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An assessment of thermal desorption as a remediation technique for per- and polyfluoroalkyl substances (PFASs) in contaminated soil

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Anna-Stina Lind

ABSTRACT

An assessment of thermal desorption as a remediation techniques for per- and polyfluoroalkyl substances (PFASs)-contaminated soil

Anna-Stina Lind

Per- and polyfluoroalkyl substances (PFASs) are a diverse group of persistent organic pollutants. PFASs have a wide area of applications such as stain repellent for paper, textile, furniture and industrial products such as aqueous film forming foams (AFFFs) used for firefighting. However, during production, usage and disposal, PFASs can be released into the environment and can therefore be a threat to humans and the ecosystems. Thus, it is important to develop soil remediation techniques for PFASs. The aim of this thesis has been to evaluate if thermal desorption can be used as a remediation method for PFASs-contaminated soil. The idea of thermal desorption is to vaporize the PFASs by high temperature, extract the PFASs from the soil by vacuum pumping and then trapping the PFASs into an air filter. The air filter can then be removed and incinerated at a high temperature to degrade PFASs. The thermal desorption has been performed in an oven at various temperatures (i.e. 150 °C, 250 °C, 350 °C, 450 °C and 550 °C) during time periods of 15 min, 45 min and 75 min for clay soil, loamy sand soil and a mixed soil from Arlanda airport. After the thermal desorption the PFASs have been extracted in methanol and then measured with an Ultra-performance liquid chromatography tandem mass-spectrometer (UPLC-MS/MS). The results show that the method is a success. 6 of 14 PFASs in the soil from Arlanda airport and all PFASs in the clay soil and the loamy sand soil reached a removal efficiency above 90 %. The results also show that all PFASs in all soils have been desorbed below the guide line value for perfluorooctane sulfonate (PFOS) for less sensitive land use, 3 mg/kg dw, given by Swedish Geological Institute (SGI). All samples have reached this limit above thermal desorption in 450 °C with treatment time 75 min.

Keywords: Thermal desorption, per- and polyfluoroalkyl substances, PFASs, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFBS, PFHxS, PFOS, 6:2 FTSA, 8:2 FTSA, FOSA, PCB, PAH, UPLC MS/MS

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REFERAT

En utvärdering för termisk rening av jord förorenad med per- och polyfluoralkylsubstanser (PFASs)

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Per- och polyfluoralkylsubstanser (PFASs) är en stor grupp av svårnedbrytbara organiska föroreningar. I polyfluoralkylsubstanser har minst en fluoratom ersatt en väteatom, medan alla väteatomer har ersatts med fluoratomer i perfluoralkylsubstanser. Den starka klor-fluorbindningen som uppstår gör dem oerhört resistenta mot nedbrytning. PFASs kan bioackumulera i organismer och vissa PFASs har visat toxiska effekter på människor. Brandskum av typen AFFF (Aqueous Film Forming Foam) innehåller PFASs och används på flygplatser för att släcka bränslebränder, flygplatserna är därmed punktkällor för PFASs. På grund av att PFASs används i brandskum lakas det ut i marken och kommer följaktligen i kontakt med grundvattnet. När PFASs kontaminerat grundvattnet är det risk för att dessa föroreningar hamnar i våra vattenkranar då många akviferer används som dricksvattenkällor. Det är därmed viktigt att utvärdera marksaneringstekniker för PFAS för att förhindra ytterligare spridning. Syftet med denna studie är att utvärdera om termisk desorption kan användas som en saneringsmetod för mark förorenad av PFASs. Saneringsmetoden har visat sig framgångsrik på andra föroreningar såsom polyklorerade bifenyler (PCB) och polycykliska aromatiska kolväten (PAH). Den termiska desorptionen går ut på att hetta upp PFASs ända till att ämnena förångas. Då kan föroreningen extraheras från jorden genom vakuumpumpning och koncentreras i ett filter. Filtret avlägsnas sedan och förbränns i hög temperatur.

I det här experimentet har jordarna frystorkats och homogeniserats innan den termiska desorptionen utfördes. Den termiska saneringen har genomförts i ugnar som har kunnat värma upp till åtminstone 550 °C. Proverna har därefter genomgått en upparbetningsprocess för att mäta de resterande mängderna av PFASs. Efter det har proven analyserats i en vätskekromatograf kopplad till en masspektrometer (UPLC MS/MS) för att se hur mycket PFASs som var kvar i de termiskt behandlade jordproverna. Resultaten visade att för alla PFAS-ämnen i alla tre jordar, hade den termiska reningen lyckats sanera föroreningarna till en nivå som ligger under riktvärdena från Sveriges Geotekniska institut (SGI) för mindre känslig markanvändning för PFOS. I sandjorden (*Högåsa*) och lerjorden (*Vreta kloster*) hade alla PFASs nått en reningsgrad över 90 % över 450 °C efter 75 minuter. För jorden från Arlanda var saneringen inte lika framgångsrik, 6 av 14 ämnen blev sanerade till över 90 % för 550 °C efter 75 minuter. Slutsatsen är därför att metoden fungerar.

Nyckelord: Termisk rening, Per- och polyfluoralkylsubstanser, PFASs, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFBS, PFHxS, PFOS, 6:2 FTSA, 8:2 FTSA, FOSA, PCB, PAH, UPLC MS/MS.

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PREFACE

This Master's thesis is equivalent to 30 ETCS and is the final part of the Master Programme in Environmental and Water Engineering at Uppsala University and the Swedish University of Agricultural Sciences in Uppsala. My supervisor was Ph.D. student Mattias Sörengård and my subject reviewer was Associated Professor Lutz Ahrens, both at the Department of Aquatic Sciences and Assessments at the Swedish University of Agricultural Sciences. Examiner was Associate Professor Fritjof Fagerlund from the department of Geological Sciences at Uppsala University. The project was carried out as a part of the Science Project PFAS-pure that is financed by Vinnova.

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POPULÄRVETENSKAPLIG SAMMANFATTNING

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Kan jord som är förorenad med per- och polyfluoralkylsubstanser (PFASs) renas med hjälp av värme?

Per- och polyfluoralkylsubstanser (PFASs) är ämnen som bevaras länge i naturen då de bryts ned långsamt eller inte alls. De har använts i många typer av produkter till exempel i ”non-stick”-stekpannor, i färg, på insidan av pappersmuggar och i ett speciellt brandskum som används på flygplatser. Undersökningar behöver göras för att se om naturen kan renas från de här ämnena. Därför har det gjorts experiment på om värme kan rena mark där det finns PFASs.

Per- och polyfluoralkylsubstanser (PFASs) har producerats sedan 1950-talet och är en grupp ämnen med egenskaper som gör dem användbara men också långlivade. En av de egenskaper som gör PFASs svårnedbrytbara är att de innehåller en speciell kemisk bindning. Denna består av en kol-atom och en fluor-atom som dras till varandra och det bildas en stark kraft mellan dessa vilket gör det svårt att skilja de åt. Alla PFAS-molekyler innehåller minst en sådan kemisk bindning. Den här gruppen består även av en fettavvisande del och en vattenavvisande del, de är så kallade surfaktanter. En vanlig surfaktant som de flesta har hemma är diskmedel, alltså ett medel som attraheras av både vatten och olja. Det är den här egenskapen som gör att PFASs är bra på att stöta bort både vatten och oljebaserade produkter. På grund av att de är långlivade och kan stöta bort flertal ämnen gör att PFASs har producerats i stora mängder. De har använts i brandskum, stekpannor, färg, smink och pappersmuggar för att nämna några produkter.

PFASs har spridits sig ut i naturen som en följd av den storskaliga produktionen. De har läckt ut från bland annat flygplatser som använder brandskum med PFASs i. Två ämnen, PFOS och PFOA, är redan förbjudna på grund av att de är giftiga. Dessa kan dock fortfarande spridas till vårt dricksvatten eftersom att när dessa ämnen användes fastnade en del på markpartiklarna istället för att transporteras till närmsta vattendrag. Då PFASs stannar längre i marken än i de närliggande vattendragen och mycket grundvatten används till dricksvatten, är det viktigt att undersöka metoder som kan avlägsna PFASs ur marken.

Flera forskare har undersökt vilka besvär PFASs kan ge, framförallt har de undersökt de PFASs som numera har förbjudits. Forskarna kom fram till att om PFASs ansamlas i människokroppen kan det leda till låg födelsevikt för foster, infertilitet hos kvinnor som en bieffekt till en sjukdom (endometrios) som kan ha orsakats av höga halter av PFASs, ökad impulsivitet hos barn och även en ökad risk för cancer i njurar och testiklar.

Det finns flera eventuella metoder som skulle kunna användas för att ta bort PFASs ur marken. Den metod som undersöks i det här experimentet kallas termisk desorption och innebär att marken hettas upp. PFASs blir ånga som kan fångas upp och därefter förstöras. Andra metoder skulle kunna vara att gräva upp den jord där det finns PFASs och skölja rent den. Det finns även en metod som innebär att föroreningar blir kvar i marken. Metoden går ut på att det tillsätts ämnen i marken, till exempel betong, som gör att de inte kan spridas vidare.

I det här experimentet har jord hämtats från tre olika platser runt om i Sverige. Lerjord från Vreta kloster, sandjord från Högåsa och en blandjord från Arlanda Flygplast. Ämnesgruppen PFASs består av väldigt många ämnen men för att göra experimentet mer hanterbart valdes bara några stycken. I sandjorden och lerjorden tillsattes det en exakt mängd av 14 stycken PFASs. I jorden från Arlanda tillsattes dock inget, där ansågs det att det redan fanns tillräckligt med PFASs. Jordproverna hettades antingen upp till 150 °C, 250 °C, 350 °C, 450 °C eller 550 °C. För varje temperatur var proverna inne i olika lång tid. Tre tidsperioder användes 15 minuter, 45 minuter och 75 minuter. Det användes särskilda ugnar till experimenten som kan värmas upp till höga temperaturer. När jorden hade blivit upphettad och svalnat igen gjordes analyser av vad som fanns kvar i proverna. Undersökningarna gjordes genom att separera PFASs från jorden med hjälp av lösningsmedlet metanol. Efter att separeringen var utförd hamnade den PFASs som förut var i jorden i metanolen. Därefter blev metanolen koncentrerad till en mindre mängd vätska och sedan kunde PFASs-halterna mätas med en särskild apparat som heter masspektrometer.

Resultatet blev bra och reningen lyckades för många ämnen. Resultaten visade att de jordar där PFASs blivit tillsatt var skillnaderna små, det var bara jorden från Arlanda som fick annorlunda resultat. Av detta har slutsatsen dragits, att jordtypen inte spelar roll för hur bra reningen blir av mark förorenad med PFASs. De temperaturer där reningen fungerade bäst var mellan 350 °C och 550 °C. Slutsatsen blev då att värme kan användas till att rena mark från PFASs och för många ämnen blev proverna renade över 90 %.

ABBREVIATIONS

AFFFs	Aqueous Film Forming Foams
PFASs	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFPeA	Perfluoropentanoic acid
PFHxA	Perfluorohexanoic acid
PFHpA	Perfluoroheptanoic acid
PFOA	Perfluorooctanoic acid
PFNA	Perfluorononanoic acid
PFDA	Perfluorodecanoic acid
PFUnDA	Perfluoroundecanoic acid
PFBS	Perfluorobutanesulfonic acid
PFHxS	Perfluorohexanesulfonic acid
PFOS	Perfluorooctanesulfonic acid
6:2 FTSA	6:2 Fluorotelomer sulfonic acid
8:2 FTSA	8:2 Fluorotelomer sulfonic acid
FOSA	Perfluorooctane sulphonamide
POP	Persistent Organic Pollutant
PCB	Polychlorinated biphenyls
PAH	Polycyclic aromatic hydrocarbons
SGI	Swedish Geological Institute
NaOH	Sodium Hydroxide
HCL	Hydrochloric acid
PHC	Polyhalogenated compound
UPLC MS/MS	Ultra-performance liquid chromatography tandem mass-spectrometer
VOC	Volatile organic compound

CONTENT

1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) - are a large group of organic substances characterized by their strong carbon-fluorine bonds (C-F bonds). PFASs can be partially or completely fluorinated, vary in size, structure and chemical properties (Buck et al., 2011). They have bioaccumulation potential (Chu et al., 2015) and they are fluorinated surfactants (Buck et al., 2011). A surfactant is a substance that can reduce the surface tension of water and other liquids (Oxford English Dictionary, 2017). Due to these characteristics, PFASs are used in a wide variety of products (Hale et al., 2017; Xiao, 2017). Concerns have been raised because the large production volumes of PFASs combined with their problematic features such as environmental persistency due to the strong C-F bond and their bioaccumulation potential (Rahman et al., 2014). They have also proven to have adverse implications on humans and biota (Ahrens, 2011). PFASs have been found in humans, wild animals, soil and drinking water, and are considered ubiquitously distributed in the environment (Buck et al., 2011).

The release of PFASs into the environment is a risk for humans and wildlife (Ahrens, 2011). There are several studies that mention dangerous complications related to present PFASs contamination (Rahman et al., 2014; Ashley-Martin et al., 2017; Wang et al., 2017). The reasons for the PFASs-contaminated soil and groundwater are that there are many products containing PFASs in large quantities and they are sometimes used in a way so that the PFASs can easily be spread into the nature (Baduel et al., 2015).

In the soil, the PFASs sorb to the soil particles (Hellsing et al., 2016) and therefore they do not spread at the same speed in the unsaturated soil compared to when the PFASs have reached the saturated soil (Gellrich et al., 2012). To be able to reduce the release of PFASs into the environment, point source PFAS soil remediation sometimes needs to be performed. Although there are today very few studies that have assessed remediation techniques for PFASs-contaminated soil. There are however several soil remediation methods that have been discussed to be effective for PFAS contaminated soil, where thermal desorption was suggested as theoretically very promising (Berglind et al., 2013).

The aim of this study is to evaluate if thermal desorption can be used as a successful remediation method for PFAS contaminated soil. Thermal desorption has previously been shown to successfully remediate other persistent organic pollutants (POP) such as polychlorinated biphenyls (PCBs) (Zhao et al., 2017), however, it has never been tested for PFASs.

1.1 RESEARCH QUESTIONS

- Which temperatures are able to remediate PFASs in the soil to a sufficient level?
- How do the PFAS concentrations and composition profile change over time after thermal treatment?
- Does the soil type have any effect on PFAS removal efficiency?

1.2 DELIMITATIONS

These experiments assessed the thermal desorption remediation method for PFASs-contaminated soil. During the experiments, 14 common PFASs were evaluated, however, this is only a fraction of the large PFAS group which contains over 3000 substances on the global market (Falk-Filipsson et al., 2015).

The focus has been on evaluating if the thermal desorption works for removing these substances from soil. No other aspect of the remediation method has been evaluated e.g. no air samples have been analysed to assess how much of the PFASs vaporized or how much of total organic fluorine that has been removed from the soil.

2. BACKGROUND

2.1 MANUFACTURING AND USE

PFASs have been used since the 1950's for numerous products and applications (Hale et al., 2017). Their properties make them an excellent substance to put in a wide variety of products (Stahl et al., 2013). They been used in firefighting foams, in food-contact paper, as protective coating on textile, in herbicide, in pesticides and even in cosmetics (Hale et al., 2017). They have also been used in products like "non-stick" frying pans and paints (Xiao, 2017). Most of the PFASs are synthetically produced but there are a few that might exist naturally, such as from volcano activities (Ahrens, 2011)

2.2 PFAS PROPERTIES

The physical and chemical properties of PFASs are diverse since PFASs are a large group of substances (Xiao, 2017). They have a few properties in common, all have at least one fluor (F) atom bound together with a carbon atom (Buck et al., 2011). This carbon-fluor bond is a very strong bond (Kim et al., 2015) and it is this bond that makes the PFASs very persistent to thermal, chemical and biological degradation (Krafft and Riess, 2015). The polyfluoroalkyl substances can degrade in the environment, tough but only or most likely to a perfluoroalkyl substance (Buck et al., 2011).

The difference between perfluoroalkyl substances and polyfluoroalkyl substances are that in the perfluoroalkyl group all hydrogen atoms are replaced with fluorine atoms and in the polyfluoroalkyl group at least one, but not all hydrogen atoms, are replaced with a fluorine atom or atoms (Buck et al., 2011). The two most common perfluoroalkyl substances are the perfluorinated sulfonic acids (PFSAs) and perfluorinated carboxylic acids (PFCAs) (Rayne and Forest, 2009). One of each from those groups, PFOA and PFOS, have been phased out because they are toxic and are bioaccumulating in humans and biota (Borg and Håkansson, 2012).

The PFCAs and PFSAs can be divided into short-chained and long chained PFASs (Buck et al., 2011). Buck et al. writes that the long chained PFCAs have 7 or more fluorinated carbon atoms and the PFSAs have 6 or more fluorinated carbon atoms. The difference in definition between the two perfluoroalkyl acids depends on the fact that the long chained PFCAs and PFSAs can bioaccumulate easier.

2.3 ENVIRONMENTAL AND BIOLOGICAL EFFECTS

Short-chained PFASs are more mobile in soil than long chained PFASs (Gellrich et al., 2012; Hellsing et al., 2016). The short chained PFASs also have lower bioaccumulation potential and viewed upon as less toxic (Gellrich et al., 2012). Short-chained PFASs are however still as persistent as the long chained PFASs in the environment (Krafft and Riess, 2015). After two of the long chained PFASs have been banned (PFOA and PFOS) (Gomis et al., 2015), the use of short-chained PFASs and precursors has increased (Ahrens et al., 2015). There is also still leaching out a lot of PFOS and PFOA from contaminated soil because they were historically used in such high abundance (Filipovic et al., 2015). The banned PFASs are therefore still ending up in our drinking water, and they also have precursors that could degrade and increase the concentrations of them in the soil over time (Gellrich et al., 2012).

A common point source for PFASs is the Aqueous Film Forming Foams (AFFFs) (Anderson et al., 2016; Barzen-Hanson et al., 2017; Mejia-Avendaño et al., 2017). AFFFs have extensively been used to quench hydrocarbon fuel fires at different practice facilities such as airport and military bases (Xiao et al., 2017). Other point sources are landfills, waste disposals, the use of products containing PFASs and from drains in sewage treatment plants (Borg and Håkansson, 2012).

According to Hellsing et al. (2016) the use of AFFFs have contaminated the soil near firefighting training sites. When the PFASs have spread to the soil they can bioaccumulate in soil organisms and plants (Rich et al., 2015; Navarro et al., 2017). After the PFASs has reached the soil, they can potentially leach down into the groundwater and thereafter contaminate drinking water reservoirs (Hellsing et al., 2016). In a study from Uppsala, Sweden, it has been shown that drinking water reservoirs have been contaminated and thereafter PFASs levels in human blood serum have increased over time because of PFASs contaminated drinking water (Gyllenhammar et al., 2015).

There are several toxicological effects to be acknowledged because of the spread of PFAS contaminations. According to Wang et al. (2017), there is a possible relation between infertility as an effect of endometrioses, where the endometrioses could have been caused by PFASs contamination. Endometrioses is a gynecologic disease that is characterized by endometrial glands growing on the outside of the uterus (Wang et al., 2017). A correlation between PFASs in maternal blood or blood from the umbilical cord and low birth weight has also been found (Ashley-Martin et al., 2017). A study on PFOA-levels in humans was done on the local population in mid-Ohio valley (Rahman et al., 2014). In this community PFOA existed in the drinking water according to Rahman et al. (2014) and it was a chemical plant in the area. The people in mid-Ohio valley, especially the people who worked in the factory, had a higher rate of cancer in kidneys and testicles. Other studies, also according to Rahman et al. (2014), have found a correlation between PFAS levels in humans and early menopause, increased impulsivity in children, delayed puberty, low semen quality in young men.

2.4 SOIL REMEDIATING TECHNIQUES

There are other potentially good techniques to remediate PFASs-contaminated soil than thermal desorption, e.g. stabilization and solidification, soil wash and incineration (Berglind et al., 2013). Soil washing aims to clean PFAS contaminated soil by washing it with water or water mixed with solvents (Englöv et al., 2007). The solution is circulated *in situ* within the contaminated area according to Englöv et al. (2007), to mobilize the contamination and partition the PFAS to the aqueous phase. When the PFASs are in the aqueous phase, the liquid is taken out from the soil and then cleaned in order to remove the contamination and any other added chemical, often by filtration through activated carbon. The *in situ* soil wash method is primarily used in the unsaturated zone but can also be applied in the saturated zone.

Incineration is another method that destroys the contaminants by burning the polluted soil. This method is usually done *ex-situ*, first, by excavating the affected soil and then combust it in an incineration unit (Vidonish et al., 2016).

Stabilization and solidification is a remediation method based on adding a sorbent material that stabilizes the contamination (Spence and Shi, 2004). An example of such a material is activated carbon. A study in Norway tested different sorbents and got the result that the best stabilization was achieved when activated carbon was added to the soil (Hale et al., 2017). When the contamination is stabilized, it can be further solidified into a monolith, example by adding a binder, often Portland cement, to the contaminated soil (Pereira et al., 2001).

2.5 THERMAL REMEDIATION

Multiple methods have been developed for thermal treatments in soil e.g. thermal desorption and incineration (Kuppusamy et al., 2017). Microwave frequency heating is also used as a thermal treatment method (Lim et al., 2016). In this study, thermal desorption was evaluated. There are two ways to operate thermal desorption: *ex-situ* and *in situ*. E*x situ* means excavation of the polluted soil and treat the soil in a facility above ground. *In situ* means that the soil is remediated while the soil is undisturbed and the treatment equipment is located in the soil (Vidonish et al., 2016). The theory of *in situ* thermal desorption is to vaporize the contaminant by heating the soil to increase the vapour pressure of the contaminant, and then be able to extract the pollutant from the soil by a vacuum pump (Figure 1). After the desorption process is finished, the air filter can remove the contaminant from the air which later can be disposed of, e.g. by incineration (Lim et al., 2016).

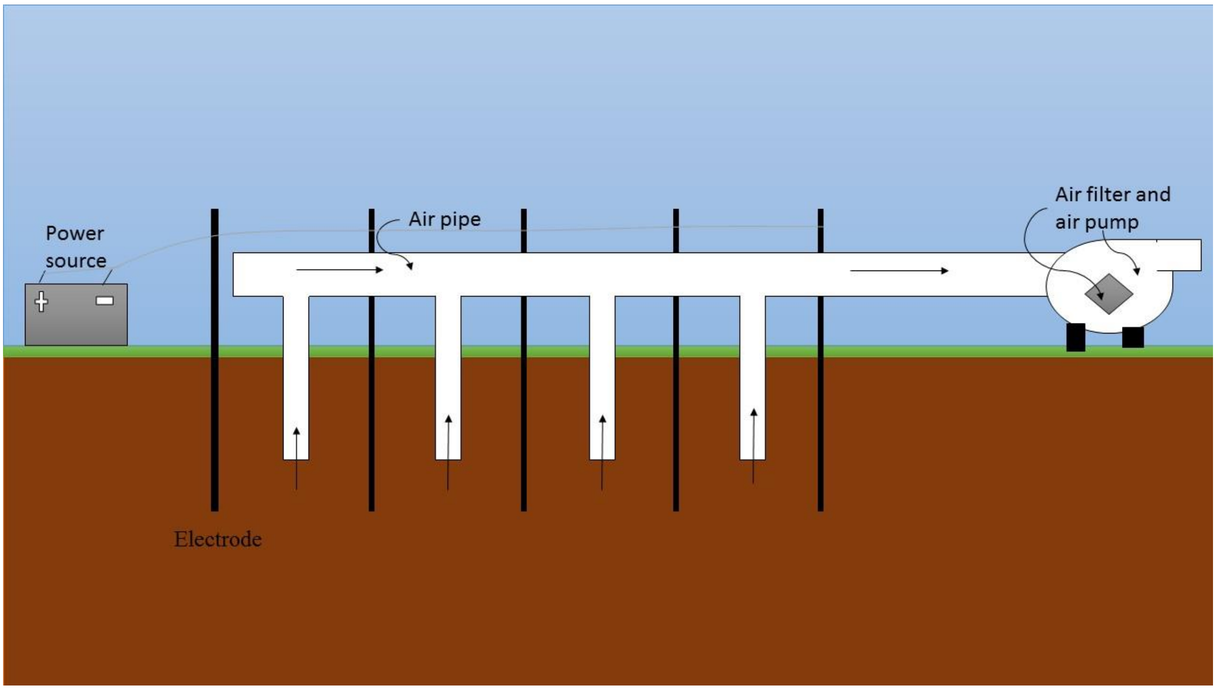

Figure 1. *A model over how thermal desorption theoretically works.*

The advantages of thermal desorption are the high removal efficiency (RE), where RE above 99 % can be achieved (Vidonish et al., 2016). Another study writes that thermal desorption treats contaminated soil with high efficiency regardless of chemical species (Gitipour et al., 2015). It can be a fast method, where *ex situ* thermal desorption has treated contaminated soil within minutes (Vidonish et al., 2016). The disadvantages are the high costs and low RE when the moisture content in the soil is high (Lim et al., 2016). *In situ* thermal desorption is more costly than the *ex-situ* thermal desorption (Vidonish et al., 2016). Other negative aspects according to Vidonish et al. (2016) are the large energy demand, both for the *in situ* method and the *ex situ* method, and the long treatment times for the *in situ* thermal desorption. The time can be between a few weeks and a few years. Thermal desorption also decomposes organic matter and therefore disrupts the soil ecosystem on site. Even if *in situ* thermal desorption takes longer and is more costly the *in situ* thermal desorption might be favourable in sensitive areas because it seems to have less impact on the environment than *ex-situ* thermal desorption (Vidonish et al., 2016).

No previous studies have been done on thermal desorption for PFASs contaminated soil. Although, there has been done thermal desorption on other persistent organic pollutants such as Polychlorinated biphenyls (PCBs) (Qi et al., 2014). According to Qi et al. (2014) the thermal desorption RE was evalueted for PCBs for 60 min treatment time between the temperatures 300 °C to 600 °C in six temperature steps (i.e. 300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C and 600 °C). The RE increased the most between 300 °C to 400 °C, the RE for 400 °C was approximately 95 %, and at higher temperatures the RE increase was marginal. Another study also evaluated thermal desorption on PCB-contaminated soil and found similar results with a maximum RE increase between 300 °C and 400 °C after 60 min of treatment time (Liu et al., 2015). According to Liu et al. (2015), they spiked their samples with different concentrations of sodium hydroxide (NaOH) and found that especially for lower temperatures the NaOH had increased the thermal desorption via base-catalyzed decomposition. Another analytical variation on thermal desorption evaluation methodology was done on PCB-contaminated soil where Mascolo et al. (2013) used thermal desorption together with a gas chromatography coupled to a tandem mass spectrophotometer and found that this method reduced the analyzing time and the time to handling samples. The disadvantage of this method is the fact that it did not have low detection limits.

This is an example of the pollutions from a firefighting training site in Canada, where PFAS-containing AFFFs were used (Yao et al., 2015). The compound groups found according to Yao et al. (2015) were polyhalogenated compound (PHCs), volatile organic compound (VOCs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and metals. In Table 1 there is an overview over how well and at what temperature thermal desorption worked for these compounds.

Table 1. *An overview of previous studied substances treated with thermal desorption.*

Substances	*Temperature*	*Removal efficiency*	*Time*	*Location*	*Reference*
PCBs	400 °C	95 %	60 min	Bench-scale in laboratory	(Qi et al., 2014)
PAHs	450 °C- 950 °C	99%	17 min	Field site, *Ex situ* Thermal desorption	(Xia et al., 2013)
Fossil fuels	150 °C	87%	25 min	Bench-scale in laboratory	(Gitipour et al., 2015)
Metals	Not working	Not working	Not working	Not working	(Guemiza et al., 2017)

3. METHOD

3.1 TARGET COMPOUNDS

Fourteen PFASs, Table 2, that are widely used and often detected in the environment were included in the study (Rahman et al., 2014). They were of interest in the assessment of thermal treatment because they are often found in PFAS polluted soil and the point source contamination risk can leach to the groundwater (Ahrens, 2011). The water used in the experiments was de-ionized and run through a PFASs filter.

Table 2*. PFASs included in this study and their corresponding vapour pressures.*

Acronym	*Name*	*Chemical formula*	*Vapour pressure log P_L (Pa)*
PFBA	Perfluorobutanoic acid	$C_3F_7CO_2H^c$	3.59^a
PFPeA	Perfluoropentanoic acid	$C_4F_9CO_2H^c$	3.13^a
PFHxA	Perfluorohexanoic acid	$C_5F_{11}CO_2H^c$	2.66^a
PFHpA	Perfluoroheptanoic acid	$C_6F_{13}CO_2H^c$	2.20^a
PFOA	Perfluorooctanoic acid	$C_7F_{15}CO_2H^c$	1.73^a
PFNA	Perfluorononanoic acid	$C_8F_{17}CO_2H^c$	1.27^a
PFDA	Perfluorodecanoic acid	$C_9F_{19}CO_2H^c$	0.82^a
PFUnDA	Perfluoroundecanoic acid	$C_{10}F_{21}CO_2H^c$	0.34^a
PFBS	Perfluorobutanesulfonic acid	$C_4F_9SO_3H^c$	2.88^a
PFHxS	Perfluorohexanesulfonic acid	$C_6F_{13}SO_3H^c$	1.77^a
PFOS	Perfluorooctanesulfonic acid	$C_8F_{17}SO_3H^c$	0.83^a
6:2 FTSA	6:2 Fluorotelomer sulfonic acid	$C_8H_4F_{13}SO_3H^c$	-0.96^a
8:2 FTSA	8:2 Fluorotelomer sulfonic acid	$C_{10}H_4F_{17}SO_3H^b$	-2.08^a
FOSA	Perfluorooctane sulfonamide	$C_8F_{17}SO_2NH_2^c$	-0.61^a

[a](Wang et al., 2011), [b](Chemspider, 2017), [c](Gobelius, 2016)

3.2 SOILS

Thermal desorption was assessed on three different soil types; a spiked clay soil, a spiked loamy sand soil and a naturally PFAS contaminated soil from a firefighting training site at the Swedish airport Arlanda. The inclusion of wide variety of soil types were strengthening the assessment of thermal desorption because the soils had a broad range of particle sizes and PFAS concentration which can give a complete perspective on the methods efficiency. The soils were sampled at three different locations in Sweden, table 3. The soil from *Vreta kloster* originated from a site with long term field experiments in *Eastern Götaland County* and can be characterized as a clay soil, Table 3 (Kirchmann et al., 2005). The soil from *Högåsa*, originating from another long term field experiment in the same *Eastern Götaland County* and can be characterized as a loamy sand soil, Table 3 (Kirchmann et al., 2005). Both were sampled at a depth of 0.45-0.55 m. The naturally contaminated soil from Arlanda airport was sampled at 0-0.15 m depth and was the same soil as analysed from site ID 3 in Gobelius (2016).

The clay soil and the loamy sand soil were spiked separately and identically with a mixture of PFAS standards. 500 g dry weight (dw) of soil together with 500 mL Millipore water were added in a 1 L PP-bottle and spiked with 114 ml of 0.10 mg mL^{-1} mixture of 14 PFASs in methanol to a target soil concentration of 0.60 mg kg^{-1} dw, a normal PFAS contamination level. The soil, water and PFASs mixture was homogenized in an end-over-end shaker (Reax 2, Heidolph) at 200 rpm for 7 days. The water mixture was freeze-dried for 7 days, and subsequently grinded with a mortar into a finer particle size and homogenized in the same end-over-end shaker at 200 rpm for 7 days. The dried homogenized soil was stored air-tight at 4 °C for 1 month to age before further experimental execution. The soil from Arlanda airport was not spiked with PFASs because according to Ahrens et al. (2015) there is a fire training facility at Arlanda airport. This training facility had used AFFFs and therefore it was thought that this soil did contain enough PFASs.

Table 3. *Soil used in the experiments (partially modified from Kirchmann et al., 2005).*

	Vreta kloster	*Högåsa*	*Stockholm Arlanda Airport*
Date of collection	July 2016	July 2016	July 2016
Longitude/Latitude	15 ° 30´ E, 58° 29´ N	15 ° 27´ E, 58° 30´ N	17 ° 56´ E, 59° 39´ N
Sand (%)	1.1 %	82.2 %	n/d
Silt (%)	23 %	14.8 %	n/d
Clay (%)	75.9 %	3 %	n/d
pH	7	6	n/d
TOC	0.31 %	0.26 %	3.3 %

3.3 EXPERIMENTAL DESIGN

The general idea has been to perform thermal desorption on different soil types, ensuring that the method could be applicable on many types of sites. After the thermal desorption the remaining concentrations of PFASs were extracted and then analysed in a UPLC MS/MS. This was done to see how well the remediation process exerted on PFASs-contaminated soil. Vapour pressure will be used to assess the results. Vapour pressure according to Britannica Academic (2017) is the pressure applied by a vapour when it is in equilibrium with the other phases. It is a measurement of the ability of a substance to transform into vapour phase and it increases with rising temperature.

3.4 EXPERIMENTAL SET-UP

The soils were freeze-dried and then the loamy sand soil, the clay soil and the natural soil from Arlanda were homogenized with a mortar and a pestle. Brown glass bottles (wide mouth, 40 mL) were rinsed three times with methanol and thereafter filled with 4 grams of soil. 160 samples were prepared for the thermal desorption remediation including negative and positive control samples (Table 4 and Table 5). All the different types of samples were produced in triplicates to ensure good quality of the measurement. The negative controls were non-spiked clay soil from *Vreta kloster*. The negative controls were used to evaluate if a cross contamination occurs through the air inside the oven. The positive control samples were never placed in the oven and used to calculate the removal efficiency. They consisted of samples from the spiked loamy sand soil, spiked clay soil, the mixed soil from Arlanda and the unspiked clay soil used for the negative controls.

Table 4. *Replicates of soil samples prepared for the experiments.*

	Vreta kloster (spiked)	*Högåsa (spiked)*	*Stockholm Arlanda Airport (unspiked)*
150 °C	9	9	9
250 °C	9	9	9
350 °C	8 (One broke)	9	9
450 °C	9	9	9
550 °C	9	9	9
Positive controls	3	3	3

Table 5. *Number of negative control replicates prepared for the experiment.*

	Vreta kloster (unspiked)
Negative controls (150 °C)	3
Negative controls (250 °C)	2 (One broke)
Negative controls (350 °C)	3
Negative controls (450 °C)	3
Negative controls (550 °C)	3
Positive controls (untreated and unspiked soil from Vreta kloster)	3

The soil filled bottles were placed in a high temperature oven (ThermoLyne 62700 Furnace). The ovens height were 19 cm, their width 22 cm and deep 33 cm. Figure 2 shows a schematic figure of the experimental thermal remediation process. The samples stayed in the oven for 15 minutes, 45 minutes and 75 minutes, respectively, and at the temperatures of 150 °C, 250 °C, 350 °C, 450 °C and 550 °C. For cooling after treatment, the soil filled bottles were placed in an autoclavable desiccator. There has also been used triplicates for every time-span and temperature. This gives the study a reliable amount of data to evaluate and therefore give trustworthy results.

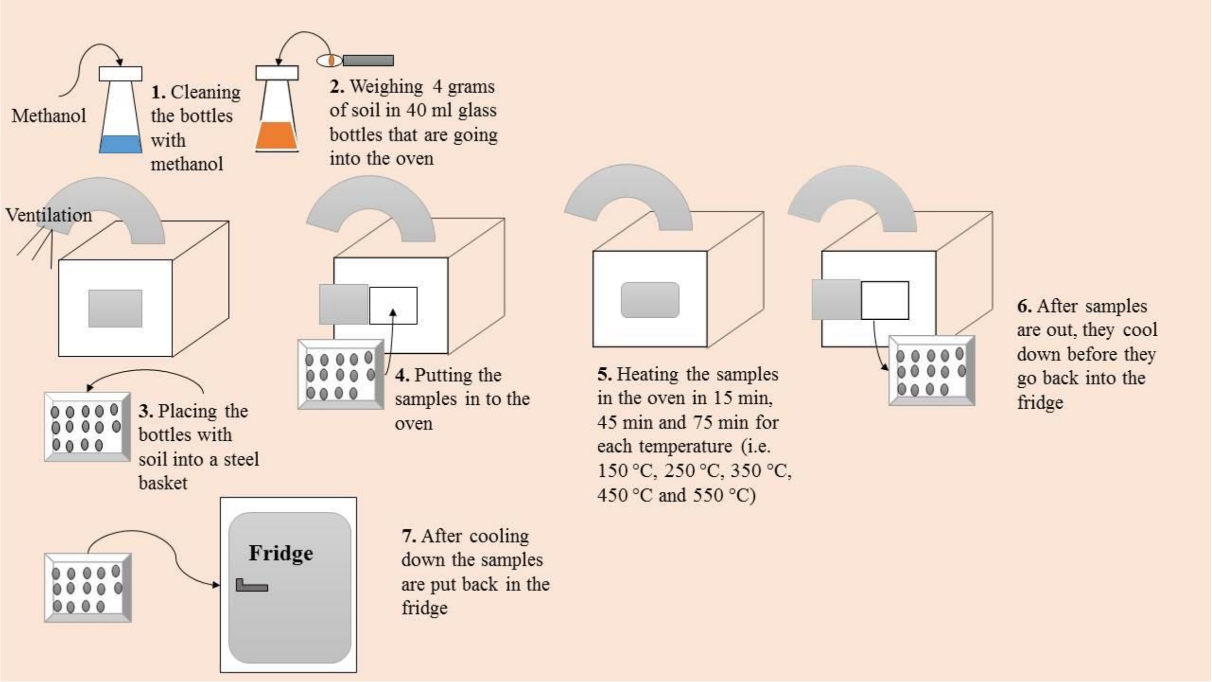

Figure 2. Experimental set up of the thermal remediation.

3.5 PFAS SOIL EXTRACTION, CLEAN-UP AND ANALYSIS

The efficiency of the thermal desorption was evaluated by measuring the remaining PFAS concentration after thermal desorption remediation and then compared to the positive control samples. The remaining PFAS concentration in the soil samples were extracted using solvent liquid extraction (Figure 3), along with internal standard (IS) dilution method, accordingly to Ahrens et al. (2009).

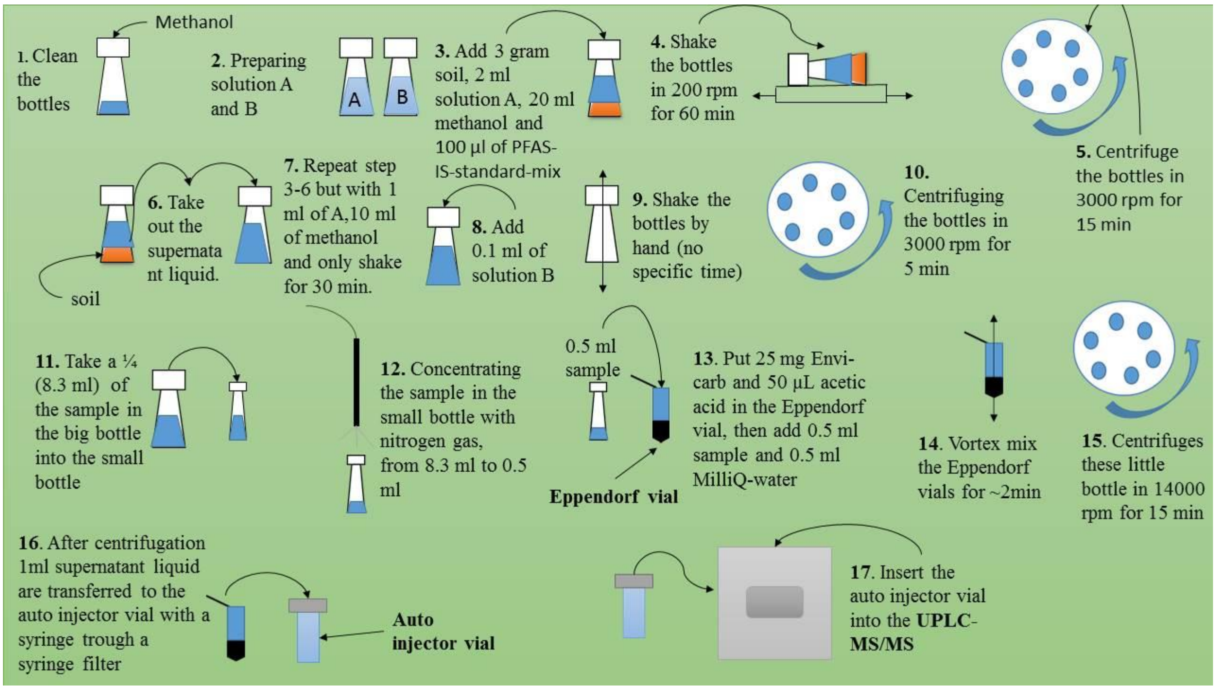

Figure 3. A schematic description of how the PFASs were extracted from thermally treated dry soil samples and reference samples.

Solution A and B were prepared as extraction solutions. Solution A consisted of sodium hydroxide (NaOH), methanol and Millipore water. 0.5 g of NaOH was diluted with 50 mL Millipore water and 200 mL methanol. Solution B consisted of a 4 molar (M) (HCl), diluted with Millipore water from 10 M HCl to 4 M HCl.

3 g ($\pm$ 0.2 g) of soil was weighed into a 50 mL PP-tube (rinsed with methanol three times). 2 mL of solution A was added and the suspension was soaked and extracted for 30 min. Thereafter, 20 mL methanol and 100 µL of PFAS-IS-standard mix were added. The PFAS-IS-standard mix consists of a mix of isotopically labeled PFAS in methanol and the concentration was 5 ng/mL. The IS accounts for losses in the all losses of PFAS in the following steps of the extraction, clean-up and analysis.

The PP-tubes containing the samples were shaken at 200 rpm for 60 min in a laboratory shaker (Gerhardt, United Kingdom) and thereafter centrifuged at 3000 rpm for 15 min in an Eppendorf 5810. After centrifugation, the liquid has separated from the soil and was called supernatant liquid. The supernatant liquid was transferred from the 50 mL PP-tube to another empty 50 mL PP-tube (rinsed with methanol three times). The extraction was repeated one more time, step 3-7 in Figure 3.

1 mL of solution A was left to soak for 30 min, 10 mL of methanol was added (but no PFAS-IS-standard mix was added) and thereafter shaken for 30 min at 200 rpm. The soil samples were centrifuged (Eppendorf 5810) at 3000 rpm for 15 min. The supernatant liquid was transferred a second time to the same 50 mL PP-tube (rinsed with methanol three times) as the first batch of supernatant liquid. 0.1 mL of solution B was added to the samples. The PP-tubes were shaken by hand and thereafter put into the centrifuge (Eppendorf 5810) for 5 min at 3000 rpm. After centrifugation, about a quarter of the supernatant liquid, 8.3 mL, was transferred to a 15 mL PP-tube (rinsed with methanol three times).

The sample liquids were concentrated, from 8.3 mL to 0.5 mL, by blowing nitrogen gas into the 15 mL PP-tube. During the concentration, the 15 mL PP-tube walls were rinsed with methanol twice to ensure that there were no PFASs attached to the walls. After the concentration, the sample was transferred into 1.7 mL Eppendorf vials which contained 25 mg Envi-carb powder (Supelco, USA) and 50 µL acetic acid (Merck, Germany). The step was called clean-up, and aims to reduce interfering substances in the analysis such as dissolved organic carbon (DOC). Thereafter, the samples were shaken (VWR VX-2500) for 2 min and centrifuged (Eppendorf 5424 R) for 15 min at 14000 rpm. 1 mL of the supernatant liquid was filtered through 0.45 µm recycled cellulose (Sartorius) syringe filter into auto-injector vials (Eppendorf, Germany). The samples were analyzed using ultra-performance liquid chromatography tandem mass-spectrometer (UPLC MS/MS) (ThermoFisher, Quantiva UltiMate 3000), and the chromatograms were evaluated in Tracefinder using a nine-point calibration curve: 0.01ng/mL-100ng/mL.

3.6 DATA EVALUATION

During the data evaluation process, the data was transformed from ng PFAS/mL (E) to mg PFAS/kg dry weight (dw) (C). The data was normalized with each initial sample weight (W), Equation (1), which was approximately 3 gram and divided with 1000. The data did not need to be compensated for because the resulting volumes were comparable. If a compensation has to be implemented the exported data value (E) was multiplied with the internal standard correction factor (L). In this assessment the internal standard correction factor was set to 1. Since all samples were performed in triplicates, the mean value of these were calculated and those values were used and presented in the graphs in the result section. To calculate the PFASs desorption removal ratio (C/C_0), the sample value (C) was divided with the value from the positive controls (C_0), Equation (2). The removal efficiency (RE) was furthermore calculated in percent, Equation (3).

$$C\ [\frac{mg}{Kg}\ dw] = \left(\frac{E\left[\frac{ng}{mL}\right] \times L\ [mL]}{W\ [g]}\right)/1000 \qquad (1)$$

$$C/C_0 = \left(\frac{C\left[\frac{mg}{Kg}TS\right]}{C_0\left[\frac{mg}{Kg}TS\right]}\right) \qquad (2)$$

$$RE\ [\%] = \left(1 - \left(\frac{C\left[\frac{mg}{Kg}TS\right]}{C_0\left[\frac{mg}{Kg}TS\right]}\right)\right) \times 100 \qquad (3)$$

The strategy of the Figures and Tables generated were to show in a accurate way if this method worked for PFASs-contaminated soil. There has been focus on assessing the temperature and the time aspect of this method and which of those had the greatest impact on thermal desorption remediation. Therefore Figures containing the changes of PFAS composition regarding time and temperatures were generated. The changes of removal ratio [C/C_0] and the removal efficiency (RE) regarding temperature were also considered important to include. These were only created with regard to temperature since time seemed to have less impact than temperature. There were also Figures and Tables created to control the quality of the data.

4. RESULTS

4.1 THERMAL DESORPTION

Thermal desorption was applied on all three soils and the remaining PFASs concentrations were analysed for these experiments. The evaluation of the data demonstrated that the remediation had removed a considerable amount of PFASs after 75 minutes, although the difference between 45 minutes and 75 minutes were small. All further results were therefore based on the time-period of 75 minutes.

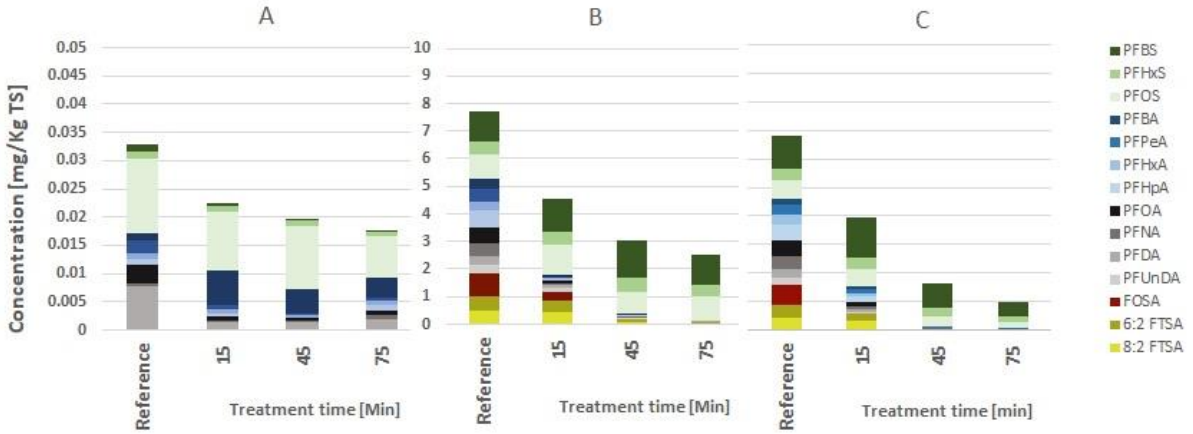

Figure 4. *The composition after thermal treatment in 350 °C at different treatment duration times for A) Naturally PFAS contaminated soil from Arlanda, B) Clay soil from Vreta kloster and C) Loamy sand soil from Högåsa.*

The composition of substances after thermal desorption at 350 °C for 15 minutes, 45 minutes and 75 minutes, Figure 4, proclaim that the concentrations decreased for each time-period. The results were calculated by Equation 1. This temperature, 350 °C, was chosen to represent the impact time had on thermal desorption remediation since many PFASs reached a high removal ratio at this particular temperature. The naturally contaminated soil contained less concentrations and fewer PFASs than the spiked soils. Reference samples were thermally untreated soil used to evaluate the differences that occurred during the remediation.

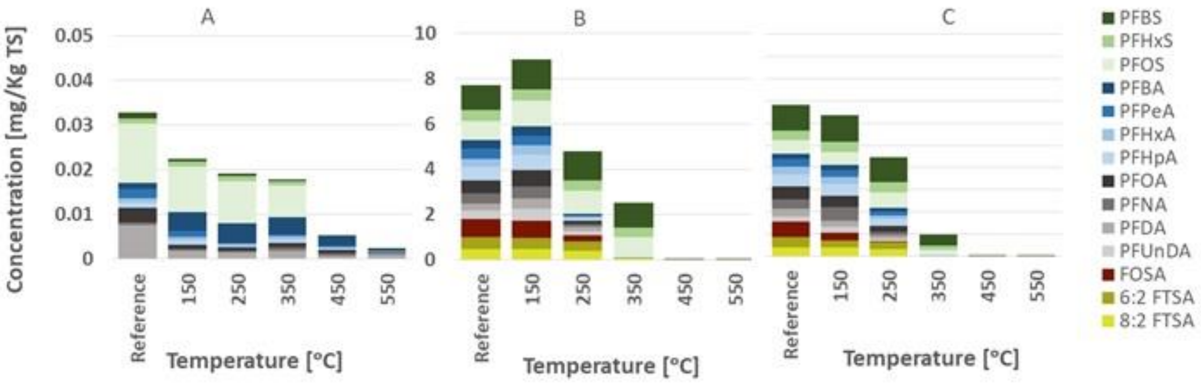

Figure 5. *The PFAS composition after the thermal desorption in 75 min at different treatment temperatures A) Naturally PFAS contaminated soil from Arlanda, B) Clay soil from Vreta kloster, C) Loamy sand soil from Högåsa.*

The composition of substances after thermal desorption at 75 minutes for 150 °C, 250 °C, 350 °C, 450 °C and 550 °C, Figure 5, shows that increased temperatures had an impact on the concentrations of PFASs in the soils. In the naturally PFAS contaminated soil (*Stockholm Arlanda Airport*), the PFCAs and PFSAs were the most prominent substances. PFSAs degraded first and then the PFCAs, in the naturally contaminated soil (Figure 5, A). In the clay soil (Figure 5, B) and the loamy sand soil (Figure 5, C), FOSA and FTSAs degraded initially, thereafter the PFCAs and last the PFSAs.

4.2 REMOVAL EFFICIENCY

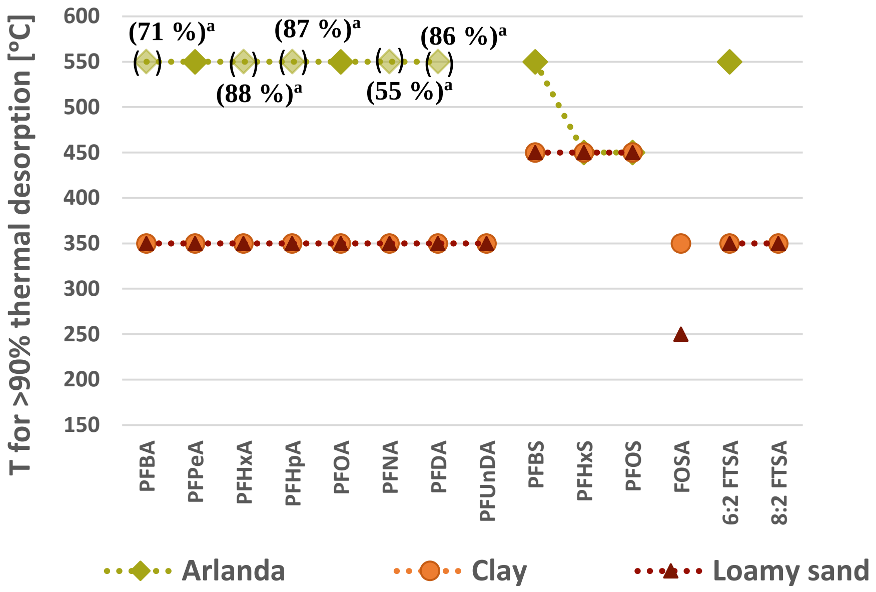

Figure 6. *Temperatures (T) for >90% thermal desorption of naturally PFAS contaminated soil from Arlanda, clay soil from Vreta kloster and loamy sand soil from Högåsa. The half transparent dots within brackets did not reach above 90 % removal ratio. They mark the temperature where those substances reached their highest removal.*

These results, in Figure 6 and appendix in Table 8, that were based on calculations with Equation 3 illustrated that the clay soil (*Vreta kloster*) and the sand soil (*Högåsa*) had generally a removal efficiency above 90 % at temperatures over 350 °C. PFCAs and PFSAs had unified results for the clay soil and the loamy sand soil. The PFCAs reached above 90 % removal efficiency at 350 °C and PFSAs at 450 °C. The other two groups, FOSA and FTSA, had varying results for all three soils. For the naturally PFAS contaminated soil (*Stockholm Arlanda airport)*, only a few values reached above 90% removal efficiency.

There were PFASs present in the loamy sand soil (*Högåsa*) and the clay soil (*Vreta kloster*) that were not found in the naturally PFAS contaminated soil (*Stockholm Arlanda Airport*), and they were marked with a line in Table 8.

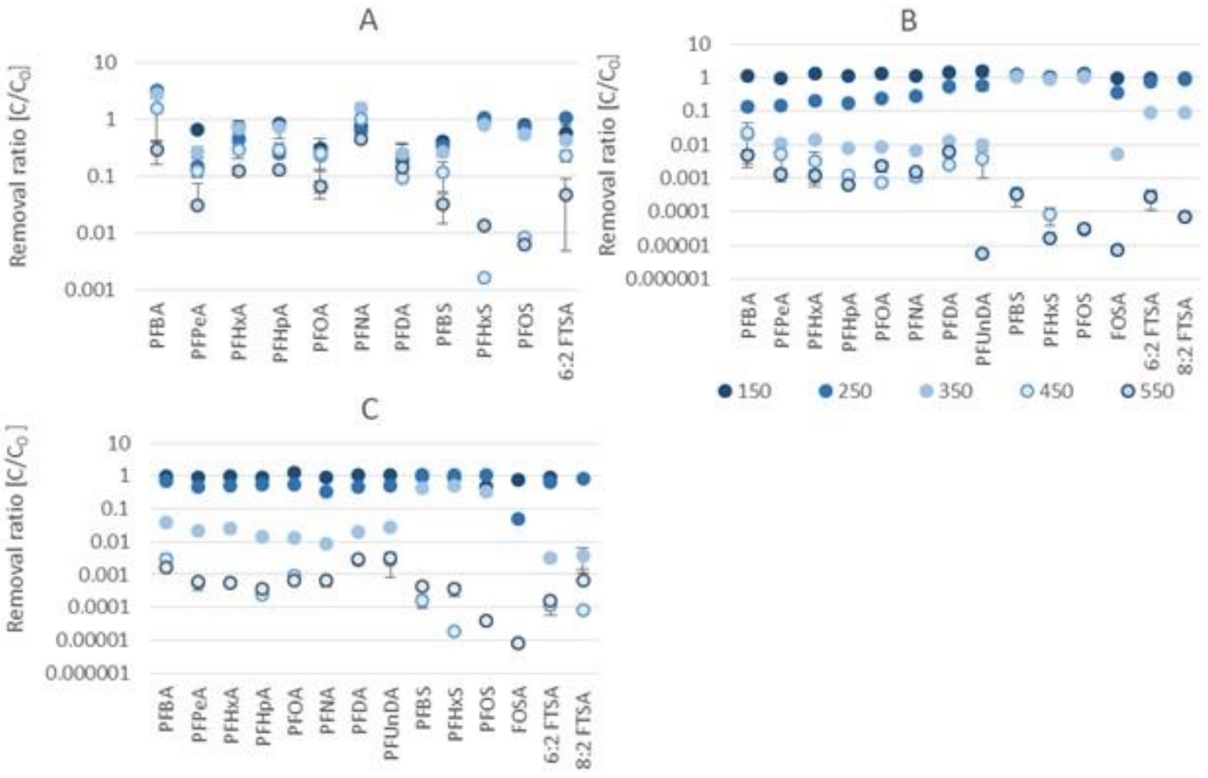

Figure 7. *The PFASs mean desorption [C/C0] for A) Mixed soil from Arlanda airport, Stockholm B) Clayish soil form Vreta kloster and C) Loamy sand soil from Högåsa at thermal treatments ranging from 150 to 550 °C. Error bars were the standard deviation of the triplicate samples.*

The thermal desorption removals of PFASs for each soil at 150 °C -550 °C, Figure 7, were calculated with Equation 2 and showed that the removal ratios were below 0.01 for the two highest temperatures in the loamy sand soil (*Högåsa*) and the clay soil (*Vreta kloster)* (i.e. 450 °C and 550 °C). In Figure 7 B and C, the results were incoherent between 150 °C -350 °C and the removal ratio was closer to 1.

PFBA in the naturally PFAS-contaminated soil (*Stockholm Arlanda Airport*), Figure 7 A, had removal ratios above 1 for the first four temperatures (i.e. 150 °C-450 °C) and these results indicate increased concentrations after ended remediation. At 550 °C PFBA decreased until the removal ratio was below 1 in the naturally contaminated soil. PFNA had also a high removal ratio for all temperatures and at 550 °C it had reached a removal ratio at approximately 0.5 in the naturally contaminated soil. The other substances in the naturally PFAS contaminated soil (*Stockholm Arlanda Airport)* reached removal ratios below 0.1 or even 0.01.

A substantial fraction of the PFASs in the clay soil (*Vreta kloster)*, Figure 7 B, had a removal ratio above 1 for 150 °C. PFCAs and FOSA then reached a removal rate below 0.1 at 350 ° C. PFSAs had a desorption ratio above 1 up to 350 °C and did not reach >90% removal until 450 °C. FTSAs reached removal ratio below 0.1 at 450 °C.

In loamy sand soil (*Högåsa*), Figure 7 C, most substances did not have a removal ratio above 1, on the contrary of the clay soil (*Vreta kloster).* PFCAs and PFSAs reached valid results at the same temperatures as in the clay soil (*Vreta kloster*). FTSAs attained removal beneath 0.1 at 350 °C and FOSA at 250 °C.

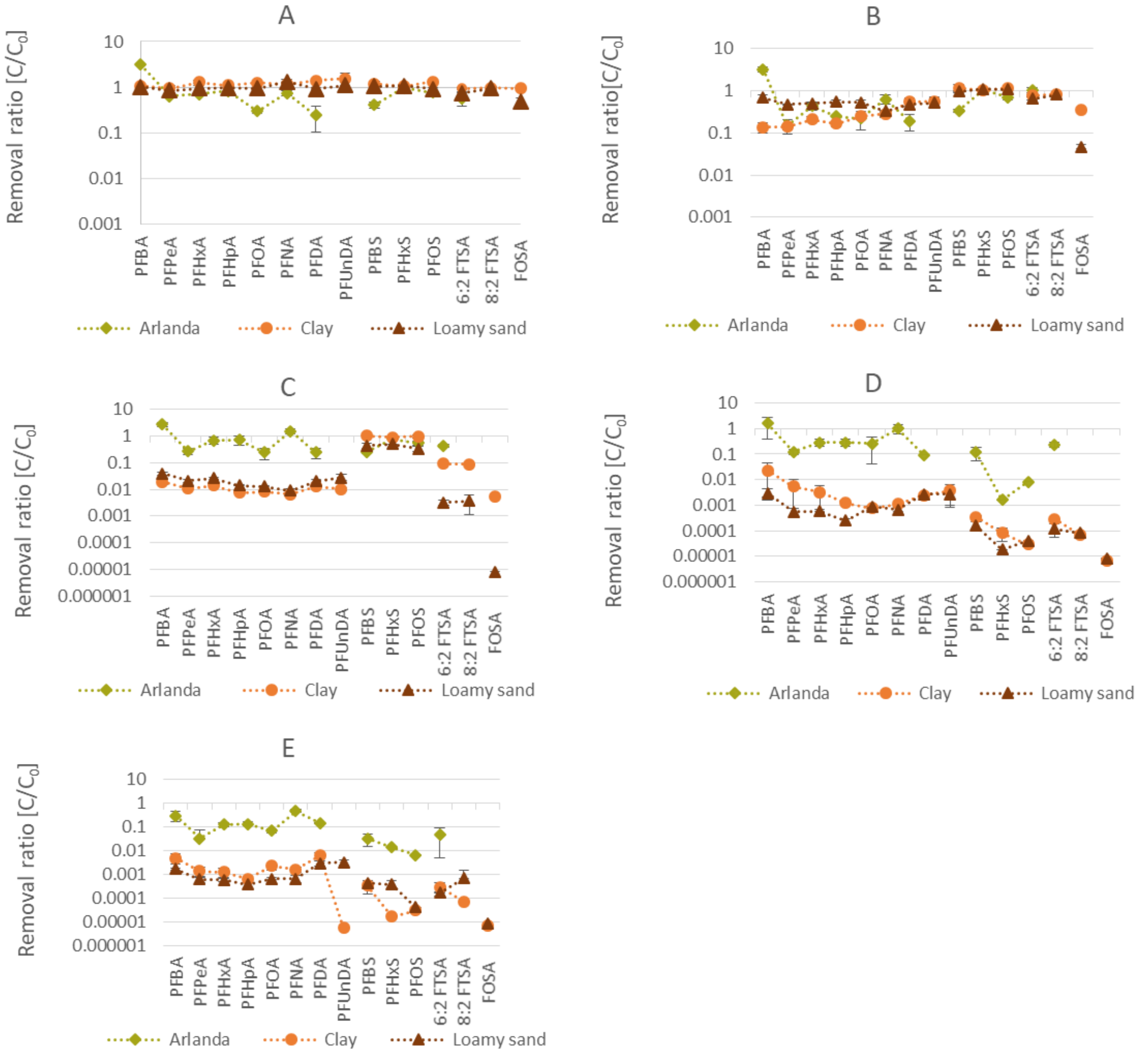

Figure 8. *The removal ratio [C/C0] for A) 150 °C, B) 250 °C, C) 350 °C, D) 450 °C and E)550 °C for individual PFASs. Error bars were the standard deviation of the triplicate samples.*

A comparison of the soils at 150 °C-550 °C, Figure 8, showed that the loamy sand soil (*Högåsa*) had the highest removal, thereafter the clay soil (*Vreta kloster*) and last the naturally PFAS contaminated soil (*Stockholm Arlanda Airport*). The results presented in Figure 8 have been calculated with Equation 2.

Thermal desorption in 150 °C, Figure 8 B, had a removal ratio at 1 or above for all soils. When the removal ratio was 1, it showed no change between the concentrations in the positive control samples and the measured concentration after the thermal desorption. That was a clear indication that the method had not been successful for this temperature (Figure 8, A). The results for thermal desorption in 250 °C were improved compared to 150 °C, PFSAs however still had a removal of 1 or only a little below.

The PFCAs, FTSAs and FOSA, at 350 °C, reached removal ratios below 0.1, Figure 8 C, and PFSAs had a removal ratio around 1 or slightly below in the clay soil (*Vreta kloster*) and the loamy sand soil (*Högåsa*). In the naturally contaminated soil (*Stockholm Arlanda Airport*) all PFASs still had removal ratios at 1 or slightly below.

At 450 °C, Figure 8 D, all substances in the clay soil (*Vreta kloster*) and the loamy sand soil (*Högåsa*) had removal ratios below 0.01. All PFASs in the naturally contaminated soil

(*Stockholm Arlanda Airport*) except PFBA and PFNA, Figure 8 D, had reached a removal ratio close to 0.1. PFBA and PFNA were still at a removal ratio equal to 1 for this soil. After the remediation in the highest temperature (550 °C), Figure 8 E, the thermally desorption had reached a removal ratio below 0.1 for nearly all substances in all soils.

4.3 QUALITY CONTROL

4.3.1 Negative control sample

A comparison of uncontaminated thermally treated clay soil (negative control samples) and uncontaminated untreated clay soil (positive control samples), Table 6, demonstrated that the total amount of PFASs decreased during the thermal desorption except for PFBA and PFDA. The bars for the untreated and unspiked clay soil, Figure 9 in appendix, were equally high as the bars representing the thermal treatment of 150 °C. PFBA had increased at 150 °C while the longer chained PFCAs decreased and therefore were the bars equally high. PFDA was also a substance that was irregular, it decreases until 350 °C and thereafter it increase again. The assessment of the negative control samples shows that there had not occurred a cross-contamination.

Table 6. *Negative PFAS control samples containing unspiked clay soil from Vreta kloster, showing different temperatures including standard deviations.*

PFAS acronym	*ref. [µg/kg dw]*	*150 °C [µg/kg dw]*	*250 °C [µg/kg dw]*	*350 °C [µg/kg dw]*	*450 °C [µg/kg dw]*	*550 °C [µg/kg dw]*
PFBA	2.40 ± 1.18	12.0 ± 2.2	1.58 ± 0.0035	8.13 ± 2.38	0.344 ± 0.059	0.40 ± 0.039
PFPeA	1.219 ± 0.24	0.88 ± 0.33	0.55 ± 0.110	0.41 ± 0.44	0.208 ± 0.047	0.242 ± 0.052
PFHxA	0.67 ± 0.059	0.59 ± 0.18	0.328 ± 0.103	0.44 ± 0.083	0.203 ± 0.107	0.20 ± 0.027
PFHpA	1.185 ± 0.35	0.73 ± 0.24	0.35 ± 0.089	0.244 ± 0.052	1.14 ± 1.26	0.29 ± 0.069
PFOA	3.46 ± 0.67	0.94 ± 0.28	1.846 ± 0.56	0.704 ± 0.39	0.96 ± 0.80	2.32 ± 0.38
PFNA	1.52 ± 0.78	0.81 ± 0.41	0.48 ± 0.0086	0.26 ± 0.068	0.309 ± 0.036	0.404 ± 0.12
PFDA	8.78 ± 2.40	4.69 ± 3.81	1.273 ± 0.29	0.406 ± 0.21	2.22 ± 1.61	6.312 ± 2.416
PFUnDA	1.59 ± 2.24	0.022 ± 0.030	0.748 ± 1.91	0.077 ± 0.019	0.728 ± 0.15	0.47 ± 0.40
PFBS	0.47 ± 0.055	1.75 ± 0.97	0.302 ± 0.014	1.167 ± 0.35	0.403 ± 0.182	0.56 ± 0.26
PFHxS	0.066 ± 0.048	0.008 ± 0.000068	0.0079 ± 0.000112	0.0080 ± 0.000060	0.0117 ± 0.0053	0.107 ± 0.077
PFOS	0.0253 ± 0.00034	0.026 ± 0.00023	1.067 ± 1.041	0.027 ± 0.00020	0.027 ± 0.00042	0.026 ± 0.00041
FOSA	0.00595 ± 0.000051	0.0060 ± 0.000051	0.0060 ± 0.000085	0.0061 ± 0.000045	0.0061 ± 0.000096	0.0059 ± 0.000093
6:2 FTSA	0.45 ± 0.093	0.30 ± 0.072	0.087 ± 0.0145	0.33 ± 0.20	0.067 ± 0.023	0.119 ± 0.0753
8:2 FTSA	0.033 ± 0.00045	0.034 ± 0.00030	0.034 ± 0.00049	0.076 ± 0.038	0.035 ± 0.00056	0.034 ± 0.00050

4.3.2 UPLC-MS/MS measurement accuracy

The standard deviation for the measurement accuracy, Table 7, were the most important features in these results. The reason was that these results gave information about whether the mass spectrometer had given reliable results or not. The standard deviation was within an acceptable range except PFNA that had a standard deviation that was almost as large as the mean value. 6:2 FTSA, PFHpA and PFDA had a standard deviation slightly larger than their mean values. The standard deviations were, however, within an acceptable range.

Table 7. *A sample treated in 150 °C for 15 min containing the naturally contaminated soil (Stockholm Arlanda Airport) was measured 34 times, divided on three analytical runs, ensured the measurement accuracy for UPLC MS/MS and the integration method in the software.*

PFAS acronym	***Measurement accuracy [µg/kg dw]***
PFBA	7.14 ± 1.21
PFPeA	2.18 ± 0.52
PFHxA	1.66 ± 0.72
PFHpA	2.27 ± 1.26
PFOA	3.19 ± 1.38
PFNA	2.38 ± 1.96
PFDA	9.04 ± 5.94
PFBS	1.043 ± 0.38
PFHxS	1.54 ± 0.24
PFOS	15.4 ± 4.70
6:2 FTSA	0.52 ± 0.30

5 DISCUSSION

5.1 TIME

The experimental treatment time periods, 15 minutes, 45 minutes and 75 minutes, were chosen after reading other reports that had performed similar thermal desorption assessments on other persistent organic pollutants (PCBs and PAHs) (Mascolo et al., 2013; Qi et al., 2014; Liu et al., 2015). The other references used approximately the same time periods, between 20-60 min. The longest time period used in the experiments, 75 minutes, was chosen to represent all further results with the reason that at this treatment time length, the treatment time variable seemed to have less impact than temperature on PFAS removal. The results, Figure 4, insinuated that treatment times longer than 75 minutes, at least in laboratory scale, would not lead to a greater removal efficiency.

The largest changes for the concentrations of PFASs, Figure 4, happened between 350 °C and 450 °C. These were similar to the results from other reports, they had found that the removal efficiency increased the most between 300 °C and 400 °C (Qi et al., 2014; Liu et al., 2015). The one of these temperatures, 350 °C, that had most PFASs with high removal efficiency were chosen to show how the PFASs concentrations changed regarding time.

There were differences between the PFASs groups, the PFSAs and the short chained PFCAs desorbed after the longest treatment time period. The reason could be that longer chained PFASs and precursors had desorbed and created more molecules of short chained PFCAs and PFSAs (Ahrens et al., 2015). Other assessments (McCleaf et al., 2017) have been interested in knowing if there is a correlation between chain length and removal efficiency. In this assessment there was no correlation found regarding treatment time length.

5.2 TEMPERATURES TO REMEDIATE DIFFERENT PFASs

The reason for the degradation due to increased temperatures depends on the vapour pressure, and when the heat increases so does the vapour pressure (Wang et al., 2011). Therefore, the PFSAs changed phase and become gas at a certain temperature (Qi et al., 2014). There were not any visible trends regarding chain length and removal efficiency regarding temperature.

Below 350 °C, Figure 8, the heat was not high enough to make the PFASs desorb. It was only FOSA in the loamy sand soil that reached a removal efficiency >90 % below 350 °C, the rest of the substances in the loamy sand soil and all the substances in the other two soils reached a removal efficiency > 90 % at or above 350 °C. FOSA is the only PFAS assessed that was not ionized. There were two exceptions, PFBA and PFNA, they did not desorb directly when remediated with thermal desorption. First they increased and thereafter when the temperature was above 350 °C they started to decrease. The reason they increased first could be due to degradation of precursors and longer chained PFASs.

When a PFAS reached a removal efficiency above 90 %, Figure 5, the concentrations dropped a lot at a certain temperature. An explanation could be that it reached above its boiling point and almost all of that PFAS vaporized at the same time. It seems that for the spiked soils they follow each other’s patterns when they come to this drop but not for the naturally contaminated soil. To a certain extend it does but not at the same rate as the other two soils. In the spiked soil FOSA and the FTSAs desorb first and then the PFSAs and the PFCAs. The reason for this could be that FOSA and FTSAs were precursors, they have the lowest vapour pressure and did therefore desorb first (Wang et al., 2011). In the naturally contaminated soil the PFCAs and the PFSAs were most prominent and the reason for this could be that the soil not contain the other

PFASs used in the experiments. The naturally contaminated soil could contain other PFASs, however, that were not analysed in this assessments.

5.3 SOILS

A large difference in removal efficiency, Figure 7, was between the naturally contaminated soil and the spiked soils (loamy sand soil and clay soil). The spiked soils acted similar during the thermal desorption remediation. It seemed that the naturally contaminated soil was more difficult to remediate. There were several possible reasons for this and those were that the contamination in the naturally contaminated soil was older than the contaminations in the other two soils. The naturally contaminated soil was also slightly aggregated compared to the spiked soils and that could therefore be a possibility that this soil contained more water when it entered the oven compared to the other two soils. The naturally contaminated soil did also contain lower concentrations of PFASs and that could also be a possible reason why this soil was harder to remediate than the other two soils.

5.4 RECOMMENDATIONS

The results given in Figure 6 and Table 8 were based on an assumption that >90% removal efficiency was an adequate level and could be seen as a good removal efficiency indicator. A few recommendations can be given, for PFCAs the remediating temperature was adequate at ≥ 350 °C, for PFSAs ≥ 450 °C, FOSA ≥ 350 °C and for the FTSAs ≥ 350 °C. These recommendations were based on ideal conditions and therefore they might have to be adjusted if used in a field experiment. A firefighting training site often contain a large variety of contaminants, both from the substances that burns and the firefighting foams used to extinguish the fire. Table 1 contains information about thermal desorption exerted on PAHs, PCBs, fossil fuels and heavy metals and what temperatures used during those experiments. A recommendation can therefore be given for this compound mix, the temperature should be at least ≥ 450 °C.

The guideline values for PFOS given by the Swedish Geological Institute (SGI) were 0.003 mg/kg dw for sensitive land use, and 0.3 mg/kg dw for less sensitive land use (Pettersson et al., 2015). In Sweden according to Pettersson et al. (2015) there were two different classifications for land use, sensitive land use and less sensitive land use. Sensitive land use can be areas where apartments, houses or schools are built. Less sensitive land use is where industries and factories might be built. PFOS was the only PFASs having a threshold value. SGI is practicing the precautionary principle and had therefore given the values for PFOS as generic values (Table 8). All substances were, when reached a removal ratio that was considered sufficient, below the guide line values for less sensitive land use for PFOS.

5.5 QUALITY CONTROL

The results shown in Table 6 indicates that there were not any cross contamination through the air in the oven. There were a few values that were higher than the reference levels but they were not occurring on a regular basis so they might be viewed upon as outliers rather than a cross contamination.

The bars for the untreated and unspiked clay soil, Figure 9 in appendix, were equally high as the bars representing the thermal treatment of 150 °C. PFBA had increased at 150 °C while the longer chained PFCAs decreased and therefore were the bars equally high. PFDA was also a substance that is irregular, it decreases until 350 °C and thereafter it increase again. An explanation for this could again be degradation of precursors and PFASs with longer chains than PFDA.

The measurement accuracy, Table 7, shows reliable results but a source of error could be a carry over effect due to the UPLC MS/MS. It was most likely an effect from the sample measured before the control sample. A carry over effect means that the measuring equipment measures a little bit too high as a result of first measuring a sample with high concentration and then after measuring a sample with low concentration. The equipment could have a residue of the last sample in the system which then was visible in the measurement after. It had affected the result slightly, but since the measures went from high to low in a decreasing scale that impact have not been significant enough to make the data unreliable.

5.6 RESEARCH QUESTIONS

- Which temperatures are able to remediate PFASs in the soil to a sufficient level?
- How do the PFAS concentrations and composition profile change over time after thermal treatment?
- Does the soil type has any effect on PFAS removal efficiency?

Answers to research questions

First question was, *which temperatures are able to remediate PFASs in the soil to a sufficient level?* The answer depends on the soil and the substance. Approximately most substances are remediated between 350 °C and 550 °C. *How do the PFAS concentrations and composition change over time after thermal treatment?* It desorbs most between 15 min and 45 min and between 45 and 75 min the changes are small *Does the soil type has any effect on PFAS removal efficiency?* The conclusion I would draw was that the soil type do have an effect on PFAS removal efficiency. This was based on that the removal efficiency for the spiked soils differed significantly from the removal efficiency for the naturally contaminated soil.

An interesting next step would be to investigate what happens to the ecosystem after the thermal treatment and how the ecosystems cope with the contaminants in the soil. Do the soils contain microorganisms when heavily contaminated e.g. on a firefighting training site? If it do, how much would thermal desorption destroy that ecosystem? It would also be interesting to investigate why the naturally contaminated soil were harder to remediate than the spiked soils.

6 CONCLUSIONS

The results showed that for the clay soil (*Vreta kloster)* and the sandy soil (*Högåsa)* the remediation had been successful, all PFASs for these two soils were remediated below guideline values given by the Swedish Geological Institute (SGI). For the soil from Arlanda the success rate was lower, 6 out of 14 substances were remediated to > 90% removal. It was a good result regarding that the concentrations for all substances ended up below the guideline values of 0.3 mg/kg dw.

A few of the positive aspects for this method was high removal efficiency and rapidity if it was used *ex situ*. A negative aspect would be that they have great potential to destroy the ecosystem on the site and make the treated soil sterile (Vidonish et al., 2016). The method worked in the laboratory, but there was not possible to conclude if it would work on a real site. In a field study it likely need longer treatment time since the method was tested on dried and homogenised soil. The conclusion, however, was that the remediation method worked in laboratory scale for all three soil types at temperatures ≥450 °C after 75 minutes of thermal treatment.

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8 APPENDIX

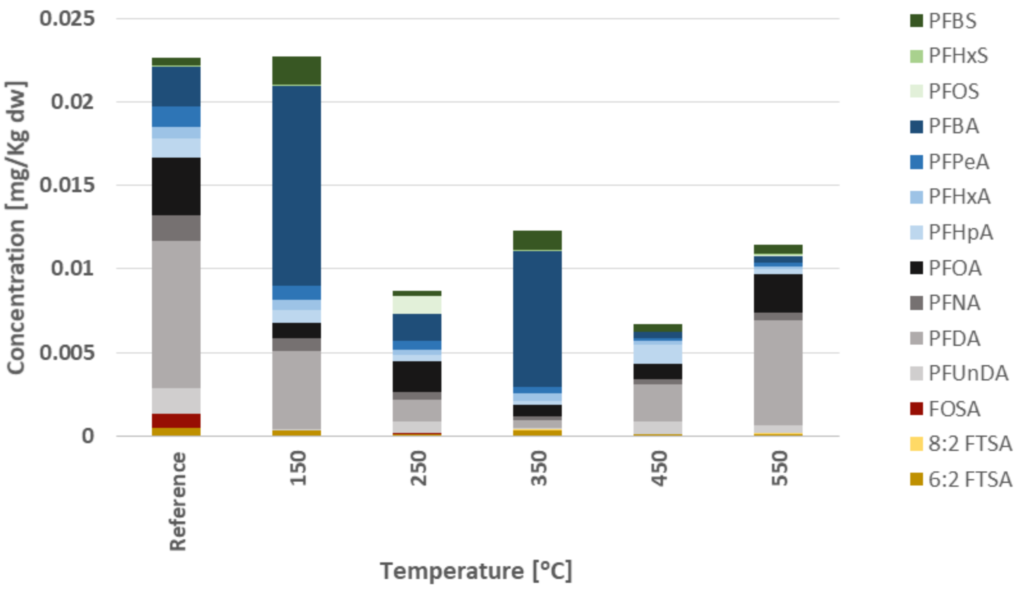

Figure 9. *The composition and concentrations of the negative control samples.*

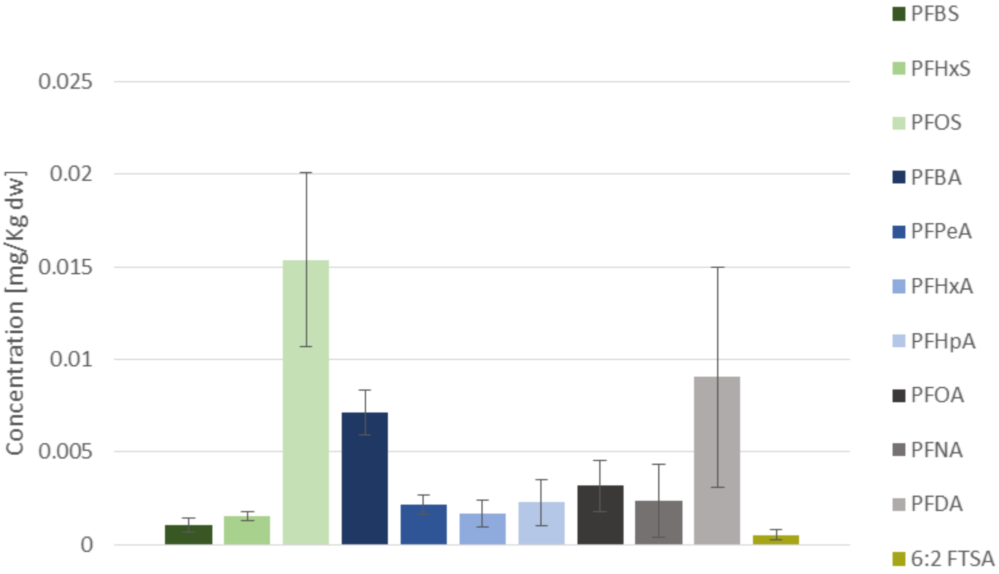

Figure 10. *The measurement accuracy for a sample treated in 150 °C for 15 min containing the naturally contaminated soil (Stockholm Arlanda Airport), measured 34 times.*

Table 8. *Lowest temperatures with >90% thermal desorption remediation efficiency.*

PFAS acronym	***Recommendation: Naturally PFAS contaminated soil***	***Removal efficiency***	***Before remediation [mg/kg dw]***	***After remediation [mg/kg dw]***
PFBA	(550) ˚C	(71%)[a]	0.0013	0.00039[a]
PFPeA	550 ˚C	96.9 %	0.0021	6.55 E-05
PFHxA	(550) ˚C	(88 %)[a]	0.0010	0.00013[a]
PFHpA	(550) ˚C	(87 %)[a]	0.0011	0.00014[a]
PFOA	550 ˚C	93.3 %	0.0033	0.00022
PFNA	(550) ˚C	(55 %)[a]	0.00050	0.00023[a]
PFDA	(550) ˚C	(86 %)[a]	0.0076	0.0011[a]
PFUnDA	-	0[b]	-	-
PFBS	550 ˚C	96.8 %	0.0013	0.00004
PFHxS	450 ˚C	99.8 %	0.0011	1.81 E-06
PFOS	450 ˚C	99.2 %	0.013	0.00011
6:2 FTSA	550 ˚C	95.3 %	0.00017	0.00001
8:2 FTSA	-	0[b]	-	-
FOSA	-	0[b]	-	-
	Recommendation: Clay soil	**Removal efficiency**	**Before remediation [mg/kg dw]**	**After remediation [mg/kg dw]**
PFBA	350 ˚C	98 %	0.38	0.0075
PFPeA	350 ˚C	98.9 %	0.46	0.0051
PFHxA	350 ˚C	98.6 %	0.33	0.0046
PFHpA	350 ˚C	99.2 %	0.61	0.0046
PFOA	350 ˚C	99.2 %	0.57	0.0048
PFNA	350 ˚C	99.3 %	0.44	0.0029
PFDA	350 ˚C	98.7 %	0.32	0.0042
PFUnDA	350 ˚C	99 %	0.35	0.0035
PFBS	450 ˚C	99.9 %	1.11	0.00040
PFHxS	450 ˚C	99.9 %	0.48	0.0013
PFOS	450 ˚C	99.9 %	0.86	2.6 E-05
6:2 FTSA	350 ˚C	91.0 %	0.51	0.048
8:2 FTSA	350 ˚C	91.0 %	0.48	0.044
FOSA	350 ˚C	99.5 %	0.82	0.0044
	Recommendation: Loamy sand soil	**Removal efficiency**	**Before remediation [mg/kg dw]**	**After remediation [mg/kg dw]**
PFBA	350 ˚C	96 %	0.20	0.0081
PFPeA	350 ˚C	97.8 %	0.38	0.0080
PFHxA	350 ˚C	97.3 %	0.32	0.0085
PFHpA	350 ˚C	98.6 %	0.57	0.0081
PFOA	350 ˚C	98.7 %	0.55	0.0073

PFNA	350 ˚C	99.1 %	0.46	0.0041
PFDA	350 ˚C	97.9 %	0.32	0.0065
PFUnDA	350 ˚C	97.2 %	0.23	0.0063
PFBS	450 ˚C	99.9 %	1.15	0.00019
PFHxS	450 ˚C	99.9 %	0.42	7.76 E-06
PFOS	450 ˚C	99.9 %	0.64	2.58 E-05
6:2 FTSA	350 ˚C	99.7 %	0.45	0.0015
8:2 FTSA	350 ˚C	99.6 %	0.42	0.0015
FOSA	250 ˚C	95.2 %	0.72	0.034

[a] *These values were the results from thermal remediation in 550 °C but they did not reach above 90 % removal efficiency*

[b] *Below detection limit*