better removal efficiency than the exit water samples.

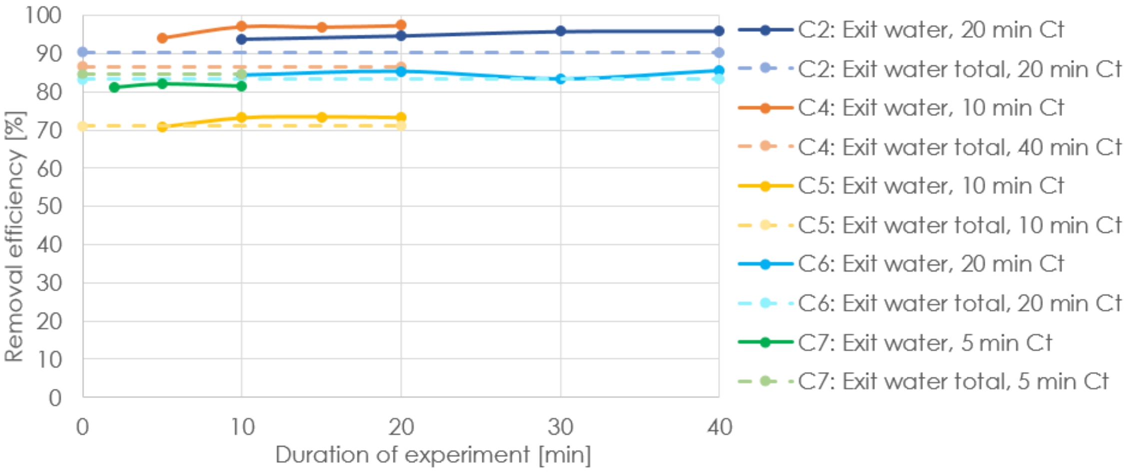


Figure 37: *Removal efficiency of $\sum$ PFASs over time for C2, C4-C7. Exit water in bold lines. In dotted line the removal efficiency of $\sum$ PFASs for the mixed total volume of exit water during the entire experiment (Exit water total).*

4.3.2 Column contact time 20 min

The column contact time of 20 min were achieved in experiment C2 and C6. In Appendix 8.8 is a table displaying all flows measured during the experiments. The table shows that by calculating the contact time from the flows, using Equation 4 in chapter 3.6, the result is that the flow is on average corresponding to a column contact time of 20 min. Corresponding results were found for contact times 10 and 5 min.

The C2 and C6 experiment corresponds to a column contact time (Ct) of 20 min. The duration of the experiment was 40 min, but already after 10 min steady state was reached according to Figure 38. The $\sum$ PFASs concentration levels differ some from C2 and C6, but the appearances of the curves are similar.

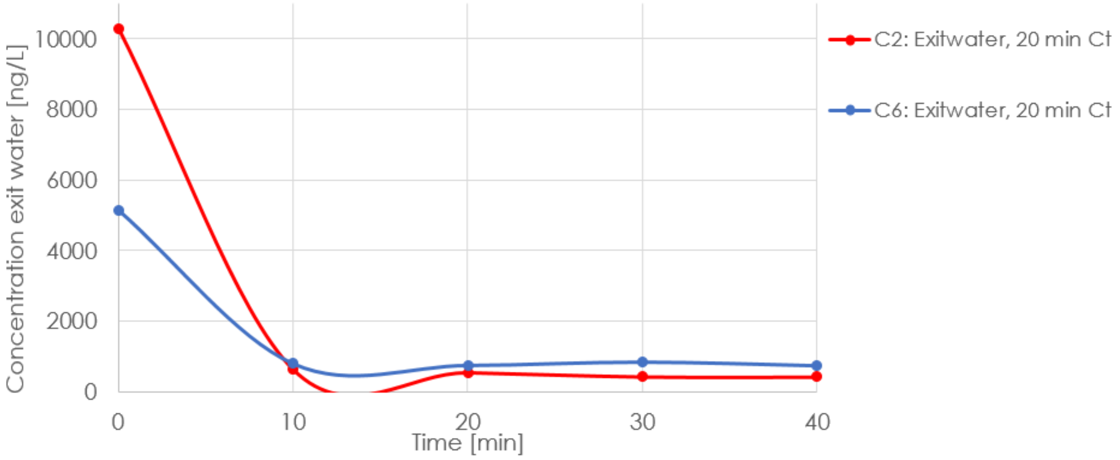


Figure 38: *$\sum$PFASs concentration of the exit water over time for C2 and C6. Air flow rate= 2 L/min, Column water level= 1 m, Contact time (Ct) = 20 min.*

4.3.3 Column contact time 10 min

In Figure 39 $\sum$PFASs concentrations of B4 and B5 are plotted over time. The raw water concentration of C4 stands out as one of the highest levels observed in the project (first time point at 0 min), but the ending result is similar to the one of B5.

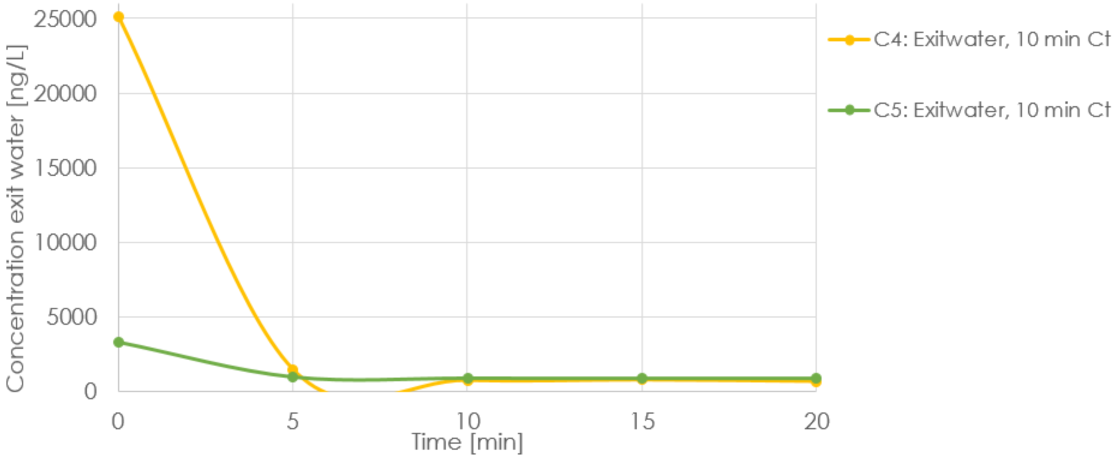


Figure 39: *Concentration levels of $\sum$ PFASs in the exit water over time for C4 and C5. Air flow rate=2 L/min, Column water level=1 m, Contact time (Ct)=10 min.*

4.3.4 Column contact time 5 min

Only one experiment was done with a 5 min column contact time. Below in Figure 40 are the $\sum$PFASs concentration levels over time for C7. The curve is similar to previous curves, but the time steps are much shorter. C7 is the only experiment that has a sample taken at 2 min. The graph shows how fast the concentrations drop and that the contact time does not have to be so long for it to reach a steady state.

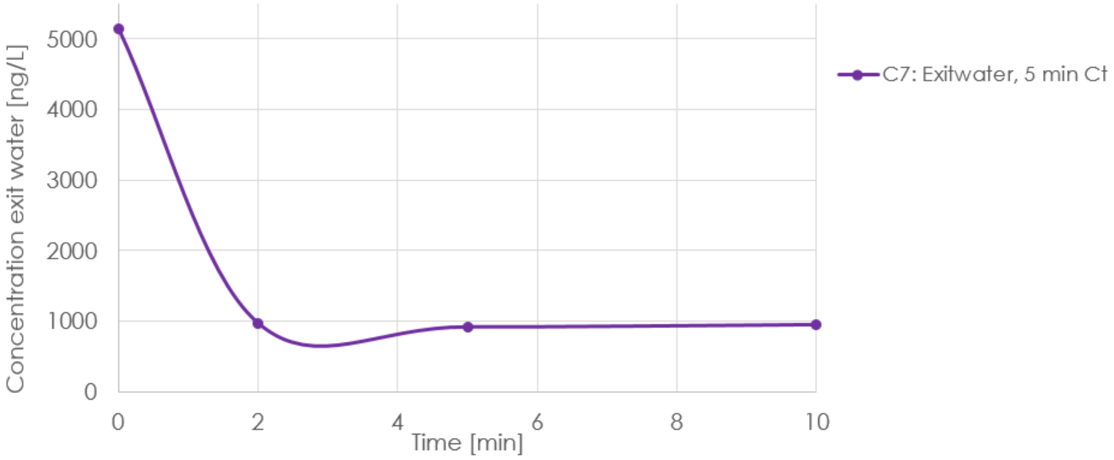


Figure 40: *Concentration levels of $\sum$ PFASs in exit water over time for C7. Air flow rate= 2 L/min, Column water level= 1 m, Contact time (Ct)= 5 min.*

4.3.5 Comparison with batch experiments

All batch experiments had a column contact time (Ct) of 60 min total. The Ct in the batch experiment corresponds to samples taken at each time step, meaning that contact time was how far the experiment had come. A comparison can be made between the batch and continuous experiments based on the column contact time. The chosen batch experiments in this chapter of comparison with the continuous ones are B2 and B5, both had an air flow rate of 4 L/min but B2 had a column water level of 1 m and B5 had one of 0.5 m. They are compared, instead of B2 and B7 which are duplicates, due to delays in the sample analysis. The aeration flow rate is 4 L/min for the batch experiments and 2 L/min for the continuous.

The column contact time of 5 min can be seen in Figure 41 where B2, B5 and C7 is graphed next to each other with the 5 min contact time. The reduction of $\sum$ PFASs concentration levels is fast. Already after 2-5 min are the removal efficiency of total PFASs 81 % for C7 and for B2 and B5 it is around 70%. The concentrations in the foam are rapidly increasing, but have not yet reach their peak.

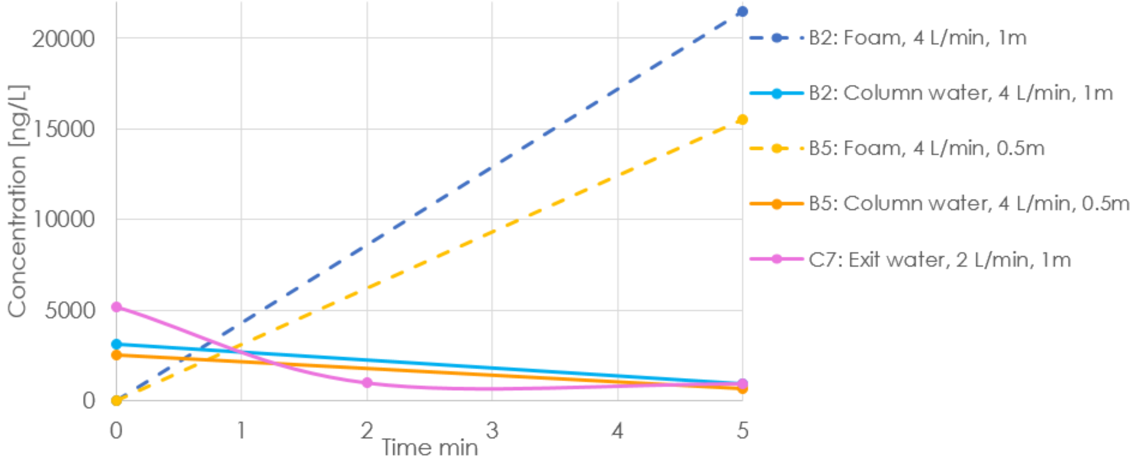


Figure 41: *$\sum$ PFASs concentrations for column contact time 5 min. {B2, B5, C7} of air flow rate {4, 4, 2} L/min and column water level of{1, 0.5, 1} m.*

Continuing with the concentrations of $\sum$ PFASs of contact time 10 min visible in Figure 42, the foam levels of B2 and B5 have reached their peak and concentrations are starting to drop. For column water of B2, B5, C4 and C5, the most rapid changes occur during the first 5 min. The column water concentration of C4 and C5 seem to have reached a steady state after 10 min. Something to also comment on is the extreme out-lier of the raw water level of C4.

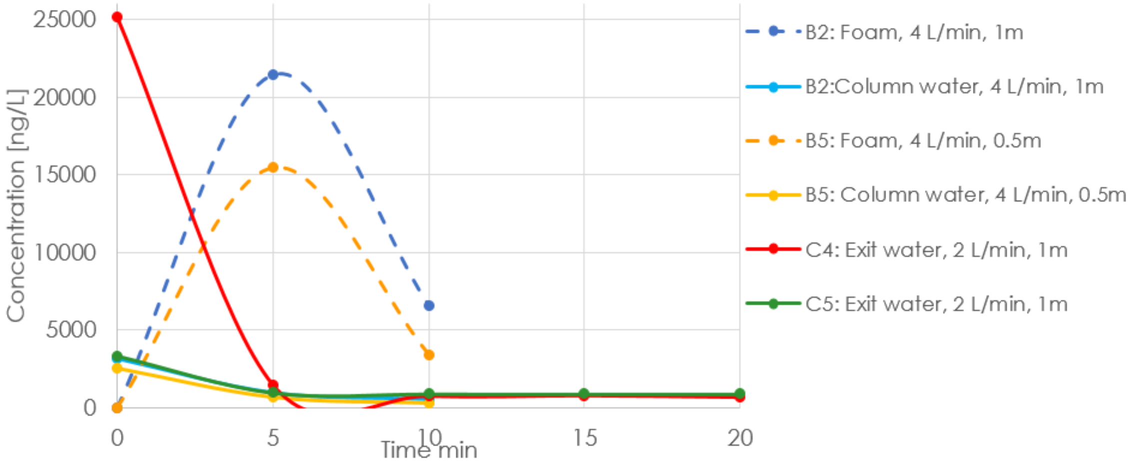


Figure 42: *$\sum$ PFASs concentrations for column contact time 10 min. {B2, B5, C4, C5} of air flow rate {4, 4, 2, 2} L/min and column water level of{1, 0.5, 1, 1} m.*

Going forward to the longest column contact times comparable is the 20 min contact time, $\sum$ PFASs concentrations graphed in Figure 43. The testing is split into quarters of the experiment duration for the continuous experiments C2 and C6, and samples were taken every 10 min. In this figure, the foam concentrations of B2 and B5 seem to have reached a steady state. Looking at the column water, one can suspect that already after 5 min a steady state is close, but at 10 min it seems to be present.

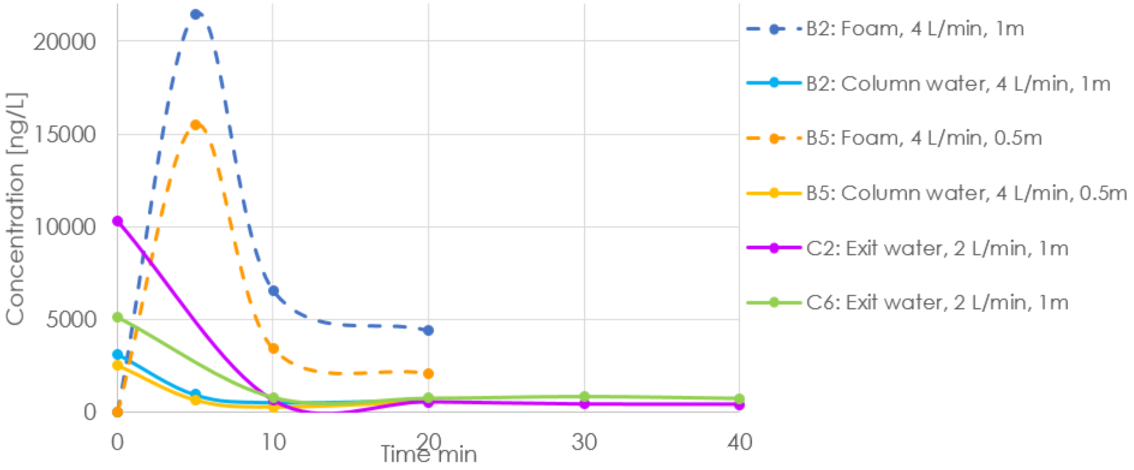


Figure 43: *$\sum$ PFASs concentrations for column contact time 20 min. {B2, B5, C2, C6} of air flow rate {4, 4, 2, 2} L/min and column water level of{1, 0.5, 1, 1} m.*

5 Discussion

5.1 Raw water

The analysis of the raw water was done using all data from both batch and continuous experiments. The analysis shows a dispersed raw water content, dependent on when it was harvested and when it was used. The raw water taken at sampling point R1 at Hovgården was harvested during different times of the day, during April-June and during various times in the inlet cycle. It was clear that sometimes the mixing in the basin by aeration was turned off and sometimes new water entered the basin during harvesting. Scattered results of the content of raw water was expected and is difficult to avoid when experimenting on leachate from a plant in operation.

There are uncertainties to why higher or lower concentrations occurred in the raw water, for example C4 with a $\sum$PFASs concentration of 25200 ng/L and PFOS of 15600 ng/L. C1-C4 for example had the same harvesting date and time, and it is possible that the PFASs had been stratified in the container over the course of all experiments, and though the container was thoroughly shaken the layers persisted. PFASs may have been adsorbed to particles in the water that are more easily stratified. B1-B12 had the same harvesting date and time, as well as B13-B16, C1-C4 and C5-C7 (see Appendix 8.4). The lowest observed raw water concentration of $\sum$ PFASs was for B9 and was about 1100 ng/L (diluted with 25% leachate).

5.2 Removal efficiency

The measurement for removal efficiency is a good way to determine in general whether one of the experiments is better at removing a percentage of the contamination than another. The measurement is a kind of a normalized value, since all experiments had different raw water concentrations, and just comparing the concentration at the end would be unreliable.

The $\sum$ PFASs removal efficiency with an average over all time steps ranks as follows:

Batch experiments
B15: 91% > B16: 90% > B13: 88% > B12: 85% > B8: 84% > B11: 82% > B3: 82% > B5: 81% > B10: 80% > B2: 78% > B7: 77% > B4: 74% > B9: 68% > B1: 62%

Continuous experiments C2: 94% > C4: 94% > C6: 84% > C7: 82% > C5: 72%

The highest $\sum$ PFASs average removal efficiency was obtained for batch experiments with salt(B15-16), dish soap(B13) or iron additives(B10-12). These are all additives that stimulates the foam building, and with this finding it is clear that the key to reduce PFASs is to build foam. The other parameter standing out was the air flow rate, where the higher air flow rates of 4 and 6 L/min (B2, B3 and B5) had higher average removal efficiency. One experiment with surprisingly high removal efficiency was B8, which was 50 % diluted, this may be some kind of extreme value.

5.3 Sample representation

Samples were diluted right after they were taken with tested Milli-Q water. All samples were refrigerated while waiting on being sent to the lab. Containers were shaken before the experiments and all samples were taken from the same exit point (vent [9]) on the column. Some extra measurements were included later on, such as rinsing the vent from the water that may be left inside from earlier testing (from B7 and forwards) and filling the column with water in between experiments to prevent precipitation (from B4 and forwards). Some unavoidable factors that may affect the sample representation still existed. For example the stratification that probably happens fairly fast after a container has been shaken, samples not being refrigerated while under transport to lab, samples being sent in months after they were harvested and the error of the scale when using it for the dilutions.

The color had shifted on some samples that were sent in later than they were taken, and oxidation was suspected. The samples that were sent in later are shown in Appendix 8.7. The PFASs content in samples stored longer time was estimated to not be affected noticeable. The main issue with storing PFASs samples is adsorption to surfaces rather than degradation of the molecules, since the molecule is very persistent. The adsorption to surfaces happens to samples analyzed without storing as well, although the extent is unclear.

One way to determine if the samples are representative of the column content is to compare the CW60 and CW60+ samples that was supposed to show the same concentration level, see Appendix 8.9. A difference between the two kinds of samples was that for CW60+ no mixing by air was made and it was undiluted while the CW60 was diluted. The difference in concentration from dilution contributes to different detection limits. The samples CW60 and CW60+ (Table 8) are not very similar. The question becomes a double one: are the samples illustrating sample representation representational? The answer is probably no. The biggest differences in concentrations occurs for short chained PFCAs (Appendix chapter 8.9 at Table 51), which also were the substances that had high concentrations. The results show that it may be difficult to compare undiluted and diluted samples that was taken during different forms (aeration or no aeration). This also questions the raw water samples that was taken in a corresponding way as the CW60+.

5.4 Ability to duplicate experiments

One of the hardest things to duplicate for both batch and continuous experiments is the way the foam is harvested. There is both so called ”dry foam” and ”wet foam”, and the question of how close to the water surface the foam is harvested is even difficult to duplicate in between time steps during experiments. The easiest way of fixing this problem is to have the same person harvest all foam and being fairly consistent.

Another factor is the raw water used. The variations have been made clear, and one possible way of reducing the variations may be to execute the pilot experiments on site to be able to use more recently harvested leachate.

5.4.1 Batch

The question of ability to duplicate all batch experiments have different components. The procedure is easily repeatable with samples taken at the same time steps controlled by a timer, same air flow controlled by rotameters and same water level controlled with a mounted rule and same vent that samples were taken from the column. There are some human error for the repeatable traits as well, such as not exact timing and errors when reading rules and meters.

There are more factors than just the procedure that can affect the repeatability. Other parameters can be stratification and aging of leachate (raw water), the built up of PFASs and other substances on the equipment and timing when taking samples.

5.4.2 Continuous

The hardest part to get precise during the continuous experiments was the outlet flow. The flow was entirely related to the ability of the pump to produce an even flow and the elevation and direction of the exit hose. If one of those three factors changed, the flow changed. Getting the continuous experiment completely repeatable is probably not possible, but continuous flow measurements of the exit water helped monitoring and being able to keep the flow steady.

Another part of the experiment that was hard to control was the water level. The water level inside the column was entirely affected by the elevation and direction of the exit hose. Before the timer and aeration of the experiment was started, water was pumped through the system at the correct pace to get a steady state of both the flow and the water level. When the level had stabilized, the hose was altered up or down depending on where the level needed to be. This procedure had a limited accuracy, and sometimes the level could not get better than ± 1 cm from the desired water level.

5.5 Batch specific

5.5.1 Altering parameters: air flow rate, column water level, dilution

In the first half of all batch experiment, B1-B9, the air flow rate, column water level and dilution were tested to see if they influenced the removal of $\sum$PFASs. Looking at the removal efficiency over time graph for B1-B5 (Figure 20) it was clear that the 2 L/min aeration (B1 and B4) had a lower removal efficiencies than the batches with 4 or 6 L/min (B2-3, B5). The batches with 4 or 6 L/min had very similar patterns of how the removal efficiency changed over time, average $\sum$ PFASs removal efficiency of B2:78% and B3:82%. It may be that 2 L/min air flow rate was too weak to remove PFASs to the same level as 4 or 6 L/min, but the reduction could only remove the substances to a certain point. Comparing B1-B5 between time step 0-40 min (Figure 20) shows that the aeration of 4 or 6 L/min were most sufficient.

The question of column volume being an important factor was also answered looking at experiments B1-B5. The experiments with the lowest removal efficiencies were B5, B4 and B3 (Figure 20) and the experiments with the highest reduction were B1 and B4. This indicates that the column volume could have an influence, but that it may have a smaller influence than the air flow rate. The batches with a smaller column volume (1.69L vs 2.38L) have lower concentrations than their corresponding batch that have the same air flow. That a smaller volume have a better ability to reduce $\sum$PFASs is reasonable, thinking about how each PFASs molecule is exposed to a larger amount of air per volume unit.

The dilution experiments, B7-B9, was made with lechate of 100%, 50% and 25% concentration. The results from the sampling however does not show the same levels of PFASs as expected. Experiments B7 and B8 were much more similar in concentration of raw water at the start of the experiment than intended. What this may depend on is unclear. It could be a consequence of stratification inside the raw water container, or an adsorption to surfaces. No changes in the procedure was made between the two experiments that could explain a concentration difference.

Surprisingly enough, the removal efficiency was best for B8, with 50% leachate/Milli-Q, even though the highest raw water concentration was found in B7. The removal efficiency of B8 was lowest 10 min into the experiment at approximately 83%, and increased over time to end up at just over 84%, seen in Figure 22. The most uneven and lowest removal efficiency was obtained by B9 with 25% lechate, but an interesting finding was that the lowest raw water $\sum$PFASs concentration found during the entire project was for this particular experiment. The removal efficiency was poorest for B9, but even though the $\sum$PFASs content was much lower than the previous two, the removal efficiency was of 64-76%. The dilution does not seem to hinder the removal completely and experiment B7-B9 showed that levels of 1000 ng/L $\sum$ PFASs can be more than cut in half.

5.5.2 Additives: iron chloride, dish soap, salt

All additives increased the removal of PFASs. B15 and B16 which used salt (NaCl) as an additive had the highest removal efficiency over time for all batch experiments. 6.20 and 12.55 grams of salt added contributed to an $\sum$ PFASs average removal efficiency of 91 and 90 %, compared to experiment B7 without any added salt that had an average $\sum$ PFASs removal efficiency of 77% (Figure 28).

The addition of dish soap as a surfactant gave an average $\sum$ PFASs removal efficiency of 88 % and the addition of iron chloride in dosages of 0.89, 1.78 and 3.60 g gave an average $\sum$ PFASs removal efficiency of 80, 82 and 85%. Looking at just the average $\sum$ PFASs removal efficiency over all time steps, the lower dose of salt had the highest average removal efficiency and the lowest reduction came from the lowest dose of iron chloride.

5.5.3 Long-term effects of aeration

Experiment B2 was conducted to examine the effects of long-term foam fractionation exposure. The aeration was run over a weekend, and the concentration over time (Figure 33) shows a raw water concentration of just over 3000 ng/L that quickly reduces to about 500-600 ng/L withing the first hour. The concentration varied between 500 ng/L to just over 1000 ng/L over the course of 90 hours. No foam was collected in between the longer sampling time steps, and this may cause the difference over the longer time periods. The long term exposure did not enhance the removal.

5.5.4 Bubble size analysis

The bubbles increased in size with increasing air flow rate, from about 1-3 mm for 2L/min to 3-8 mm for 6 L/min. The bubbles increased in size the higher in the foam they got. It is believed that a greater bubble surface area will increase the adsorption of hydrophobic PFASs to it. If this is true, the air flow rate of 6 L/min would be the most successful at removing the substances, since this batch test had the most bubbles. In batch experiment B3 and B6, an air flow rate of 6 L/min was used. B3 was successful at removing PFASs, and how B6 performed is unknown since the experiment had to be interrupted due to lack of water left in the column.

5.5.5 Dissolved ion and organic carbon analysis

The analysis showed that the conductivity, the content of HCO_3, Mn, Na and TOC was lowered during the experiments (Figure 6). The content of NH4-N, PO4-P, Cl and SO_4 was not changed or slightly elevated. The concentrations of different raw water were similar to each other, and the same results were seen for the last column water sample (CW60+). The Milli-Q water used for dilution did not show any traces of any substances.

Differences in water quality parameters was seen when comparing the water tested to the average values of tap water in Uppsala from 2019 (Figure 6). Conductivity was much higher, indicating a high salt level (sodium and chloride content was also much higher for the leachate). The ammonium was much higher in the lechate and not detected at all in the tap water, while the phosphate phosphorus was undetected in all samples. There were also a lot more total carbon content in the leachate that may indicate smaller particles that PFASs could adsorb to.

Since the salt level in the leachate seem to be higher than for tap water, it may be that properties of the leachate itself will stimulate foam building. Whether or not the aeration affects the dissolved ions or carbon content is difficult to say with such a small amount of data. Most probable is that the aeration contributes to reduction of iron, bicarbonate (HCO_3) and small reduction of the conductivity and that the content is removed with the foam. Other parameters seem to be unaffected by the aeration in the pilot, and the treatment during these experiments can not be considered to reduce any other content than the PFASs. A big difference between the pilot aeration and the current aeration on site is the biomass that contributes to treatment in the on site aeration. If leachate was treated in the pilot with longer contact time, larger volumes and some kind of increased surface area for biomass to grow on, then reduction of other substances in the water may occur at the same level as on the current site.

5.6 Continuous specific

The majority of all $\sum$ PFASs present are reduced in the first time step for all continuous experiments. The substances with longer chains are thought to be eliminated first, and if the experiment is run longer, the short chained PFASs follows. Looking at Figure 37, the highest removal efficiency from raw water to exit water (dashed line) was obtained by C2, then C4, C7, C6 and lastly C5. Looking at an average of the column contact times, the 20 min contact time has the best removal efficiency, even though the reduction is fast for all experiments. The removal efficiency increased over time at each time step for almost all continuous samples taken.

One reason why C4 have a lot higher removal efficiency than its parallel experiment C5 may be due to the very high raw water concentration of C4.

A suitable column contact time is dependent on the system used. The pilot system had limitation of the pace the pumps could produce, and longer contact times were unable to be tested. The larger the basin, the easier it gets to produce a longer contact time. For this particular system, with its limitations and abilities present, a preferred contact time would be 20 min.

5.7 Sources of error

5.7.1 Estimations of half of the detection limit

The differences in raw water concentration can make a side by side comparison of just the $\sum$ PFASs difficult. One thing to keep in mind when comparing results in this study is that the concentration never reaches 0. Since an estimation of half the detection limit has been made for all values reported with a "less than" sign, no sample ever have an absolute zero concentration. This means that a substance with a detection limit of <0.00030 μg/L in both the raw water and in the last column water sample (CW60) would show an removal efficiency of 0%. Another related issue is that the detection limit is different for different samples. If the case instead was that the raw water concentration level came back as <0.00030 and the CW60 sample came back with a higher detection limit as <0.0030, the removal efficiency after the detection limit estimation (1/2 DL) would be -900%. This effect was avoided by excluding the raw water substances that had a concentration estimated with half of the detection limit. The problem although affects experiments where the raw water content had an above detection limit and the column water samples had a below detection limit concentration with different detection limits, which complicates comparisons over time.

Another problem regarding concentration never going to absolute zero is that a small raw water concentration above detection limit can never be removed to the same percentage as a larger raw water concentration can. For example if a comparison of a raw water level of 1000 ng/L and 50 ng/L is done, the removal efficiency will always show up higher for the first example since the concentration never reaches 0. The fact that the substances had different raw water concentrations determine which substance we interpret to have the highest removal efficiency.

Even with the risk that all values with an estimation from half of the detection limit are questionable, the estimation contributes to comparisons of substances. The largest risk using the estimated data is that concentrations have been exaggerated and that the content of PFASs in the water during the experiment actually is smaller. Since the raw water samples are not estimated, the removal of PFASs can only be better than described in this thesis.

5.7.2 Differences in concentrations

Concentration may have an effect on the removal efficiency measurement and is shown when looking at the removal efficiency for chain length 7 for all batch experiments, in Figure 16. Concentration levels of PFCAs and PFSAs of chain length 7 are very different, and may compromise the removal efficiency measurement. The removal efficiency for PFCA of chain length

7 is much higher than the same chain length for PFSA. The RW level of the two different substances are different, where the PFSA substance of chain length 7 usually has a level of about 10-20 ng/L, and the PFCA has between 400-4000 ng/L. This probably means that substances with a high raw water concentration will show up as having a higher removal efficiency than substances with low raw water concentration. This, even though the amounts at the end are lower for the substance of the lower raw water concentration.

5.7.3 Dilution

If samples with larger detection limits was multiplied with a large dilution factor, the result was extreme concentration values. This was seen in the last column water sample taken for B5, which was removed from the report. The original sample was of a relatively small volume (0.0058 L) and had a dilution factor of about 45. The report limit of the sample was relatively high for PFBA, so the estimation of half of the detection limit became 35 ng/L. All substances was not detected, and PFBA for example was reported below the report limit. When later multiplying the dilution factor, the errors were also multiplied. This resulted in a PFBA concentration of about 1570 ng/L, even though no report of the samples content was reported from the lab. This is of course the cause of two estimations being multiplied and the effects of errors multiplying. The error of the reported substance and the estimation of half the detection limit increases if the sample are small. All dilution factors are inserted in chapter 8.5 in Appendix.

When comparing the CW60 and CW60+ samples (in Table 8) quite large differences are evident. These can be errors due to dilutions.

5.8 Mass balance

The mass balance made for B1, B2, B3 and B5 show different challenges. The graphs displaying B3 (Figure 31) shows the expected result with a column water level at 0 min taken from the raw water and a descending amount of PFASs at each time step. It is expected that some amount would go missing during the test, and that some smaller errors may cause the graph to shift in levels. This may also be due to the 5-60 min samples only being 5 ml and then diluted to not disturb the colume inside the column. The most unexpected graph is again the B5 graph. Even if excluding the previously stated troublesome sample at 60 min for column water, the graph is still inexplicable. The total amount at each time step between 5-40 min never exceeds 50% of the original level in the raw water. This would mean that 50% of the PFASs amount in the column would be completely unaccounted for. Also this could be depending on the representation of 5 mL from a 2.38L column.

Since all bars in the mass balance plots should be at the same level, the fact that errors exists in the experiment is evident. The error for B1 varies between +18 percent units to -20 percent units (Figure 30. These error are most likely consequences of dilution, estimation of half of the detection limit and the fact that 5 mL may be unrepresentative of an approximate 2.38L column. The raw water sample that is both undiluted and not estimated is probably the most real life accurate. The samples from 5-60 min should have about the same errors due to dilution and estimations, and are more similar and therefore easier to compare with each other.

6 Conclusion and future perspectives

The aims of the research was summarized with three questions:

1. Does aeration foam collection reduce PFASs levels in the leachate from Hovgården?
2. Does the perfluoroalkyl chain length and functional group influence the removal efficiency?
3. Is the PFAS removal influenced by additives such as salt, iron chloride or dish soap or other parameters such as air flow rate, column volume and raw water concentration?

To start with, the PFASs concentration was reduced in the lechate for all experiments. All batch experiments showed reduced $\sum$PFASs concentrations, from 62 up to 91%, with an average removal efficiency of 77%. All continuous experiments showed reduced values of sum PFASs, with removal efficiencies ranging from 72 up to 94%, with an average of 86%. The majority of sum PFASs are reduced within the first time steps for all experiments, but for the last amount to be removed the contact time needs to be longer. The column contact time of 20 min had the average highest removal efficiency.

The second question regarding functional group and chain length is answered by looking at the removal efficiency graphs that are divided in subgroups and chain lengths (Figure 16 or Appendix 8.6). It shows how the removal efficiency of $\sum$PFASs is best for longer chained PFSAs. The shorter chained substances, especially the PFCAs were tougher to remove. The precursors that also had longer chains were very unreliable whether they would be removed or if concentrations increased. Overall the chain length and functional group played a big role, also if they were detected or not in the raw water.

The last question regarding additives had a clear response: the reduction of PFASs was influenced by additives and alterations of parameters. Air flow rates of 4 and 6 L/min were more effective than 2 L/min to reduce the amount of sum PFASs. Smaller volumes got higher removal efficiency. The dilution experiments showed mixed and somewhat contradictory results, where the non-diluted experiment had removal efficiency of average 77% while the 50% diluted had an average removal efficiency of 84 %. The experiment with greatest dilution (75%) had the lowest average $\sum$PFASs removal efficiency as suspected, at 68%. The experiments with added 0.155 and 0.313% NaCl in the leachate was most effective at removing sum PFASs. The dish soap and $FeCl_3$ additives also contributed to greater PFASs reduction. The experiment with addition of dish soap had an average $\sum$PFASs removal efficiency of 88% compared to 77% without additives, and the highest concentration of $FeCl_3$(0,09% of the leachate) had an average $\sum$PFASs removal efficiency of 85%.

Some improvements and additions to the research can be made for future perspectives. It would be desirable to repeat each type of batch experiment at least one time. It also would be interesting to get the results from a batch experiment run as the traditional procedure but that did not have any harvesting of the foam, this would give some more knowledge about what may happen in the mass balance. Larger volumes of leachate would be interesting to treat, and to be able to have longer contact times for the continuous models.

7 References

Published

Bolto, Brian & Zongli Xie (June 2019). The Use of Polymers in the Flotation Treatment of Wastewater. *Processes* 7.6. Number: 6 Publisher: Multidisciplinary Digital Publishing Institute, p. 374. URL: https://www.mdpi.com/2227-9717/7/6/374 (visited on 04/15/2020).

Franke, Vera et al. (2017). *Hur kan PFAS-ämnen avlägsnas i vattenverken? En granskning av nya och befintliga vattenreningstekniker*. 2017-20. Svenskt Vatten, p. 62. URL: https://vattenbokhandeln.svensktvatten.se/produkt/hur-kan-pfas-amnen-avlagsnas-i-vattenverken-en-granskning-av-nya-och-befintliga-vattenreningstekniker/ (visited on 04/09/2020).

Kallenborn, Roland, Urs Berger, & Ulf Järnberg (2004). *Perfluorinated Alkylated Substances (PFAS) in the Nordic Environment*. Copenhagen: Nordic Council of Ministers. 114 pp. URL: https://books.google.se/books?hl=sv&lr=&id=qV6jsSMio-EC&oi=fnd&pg=PA5&dq=PFAS&ots=k8YMSvdL80&sig=e5h4HPIp8rvqb8Dzj3B7c4Qur7Y&redir_esc=y#v=onepage&q&f=true.

Lee, Yu-Chi et al. (Feb. 1, 2017). Recovery of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from dilute water solution by foam flotation. *Separation and Purification Technology* 173, pp. 280–285. URL: http://www.sciencedirect.com/science/article/pii/S1383586616316768 (visited on 04/03/2020).

Lemal, David M. (Jan. 2004). Perspective on Fluorocarbon Chemistry. *The Journal of Organic Chemistry* 69.1, pp. 1–11. URL: https://pubs.acs.org/doi/10.1021/jo0302556 (visited on 04/08/2020).

Meng, Pingping, Shubo Deng, Xinyu Lu, et al. (Dec. 2, 2014). Role of Air Bubbles Overlooked in the Adsorption of Perfluorooctanesulfonate on Hydrophobic Carbonaceous Adsorbents. *Environmental Science & Technology* 48.23, pp. 13785–13792. URL: https://pubs.acs.org/doi/10.1021/es504108u (visited on 08/20/2020).

Meng, Pingping, Shubo Deng, Ayiguli Maimaiti, et al. (2018). Efficient removal of perfluorooctane sulfonate from aqueous film-forming foam solution by aeration-foam collection. *Chemosphere* 203, pp. 263–270.

Meng, Pingping, Shubo Deng, Bin Wang, et al. (May 2017). Superhigh adsorption of perfluorooctane sulfonate on aminated polyacrylonitrile fibers with the assistance of air bubbles. *Chemical Engineering Journal* 315, pp. 108–114. URL: https://linkinghub.elsevier.com/retrieve/pii/S1385894717300347 (visited on 08/20/2020).

Ratnayaka, Don D., Malcolm J. Brandt, & K. Michael Johnson (Jan. 1, 2009). “CHAPTER 7 - Storage, Clarification and Chemical Treatment”. *Water Supply (Sixth Edition)*. Ed. by Don D. Ratnayaka, Malcolm J. Brandt, & K. Michael Johnson. Boston: Butterworth-Heinemann, pp. 267–314. URL: http://www.sciencedirect.com/science/article/pii/B9780750668439000159 (visited on 04/15/2020).

SuperManu (Oct. 12, 2007). *Scheme of a micelle formed by phospholipids in an aqueous solution*. URL: https://commons.wikimedia.org/w/index.php?curid=2902736.

Thompson, Jack et al. (Jan. 1, 2011). Removal of PFOS, PFOA and other perfluoroalkyl acids at water reclamation plants in South East Queensland Australia. *Chemosphere* 82.1, pp. 9–

17. URL: `http://www.sciencedirect.com/science/article/pii/S0045653510011835` (visited on 04/15/2020).

Online

IWA publishing, OA (n.d.). *Coagulation and Flocculation in Water and Wastewater Treatment.* URL: `https://www.iwapublishing.com/news/coagulation-and-flocculation-water-and-wastewater-treatment` (visited on 04/15/2020).

Procter & Gamble Europe household product info site (n.d.). URL: `https://www.info-pg.com/swe/variants/Sverige?prodForm=965` (visited on 05/15/2020).

SLV, OA (2018). *PFAS in drinking water and fish - risk management.* URL: `https://www.livsmedelsverket.se/en/food-and-content/oonskade-amnen/miljogifter/pfas-in-drinking-water-fish-risk-management` (visited on 04/02/2020).

— (2020). *PFAS in drinkingwater.* Library Catalog: www.livsmedelsverket.se. URL: `https://www.livsmedelsverket.se/livsmedel-och-innehall/oonskade-amnen/miljogifter/pfas-poly-och-perfluorerade-alkylsubstanser` (visited on 04/02/2020).

US EPA, OA (Mar. 30, 2016). *Basic Information on PFAS.* US EPA. Library Catalog: www.epa.gov. URL: `https://www.epa.gov/pfas/basic-information-pfas` (visited on 04/02/2020).

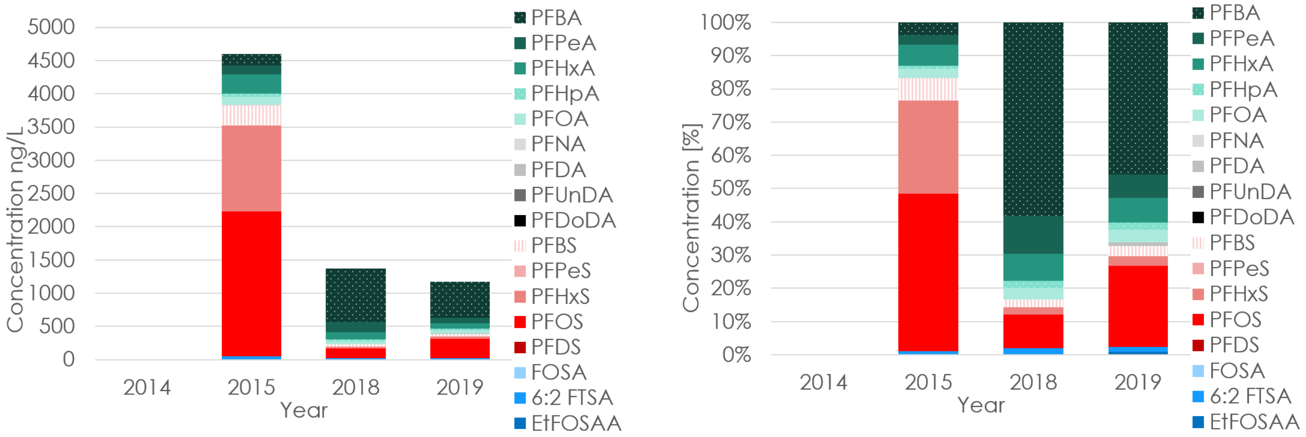
8 Appendices

8.1 Map of municipal landfill site

Figure 44: *Map of municipal landfill Hovgården. #16- Leachate treatment plant.*

8.2 Levels of PFASs in different areas of the landfill site

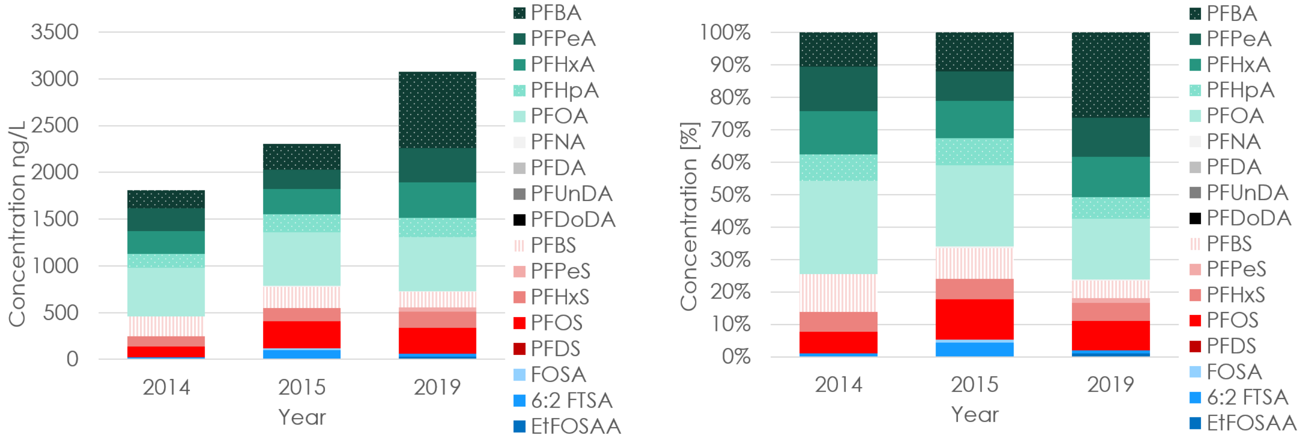
The water comes directly from partly treated areas for sampling point S0. The only treatment made before is sedimentation. Seen in Figure 45 is no detectable levels of any substances in 2014, this may be due to very high detection limits at 1000 ng/L for some substances. In 2015 a peak concentration of mainly PFSAs happens and a concentration of over 2000 ng/l PFOS and over 1250 ng/l of PFHxS is seen. For the following years 2016 and 2017 no data was retrieved, and for years 2018 and 2019 levels were lower. The total PFASs concentration of 2018 and 2019 was not exceeding 1500 ng/l and these years it was the PFCAs that was dominant. Explanations of why the levels of 2014 were undetectable, why the PFOS level in 2015 was so high and why the presence of PFSAs was lower in 2018 and 2019 is missing.



(a) Concentration distribution [ng/l] *(b) Percent distribution [%]*

Figure 45: *Distribution of PFASs from sample point S0, which contains water from sludge cells, septic basins and sedimentation ponds.*

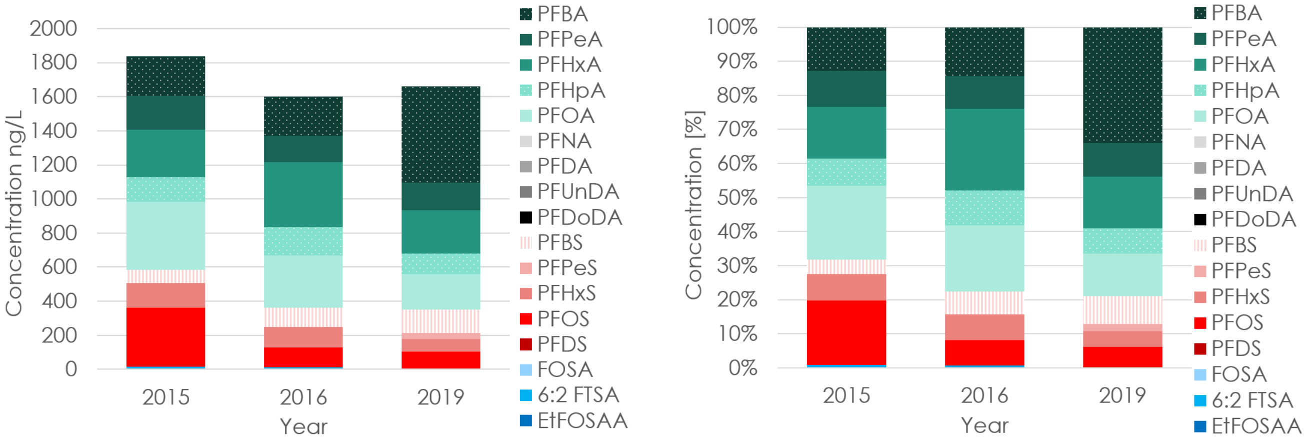
Untreated leachate from the landfill is sampled at point D0 and showed in Figure 46. Total PFASs range between approximately 1750 - 3000 ng/l.



(a) Concentration distribution [ng/l] *(b) Percent distribution [%]*

Figure 46: *Distribution of PFASs from sample point D0, which contains untreated leachate from the landfill.*

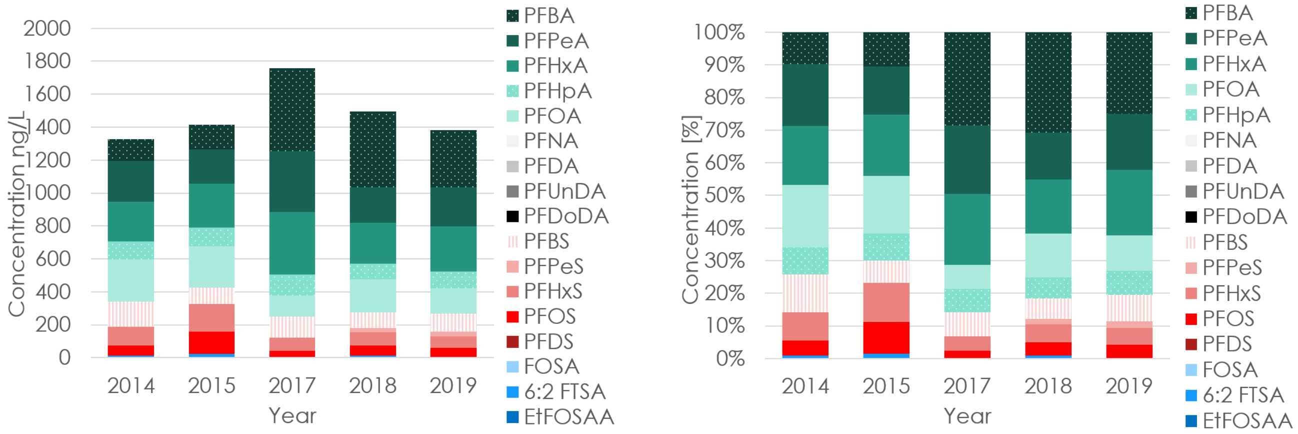
At sampling point R2 the water has passed through the lamella sedimentation and are entering the biostep. Shown in Figure 47 is total PFASs levels of 1600-1800 ng/L. That corresponds to a lower level than previous step and can probably be explained by accumulation of PFASs in the sedimented sludge. The PFOA is no longer the most common substance for all sample years, and in 2019 a peak of PFBA (chain length 3) is seen.



(a) *Concentration distribution [ng/l]* ***(b)*** *Percent distribution [%]*

Figure 47: *Distribution of PFASs from sample point R2 that is situated at the inlet of the bio reactor.*

At sample point A1, the treated water is let out to the recipient, and unfortunately high levels of PFASs remain in the water. Yearly mean values between 2014-2019 show total PFASs levels of about 1400 ng/L, as seen in Figure 48. Unfortunately, a dilution happens in the ponds after the treatment plant due to leakages from unsealed ponds. About 60% of the water entering the ponds between R4 and A1 is water that has not passed through the treatment plant. A large portion of the PFASs purification is probably just a dilution.



(a) *Concentration distribution [ng/l]* ***(b)*** *Percent distribution [%]*

Figure 48: *Distribution of PFASs from sample point A1 at the outlet of the landfill.*

8.3 List of ingredients surfactant (dish soap)

Aqua, Sodium Laureth Sulfate, Lauramine Oxide, Alcohol, Sodium Chloride, PPG-26, PEI/PEG/PPG Copolymer, Sodium, Hydroxide, Phenoxyethanol, PARFUM, Dipropylene Glycol, Benzisothiazolinone, Colorant and Colorant. The list is published by company P&G on their website (*Procter & Gamble Europe household product info site* n.d.).

8.4 Table of test leachate harvesting and containers

Table 9: *Date and time of harvesting leachate at point R1 at Hovgården, as well as number of 25 L container (dunk) used.*

Experiment	**Harvesting date and time**	**# jerrican**
B1	200428, 11:00	1
B2	200428, 11:00	1
B3	200428, 11:00	1
B4	200428, 11:00	1
B5	200428, 11:00	1
B6	200428, 11:00	1
B7	200428, 11:00	1
B8	200428, 11:00	1
B9	200428, 11:00	1
B10	200428, 11:00	2
B11	200428, 11:00	2
B12	200428, 11:00	2
B13	200511, 11:00	3
B14	200511, 11:00	3
B15	200511, 11:00	3
B16	200511, 11:00	4
C1	200518, 9:30	5
C2	200518, 9:30	6
C3	200518, 9:30	7
C4	200518, 9:30	7
C5	200603, 12:00	8
C6	200603, 12:00	9
C7	200603, 12:00	9

8.5 Dilution factors

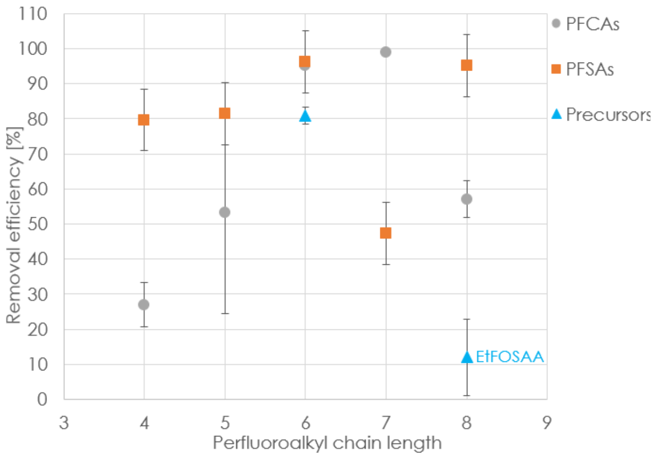
Table 10: *All dilution factors for all samples*

ID	Factor	ID	Factor	ID	Factor
B1-1-F5	26.74	B3-11-CW60	11.18	B7-6-F60	1.42
B1-2-F10	25.23	B3-12-KEM_EXIT	1.00	B7-7-CW5	42.02
B1-3-F20	16.21	B3-13-TW60	1.00	B7-8-CW10	46.32
B1-4-F40	2.64	B3-14-CW60+	1.00	B7-9-CW20	46.53
B1-5-F60	1.44	B4-1-RW0	1.00	B7-10-CW40	39.97
B1-6-RW0	1.00	B4-2-F5	11.74	B7-11-CW60	40.22
B1-7-CW60+	1.00	B4-3-F10	20.89	B7-12-KEM_Milliq	1.00
B1-8-CW5	41.64	B4-4-F20	5.13	B8-1-RW0	1.00
B1-9-CW10	41.64	B4-5-F40	3.50	B8-2-F5	2.35
B1-10-CW20	44.20	B4-6-F60	2.93	B8-3-F10	5.52
B1-11-CW40	53.37	B4-7-CW5	10.76	B8-4-F20	4.16
B1-12-CW60	39.67	B4-8-CW10	7.13	B8-5-F40	1.79
B1-13-TW60	1.00	B4-9-CW20	7.07	B8-6-F60	2.09
B1-14-MilliQ	1.00	B4-10-CW40	11.17	B8-7-CW5	38.73
B2-1-RW0	1.00	B4-11-CW60	9.28	B8-8-CW10	40.84
B2-2-F5	1.96	B4-12-TW60	1.00	B8-9-CW20	41.82
B2-3-F10	3.36	B4-12-KEMRW	1.00	B8-10-CW40	44.28
B2-4-F20	3.02	B5-1-RW0	1.00	B8-11-CW60	40.43
B2-5-F40	1.51	B5-2-F5	3.31	B8-12-CW60+	1.00
B2-6-F60	1.46	B5-3-F10	4.62	B8-13-TW60	1.00
B2-7-F90	3.05	B5-4-F20	2.84	B9-1-RW0	1.00
B2-8-CW5	42.93	B5-5-F40	2.20	B9-2-F5	3.74
B2-9-CW10	39.42	B5-6-F60	3.52	B9-3-F10	8.02
B2-10-CW20	41.97	B5-7-CW5	8.68	B9-4-F20	4.60
B2-11-CW40	37.86	B5-8-CW10	8.36	B9-5-F40	2.20
B2-12-CW60	32.42	B5-9-CW20	7.63	B9-6-F60	1.51
B2-13-CW90	34.15	B5-10-CW40	14.55	B9-7-CW5	47.59
B2-14-F+	7.76	B5-11-CW60	44.87	B9-8-CW10	39.34
B2-15-CW+	39.45	B5-TW60	1.00	B9-9-CW20	36.40
B2-16-F++	3.10	B6-1-RW0	1.00	B9-10-CW40	41.69
B2-17-CW++	6.16	B6-2-F5	1.23	B9-11-CW60	34.87
B2-18-TW++	1.00	B6-3-F10	1.30	B9-12-CW60+	1.00
B2-19-CW++	1.00	B6-4-F20	1.00	B9-13-TW60	1.00
B3-1-RW0	1.00	B6-5-F30	1.26	B10-1-KEM_RW0	1.00
B3-2-F5	1.00	B6-7-CW5	6.34	B10-2-RW0	1.00
B3-3-F10	5.27	B6-8-CW10	12.39	B10-3-F5	2.15
B3-4-F20	2.97	B6-10-CW30	6.85	B10-4-F10	4.14
B3-5-F40	1.43	B6-11-TW30	1.00	B10-5-F20	4.44
B3-6-F60	1.00	B7-1-RW0	1.00	B10-6-F40	2.66
B3-7-CW5	17.80	B7-2-F5	3.26	B10-7-F60	3.40
B3-8-CW10	13.69	B7-3-F10	4.63	B10-8-CW5	37.31
B3-9-CW20	8.66	B7-4-F20	1.54	B10-9-CW10	43.20
B3-10-CW40	14.32	B7-5-F40	1.35	B10-10-CW20	43.31

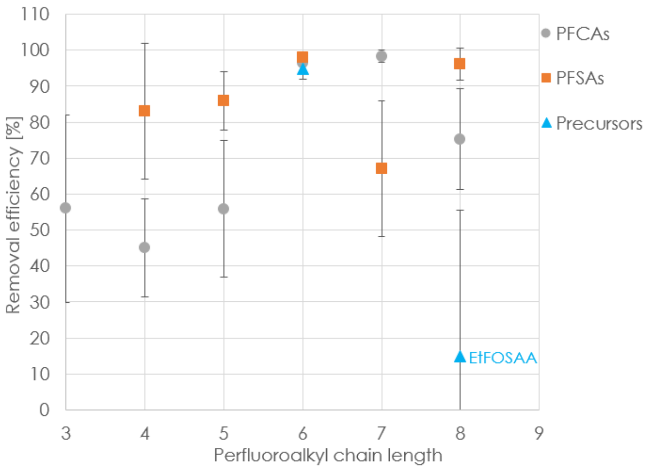
B10-11-CW40	35.37	B13-13-CW60+	1.00	C1-4-E10	26.37
B10-12-CW60	41.00	B13-14-TW60	1.00	C1-5-CW10	34.48
B10-13-KEM_CW60+	1.00	B14-1-RW0	1.00	C1-6-E15	20.02
B10-14-TW0	1.00	B14-2-F5	1.33	C1-7-E20	24.51
B10-15-CW60+	1.00	B14-3-F10	10.22	C1-8-CW20	46.27
B11-1-RW0	1.00	B14-4-F20	2.47	C1-9-F10	1.00
B11-2-F5	2.48	B14-5-F40	1.93	C1-10-F20+	1.00
B11-3-F10	4.39	B14-6-F60	1.66	C1-11-E20+	1.00
B11-4-F20	3.89	B14-7-CW5	42.34	C1-12-CW20+	1.00
B11-5-F40	2.65	B14-8-CW10	35.33	C1-13-E20+_KEM	1.00
B11-6-F60	2.04	B14-9-CW20	36.68	C2-1-RW0	1.00
B11-7-CW5	47.72	B14-10-CW40	40.46	C2-2-RW0_KEM	1.00
B11-8-CW10	47.53	B14-11-CW60	39.47	C2-3-E10	23.75
B11-9-CW20	38.95	B14-12-CW60+	1.00	C2-4-E20	25.18
B11-10-CW40	43.16	B14-13-TW60	1.00	C2-5-CW20	42.16
B11-11-CW60	42.78	B15-1-RW0	1.00	C2-6-E30	27.00
B11-12-CW60+	1.00	B15-2-F5	1.63	C2-7-E40	25.60
B11-13-TW60	1.00	B15-3-F10	2.71	C2-8-CW40	44.79
B12-1-RW0	1.00	B15-4-F20	1.23	C2-9-F10	1.00
B12-2-F5	1.50	B15-5-F40	1.18	C2-10-F20	1.00
B12-3-F10	8.75	B15-6-F60	1.00	C2-11-F30	1.00
B12-4-F20	3.15	B15-7-CW5	43.90	C2-12-F40	1.00
B12-5-F40	1.83	B15-8-CW10	45.41	C2-13-E40+	1.00
B12-6-F60	1.56	B15-9-CW20	44.64	C2-14-E40+_KEM	1.00
B12-7-CW5	51.40	B15-10-CW40	40.34	C2-15-F0-40	1.00
B12-8-CW10	38.92	B15-11-CW60	34.20	C3-1-RW0	1.00
B12-9-CW20	47.98	B15-12-CW60+	1.00	C3-2-E10	24.76
B12-10-CW40	44.08	B15-13-TW60	1.00	C3-3-E20	25.55
B12-11-CW60	44.30	B16-1-RW0	1.00	C3-4-CW20	39.63
B12-12-CW60+	1.00	B16-2-F5	1.00	C3-5-E30	25.05
B12-13-TW60	1.00	B16-3-F10	2.26	C3-6-E40	24.72
B12-14-KEM_EXIT	1.00	B16-4-F20	1.67	C3-7-CW40	44.56
B13-1-RW0	1.00	B16-5-F40	1.40	C3-8-F10	1.00
B13-2-KEM_RW0	1.00	B16-6-F60	1.66	C3-9-F20	1.81
B13-3-F5	1.07	B16-7-CW5	38.96	C3-10-F30	3.41
B13-4-F10	9.96	B16-8-CW10	39.09	C3-11-F40	2.07
B13-5-F20	7.94	B16-9-CW20	42.81	C3-12-E40+	1.00
B13-6-F40	1.63	B16-10-CW40	40.34	C3-13-E40+_KEM	1.00
B13-7-F60	3.91	B16-11-CW60	40.84	C4-1-RW0	1.00
B13-8-CW5	41.82	B16-12-CW60+	1.00	C4-2-E5	24.68
B13-9-CW10	42.30	B16-13-TW60	1.00	C4-3-E10	24.44
B13-10-CW20	40.52	C1-1-RW0	1.00	C4-4-CW10	42.00
B13-11-CW40	39.96	C1-2-RW0_KEM	1.00	C4-5-E15	25.28
B13-12-CW60	40.98	C1-3-E5	25.85	C4-6-E20	27.45

C4-7-CW20	36.92
C4-8-F10	1.18
C4-9-F20	1.22
C4-10-E20+	1.00
C4-11-E20+_KEM	1.00
C5-200604	
C5-1-RW0	1.00
C5-2-RW0-KEM	1.00
C5-3-E5	25.28
C5-4-E10	24.65
C5-5-CW10	34.56
C5-6-E15	23.72
C5-7-E20	23.22
C5-8-CW20	40.87
C5-9-F14	7.77
C5-10-F20	5.43
C5-11-E20+	1.00
C5-12-E20+_KEM	1.00
C5-13-Milliq	1.00
C6-200605	
C6-1-RW0	1.00
C6-2-RW0-KEM	1.00
C6-3-E10	25.03
C6-4-E20	26.01
C6-5-CW20	42.83
C6-6-E30	26.49
C6-7-E40	26.73
C6-8-CW40	42.03
C6-9-F20	1.25
C6-10-F40	1.41
C6-11-E40+	1.00
C6-12-E40+_KEM	1.00
C7-200605	
C7-1-RW0	1.00
C7-2-E2	24.00
C7-3-E5	25.10
C7-4-CW5	44.00
C7-5-E10	24.61
C7-6-E15	24.29
C7-7-CW15	40.54
C7-8-F15	1.75
C7-9-E15+	1.00
C7-10-E15+_KEM	1.00

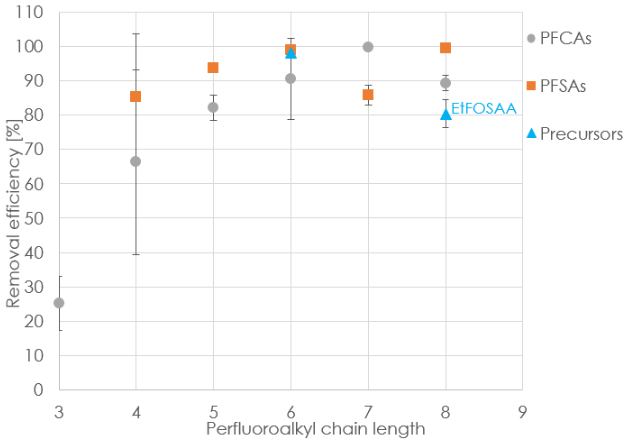
8.6 Removal efficiency for all experiments



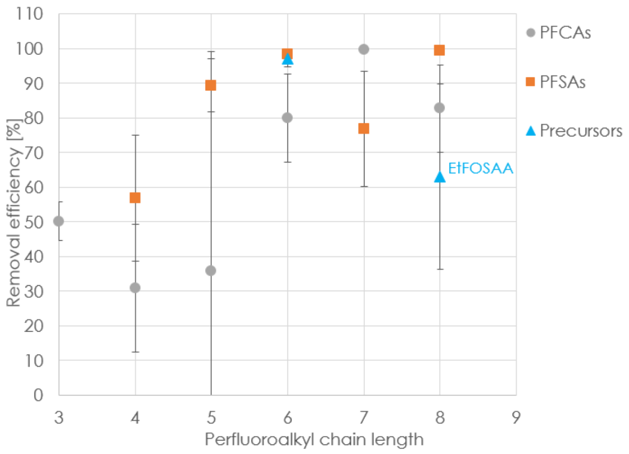
(a) RE over CL B1



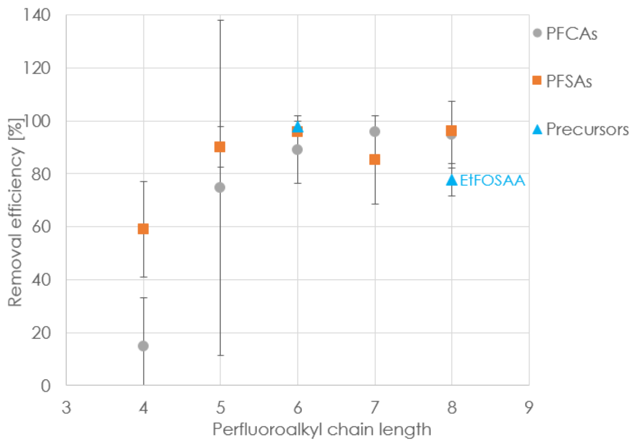
(b) RE over CL B2



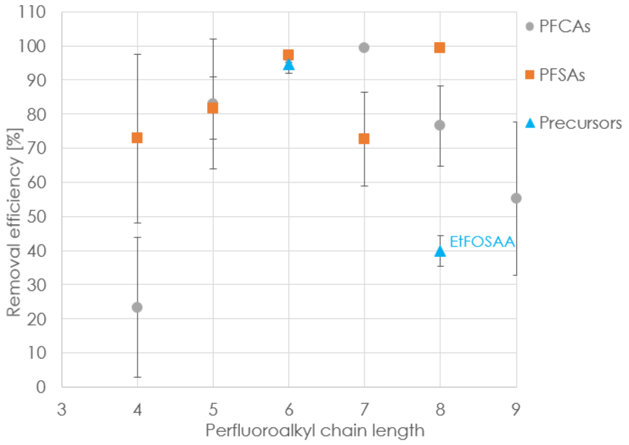
(c) RE over CL B3



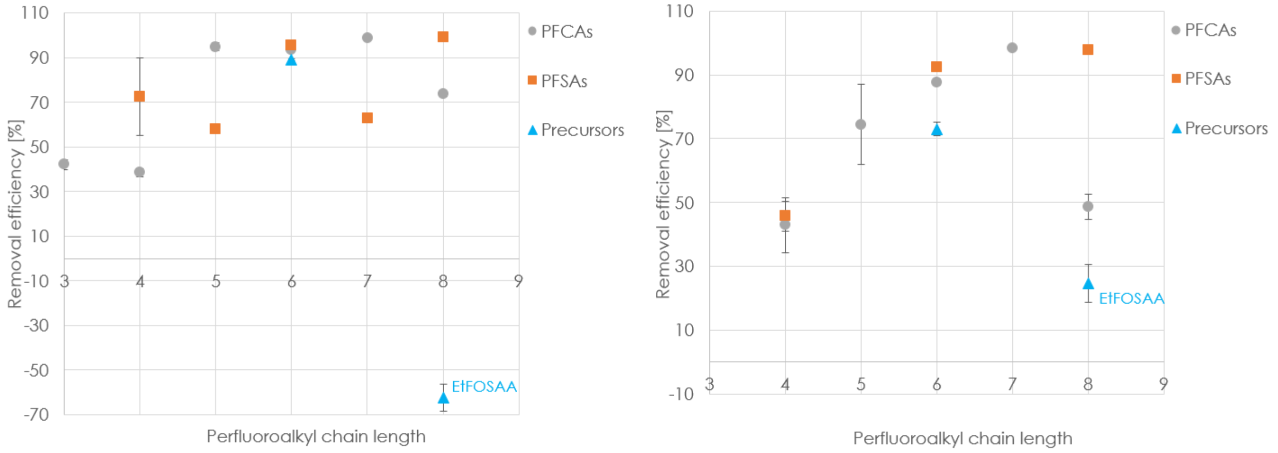
(d) RE over CL B4



(e) RE over CL B5

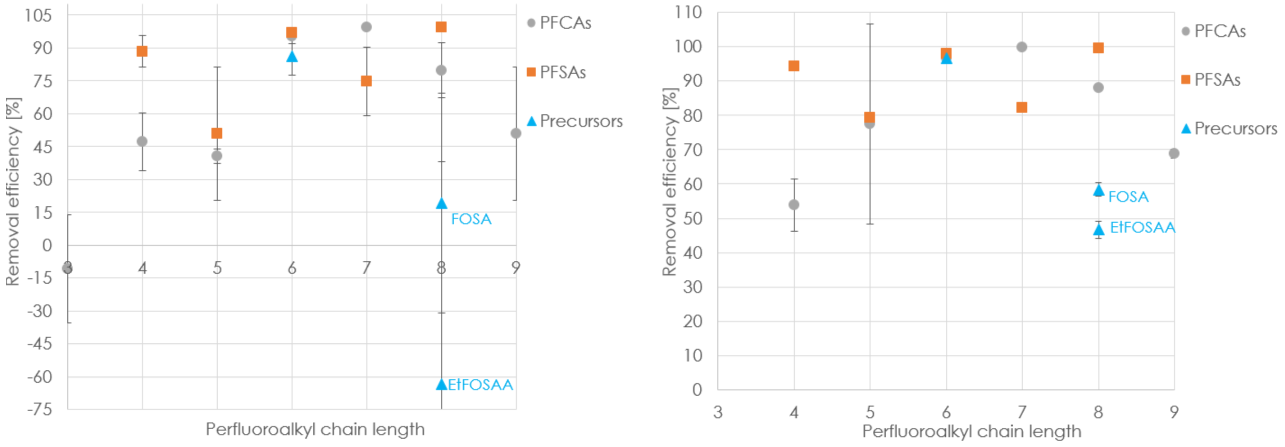


(f) RE over CL B7



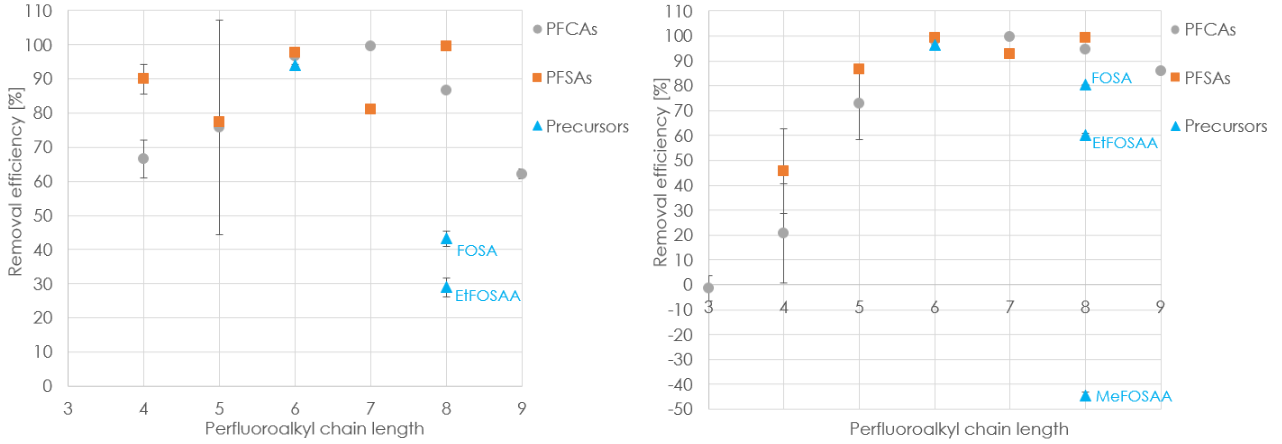
(g) RE over CL B8

(h) RE over CL B9



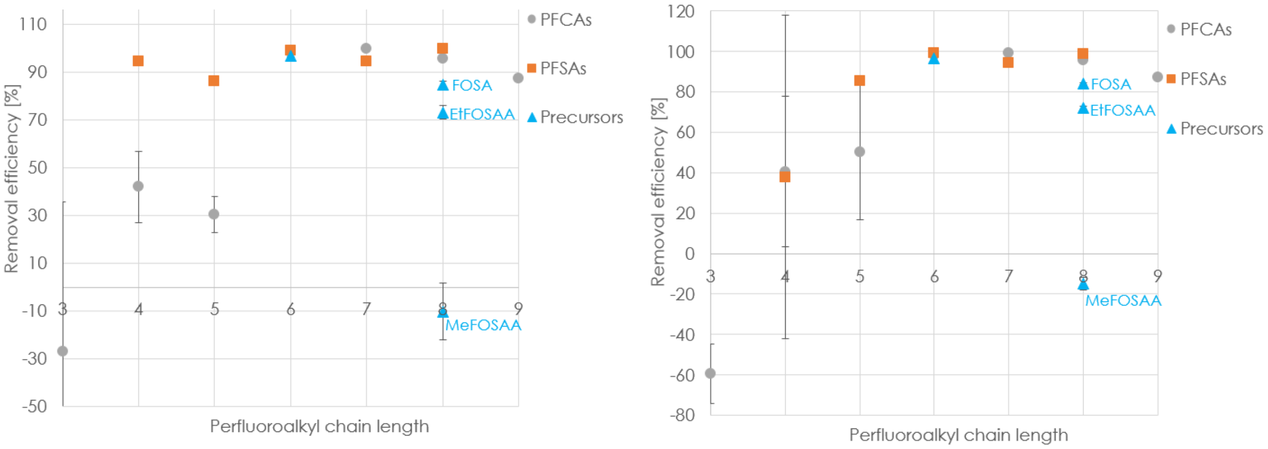
(i) RE over CL B10

(j) RE over CL B11



(k) RE over CL B12

(l) RE over CL B13



(m) RE over CL B15

(n) RE over CL B16

Figure 49: *Removal efficiency for all batch experiments over chain length. Subgroups PFCAs, PFSAs and precursors are plotted separately with associated chain length.*

8.7 Samples sent after all experiments were conducted

Table 11: *Samples sent in after all experiments were conducted. Date in top of the table.*

Sent in 25/8		Sent in 18/8		Sent in 6/7	
B1-1-F5	x	B4-8-CW10	x	B9-12-CW60+	x
B1-2-F10	x	B5-2-F5	x	B10-15-CW60+	x
B1-8-CW5	x	B5-3-F10	x	B11-12-CW60+	x
B1-9-CW10	x	B5-7-CW5	x	B12-12-CW60+	x
B2-2-F5	x	B5-8-CW10	x	B13-13-CW60+	x
B2-3-F10	x	B7-2-F5	x	B15-12-CW60+	x
B2-8-CW5	x	B7-3-F10	x	B16-12-CW60+	x
B2-9-CW10	x	B7-7-CW5	x	C4-8-F10	x
B3-2-F5	x	B7-8-CW10	x	C4-9-F20	x
B3-3-F10	x	B8-2-F5	x	C5-9-F14	x
B3-7-CW5	x	B8-8-CW10	x	C5-10-F20	x
B3-8-CW10	x	B8-12-CW60+	x	C6-9-F20	x
B3-14-CW60+	x	B9-2-F5	x	C6-10-F40	x
B4-2-F5	x	B9-3-F10	x	C7-6-E15	x
B4-3-F10	x	B9-8-CW10	x	C7-8-F15	x

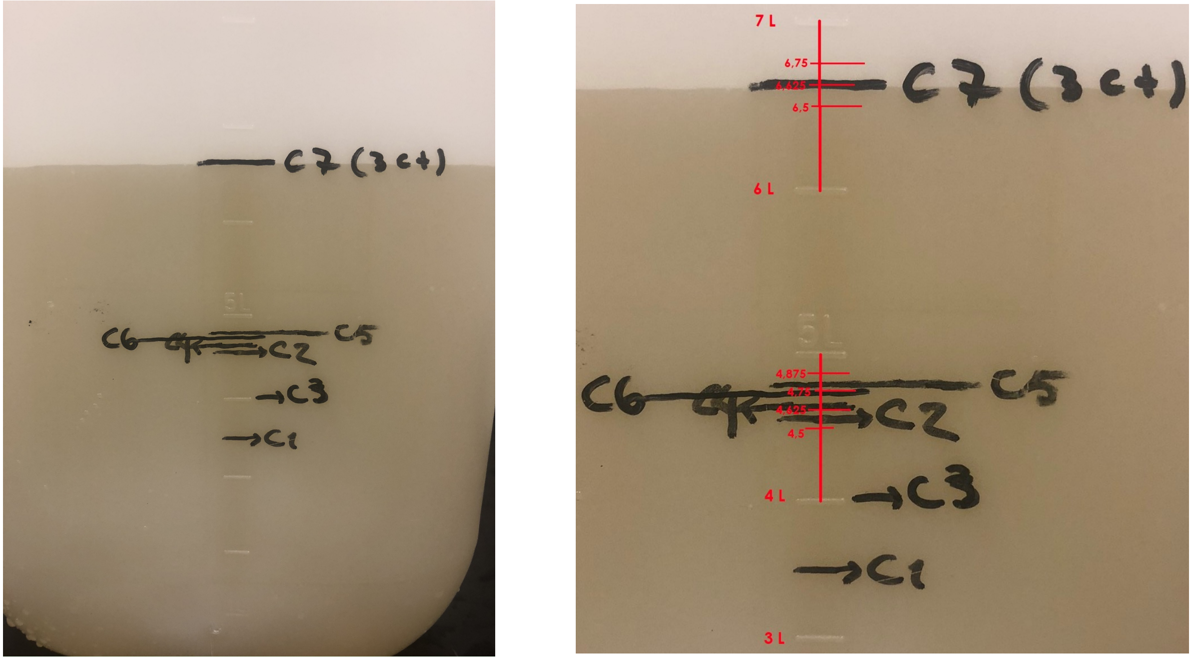
8.8 Data of flows for continuous experiments

Data of flows during each continuous experiment was gathered into Table 12. Each time point of the measurement, what the flow was at the time, the average flow during the entire experiment with standard deviation for each point, backward calculation of the column contact time (ct) and lastly estimated total exit water volume can be seen in the table. The estimated volume of exit water passed through the system was gotten from images in Figure 50.

Table 12: *All flows measured with a volumetric glass during continuous experiments*

	Time [min]	Flow [mL/min]	Average flow	Std.P	Calculated column ct [min]	Exit water volume [L]
C1	-	-	-	-		3.5
C2	0	129	119	9	20	4.6
	5	105				
	15	117				
	25	115				
	35	127				
C3	0	123	108	12	22	4.0
	5	115				
	15	114				
	25	90				
	35	97				
C4	0	244,9	227	11	10	4.6
	2	210,5				
	7	230				
	14	224				
	17	227				
C5	0	243	241	2	10	4.8
	2	242				
	7	240				
	19	238				
C6	0	115	116	8	20	4.8
	2	114				
	6	102				
	9	112				
	13	123				
	16	122				
	25	127				
C7	0	476	455	10	5	6.6
	1	441				
	2	455				
	6	462				
	8	451				
	11	451				
	13	448				

The amount of water going through the system is directly dependent on the flow of water. To see if the flow of the system was as planned, an analyze of the volumes of exit water was done. According to pre-made calculations, all experiments would produce a volume of 4.8 L, except C7 that had an experiment duration of three times the column contact time that equals a volume of 7.1 L. A lot of errors may occur, but to name a few: starting and ending flow at exact the right time, the flow being precisely correct during the entire experiment, differences in flow due to the aeration or pressure. In Figure 50 below are the images looked at when determine if the exit water volume was as predicted.

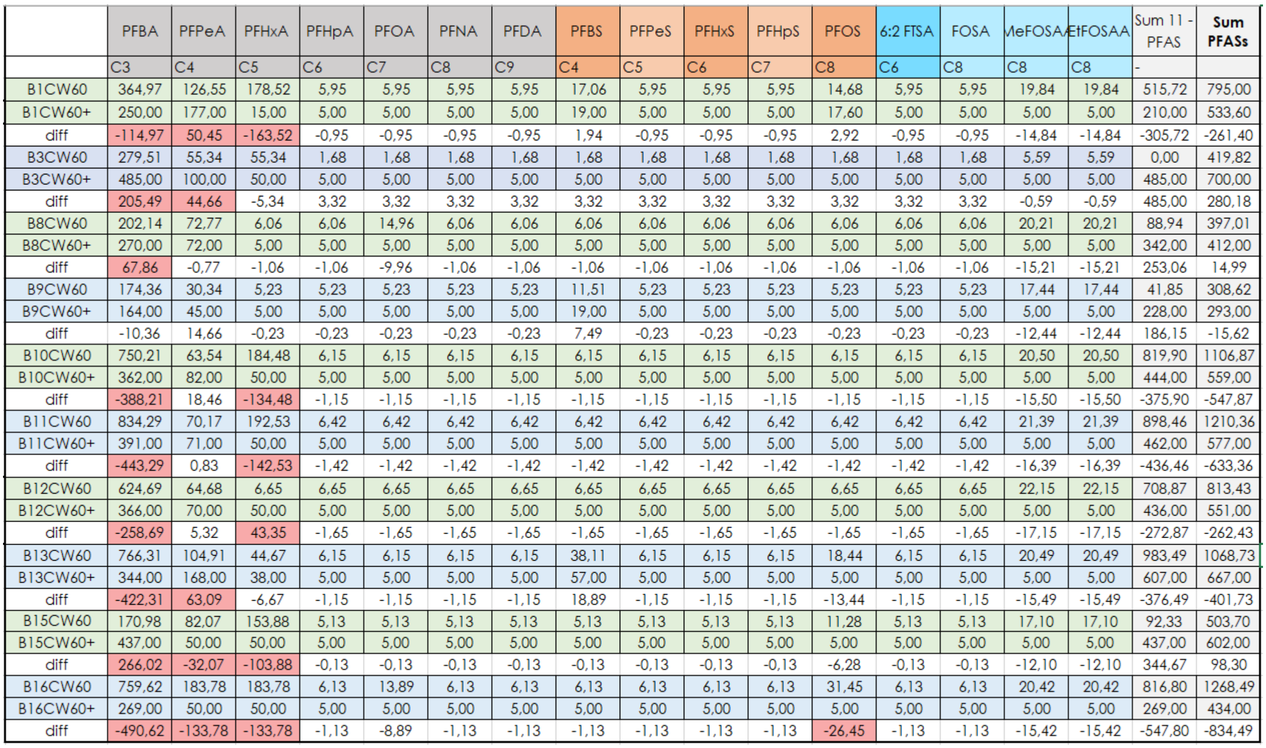


(a) *A line was drawn at the water level after each continuous experiment.*

(b) *Rough and approximate measurements of volume for each continuous experiment.*

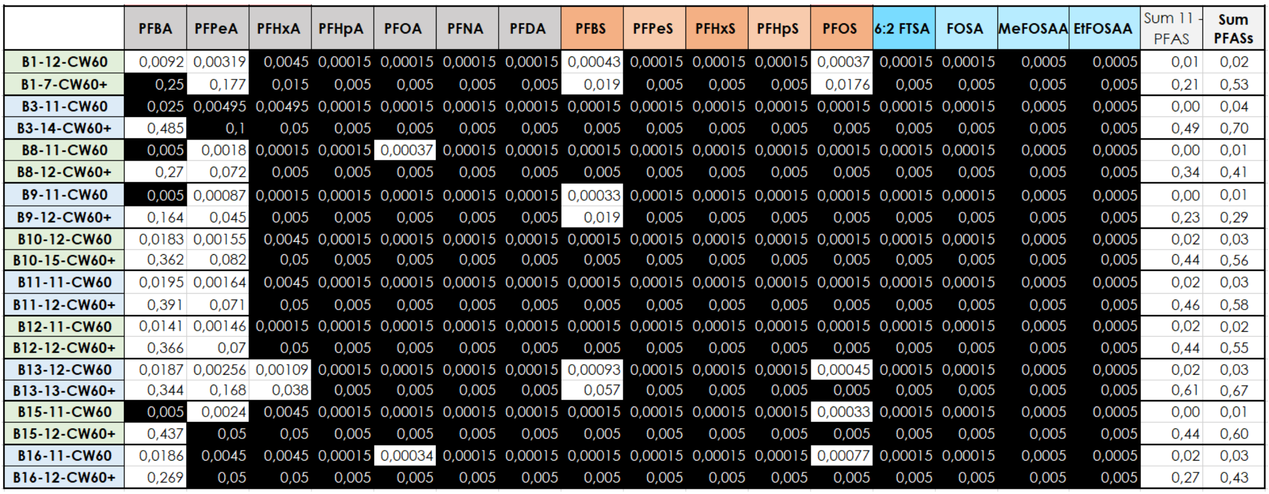
Figure 50: *Exit water in container from continuous experiments. Total volume of exit water through the system during the experiment duration marked.*

8.9 Comparison between CW60 and CW60+



	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFPeS	PFHxS	PFHpS	PFOS	6:2 FTSA	FOSA	MeFOSAA	EtFOSAA	Sum 11 - PFAS	**Sum PFASs**
	C3	C4	C5	C6	C7	C8	C9	C4	C5	C6	C7	C8	C6	C8	C8	C8	-	
B1CW60	364,97	126,55	178,52	5,95	5,95	5,95	5,95	17,06	5,95	5,95	5,95	14,68	5,95	5,95	19,84	19,84	515,72	795,00
B1CW60+	250,00	177,00	15,00	5,00	5,00	5,00	5,00	19,00	5,00	5,00	5,00	17,60	5,00	5,00	5,00	5,00	210,00	533,60
diff	-114,97	50,45	-163,52	-0,95	-0,95	-0,95	-0,95	1,94	-0,95	-0,95	-0,95	2,92	-0,95	-0,95	-14,84	-14,84	-305,72	-261,40
B3CW60	279,51	55,34	55,34	1,68	1,68	1,68	1,68	1,68	1,68	1,68	1,68	1,68	1,68	1,68	5,59	5,59	0,00	419,82
B3CW60+	485,00	100,00	50,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	485,00	700,00
diff	205,49	44,66	-5,34	3,32	3,32	3,32	3,32	3,32	3,32	3,32	3,32	3,32	3,32	3,32	-0,59	-0,59	485,00	280,18
B8CW60	202,14	72,77	6,06	6,06	14,96	6,06	6,06	6,06	6,06	6,06	6,06	6,06	6,06	6,06	20,21	20,21	88,94	397,01
B8CW60+	270,00	72,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	342,00	412,00
diff	67,86	-0,77	-1,06	-1,06	-9,96	-1,06	-1,06	-1,06	-1,06	-1,06	-1,06	-1,06	-1,06	-1,06	-15,21	-15,21	253,06	14,99
B9CW60	174,36	30,34	5,23	5,23	5,23	5,23	5,23	11,51	5,23	5,23	5,23	5,23	5,23	5,23	17,44	17,44	41,85	308,62
B9CW60+	164,00	45,00	5,00	5,00	5,00	5,00	5,00	19,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	228,00	293,00
diff	-10,36	14,66	-0,23	-0,23	-0,23	-0,23	-0,23	7,49	-0,23	-0,23	-0,23	-0,23	-0,23	-0,23	-12,44	-12,44	186,15	-15,62
B10CW60	750,21	63,54	184,48	6,15	6,15	6,15	6,15	6,15	6,15	6,15	6,15	6,15	6,15	6,15	20,50	20,50	819,90	1106,87
B10CW60+	362,00	82,00	50,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	444,00	559,00
diff	-388,21	18,46	-134,48	-1,15	-1,15	-1,15	-1,15	-1,15	-1,15	-1,15	-1,15	-1,15	-1,15	-1,15	-15,50	-15,50	-375,90	-547,87
B11CW60	834,29	70,17	192,53	6,42	6,42	6,42	6,42	6,42	6,42	6,42	6,42	6,42	6,42	6,42	21,39	21,39	898,46	1210,36
B11CW60+	391,00	71,00	50,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	462,00	577,00
diff	-443,29	0,83	-142,53	-1,42	-1,42	-1,42	-1,42	-1,42	-1,42	-1,42	-1,42	-1,42	-1,42	-1,42	-16,39	-16,39	-436,46	-633,36
B12CW60	624,69	64,68	6,65	6,65	6,65	6,65	6,65	6,65	6,65	6,65	6,65	6,65	6,65	6,65	22,15	22,15	708,87	813,43
B12CW60+	366,00	70,00	50,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	436,00	551,00
diff	-258,69	5,32	43,35	-1,65	-1,65	-1,65	-1,65	-1,65	-1,65	-1,65	-1,65	-1,65	-1,65	-1,65	-17,15	-17,15	-272,87	-262,43
B13CW60	766,31	104,91	44,67	6,15	6,15	6,15	6,15	38,11	6,15	6,15	6,15	18,44	6,15	6,15	20,49	20,49	983,49	1068,73
B13CW60+	344,00	168,00	38,00	5,00	5,00	5,00	5,00	57,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	607,00	667,00
diff	-422,31	63,09	-6,67	-1,15	-1,15	-1,15	-1,15	18,89	-1,15	-1,15	-1,15	-13,44	-1,15	-1,15	-15,49	-15,49	-376,49	-401,73
B15CW60	170,98	82,07	153,88	5,13	5,13	5,13	5,13	5,13	5,13	5,13	5,13	11,28	5,13	5,13	17,10	17,10	92,33	503,70
B15CW60+	437,00	50,00	50,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	437,00	602,00
diff	266,02	-32,07	-103,88	-0,13	-0,13	-0,13	-0,13	-0,13	-0,13	-0,13	-0,13	-6,28	-0,13	-0,13	-12,10	-12,10	344,67	98,30
B16CW60	759,62	183,78	183,78	6,13	13,89	6,13	6,13	6,13	6,13	6,13	6,13	31,45	6,13	6,13	20,42	20,42	816,80	1268,49
B16CW60+	269,00	50,00	50,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	5,00	269,00	434,00
diff	-490,62	-133,78	-133,78	-1,13	-8,89	-1,13	-1,13	-1,13	-1,13	-1,13	-1,13	-26,45	-1,13	-1,13	-15,42	-15,42	-547,80	-834,49

Figure 51: *All analyzed CW60 and CW60+ samples and the difference between them. Differences above 20 ng/L marked in red. Concentrations in ng/L.*



	PFBA	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFBS**	**PFPeS**	**PFHxS**	**PFHpS**	**PFOS**	**6:2 FTSA**	**FOSA**	**MeFOSAA**	**EtFOSAA**	Sum 11 - PFAS	**Sum PFASs**
B1-12-CW60	0,0092	0,00319	0,0045	0,00015	0,00015	0,00015	0,00015	0,00043	0,00015	0,00015	0,00015	0,00037	0,00015	0,00015	0,0005	0,0005	0,01	0,02
B1-7-CW60+	0,25	0,177	0,015	0,005	0,005	0,005	0,005	0,019	0,005	0,005	0,005	0,0176	0,005	0,005	0,005	0,005	0,21	0,53
B3-11-CW60	0,025	0,00495	0,00495	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,0005	0,0005	0,00	0,04
B3-14-CW60+	0,485	0,1	0,05	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,49	0,70
B8-11-CW60	0,005	0,0018	0,00015	0,00015	0,00037	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,0005	0,0005	0,00	0,01
B8-12-CW60+	0,27	0,072	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,34	0,41
B9-11-CW60	0,005	0,00087	0,00015	0,00015	0,00015	0,00015	0,00015	0,00033	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,0005	0,0005	0,00	0,01
B9-12-CW60+	0,164	0,045	0,005	0,005	0,005	0,005	0,005	0,019	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,23	0,29
B10-12-CW60	0,0183	0,00155	0,0045	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,0005	0,0005	0,02	0,03
B10-15-CW60+	0,362	0,082	0,05	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,44	0,56
B11-11-CW60	0,0195	0,00164	0,0045	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,0005	0,0005	0,02	0,03
B11-12-CW60+	0,391	0,071	0,05	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,46	0,58
B12-11-CW60	0,0141	0,00146	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,0005	0,0005	0,02	0,02
B12-12-CW60+	0,366	0,07	0,05	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,44	0,55
B13-12-CW60	0,0187	0,00256	0,00109	0,00015	0,00015	0,00015	0,00015	0,00093	0,00015	0,00015	0,00015	0,00045	0,00015	0,00015	0,0005	0,0005	0,02	0,03
B13-13-CW60+	0,344	0,168	0,038	0,005	0,005	0,005	0,005	0,057	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,61	0,67
B15-11-CW60	0,005	0,0024	0,0045	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00033	0,00015	0,00015	0,0005	0,0005	0,00	0,01
B15-12-CW60+	0,437	0,05	0,05	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,44	0,60
B16-11-CW60	0,0186	0,0045	0,0045	0,00015	0,00034	0,00015	0,00015	0,00015	0,00015	0,00015	0,00015	0,00077	0,00015	0,00015	0,0005	0,0005	0,02	0,03
B16-12-CW60+	0,269	0,05	0,05	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,005	0,27	0,43

Figure 52: *Raw data of all analyzed CW60 and CW60+ samples. Half of the detection limit marked with black background. Concentrations in µg/L.*