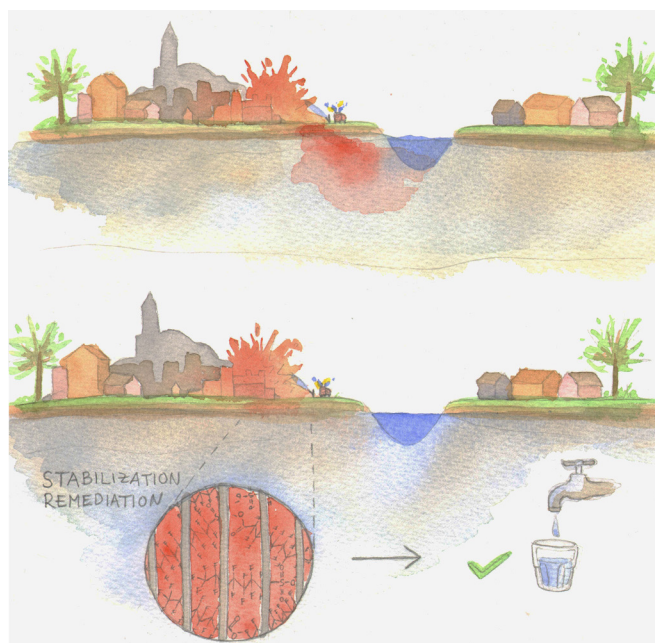




DOCTORAL THESIS No. 2020:39
FACULTY OF NATURAL RESOURCES AND AGRICULTURAL SCIENCES

Stabilization remediation of soils contaminated with per- and polyfluoroalkyl substances (PFASs)

MATTIAS SÖRENGÅRD



Stabilization remediation of soils contaminated with per- and polyfluoroalkyl substances (PFASs)

Mattias Sörengård

Faculty of Natural Resources and Agricultural Sciences

Department of Aquatic Sciences and Assessment

Uppsala

Doctoral thesis
Swedish University of Agricultural Sciences
Uppsala 2020

Acta Universitatis agriculturae Sueciae

2020:39

Cover: Pollution and stabilization remediation of contaminated soil.
(photo: L. Glimstedt)

ISSN 1652-6880

ISBN (print version) 978-91-7760-596-6

ISBN (electronic version) 978-91-7760-597-3

© 2020 Mattias Söregård, Uppsala

Print: SLU Service/Repro, Uppsala/Alnarp 2020

Stabilization remediation of soils contaminated with per- and polyfluoroalkyl substances (PFASs)

Abstract

Per- and polyfluoroalkyl substances (PFASs) are a major global concern in pollution of drinking water sources and aquatic environments. Due to the high persistence and mobility of these compounds, remediation methods for PFAS-contaminated soils are urgently needed to protect the surrounding environment and drinking water source areas. This is particularly important at firefighter training sites, due to the historical usage and release of PFAS-containing aqueous foams causing high levels of soil contamination, with high potential for leaching to groundwater and nearby environments. This thesis assessed the efficacy of stabilization remediation methodologies in mitigating PFAS leaching from contaminated soils. Screening of 44 PFAS sorbent materials showed that activated carbons (ACs) (granulated and pulverised, $n = 5$) were the best sorbent (mean removal efficiency >99.9%) for PFASs in aqueous solution. Based on these results, a commercially available injectable colloidal AC product (PlumeStop[®]) for soil stabilization was systematically assessed for PFAS retention efficiency. The best treatment efficiency for 10 different soils (fortified with 17 PFASs) treated with colloidal AC was observed for perfluorooctanoic acid (PFOA), 6:2 fluorotelomer sulfonate (6:2 FTSA) and perfluorohexane sulfonate (PFHxS), resulting in sorption increases of >80%. Assessment was also performed of a stabilization-solidification (S/S) technique that uses cementitious material to chemically stabilise PFASs and solidify the soil, decreasing hydraulic conductivity and thereby reducing PFAS leaching potential. The S/S technique was tested on PFAS-spiked soil using a cost-efficient cementitious material with a soil:binder ratio of 9:1 and seven different additives (including ACs) to 0.2% of dry weight (dw). In conservative leaching tests, treatment efficiency was highest for AC additive amended S/S remediation (*e.g.* >99.9% for longer-chain PFASs such as perfluorooctane sulfonate (PFOS)). To further assess the applicability and long-term stability of S/S treatment, a pilot-scale experiment was set up treating over six tons of field-contaminated soil using 15% cementitious binder and 0.2% dw mass-granulated AC. An artificial irrigation system was used to apply the equivalent of six years of precipitation. The treatment efficiency was >97% for four dominant PFASs homologues (perfluorohexanoic acid (PFHxA), PFOA, PFHxS and PFOS), but low (3%) for short-chain perfluoropentanoic acid (PFPeA). Ultimately, based on laboratory- and pilot-scale experiments, it can be concluded that stabilization remediation of PFAS-contaminated soils can be an efficient technique, in particular for longer-chain PFASs.

Keywords: PFAS, PFOS, PFOA, persistent organic pollutants, soil contamination, soil remediation, stabilization, activated carbon, stabilization-solidification

Mattias Sörengård, SLU, Department of Aquatic Sciences and Assessment, P.O. Box 7050, 750 07 Uppsala, Sweden

Stabilisering som saneringsteknik för mark kontaminerad med per- och polyfluoroalkylsubstanser

Sammanfattning

Per- och polyfluoroalkylsubstanser (PFAS) är ett stort globalt problem för förorening av dricksvatten och vattenmiljöer. I denna studie behandlas ämnet sanering av PFAS-förorenad mark då PFAS i många dricksvattentäkter och vattenmiljöer härrör från sådana. Eftersom PFAS inte bryts ned och har stor mobilitet från mark till grundvatten så behövs utveckling och utvärdering av möjliga saneringsmetoder för att skydda den omgivande miljön och dricksvattentäkter. Marksanering kan särskilt behövas på brandövningsplatser på grund av den historiskt stora användningen och utsläpp av PFAS-innehållande brandskum (AFFF) som har orsakat höga halter PFAS i marken med hög utlakningspotential. Denna studie syftar till att bedöma stabilisering som en möjlig teknik för att minska PFAS-utlakningen från förorenad mark. I en screeningstudie av 44 sorbentmaterial för PFAS visade resultaten att aktiverat kol (AK) (granulerad och pulveriserad (n = 5)) var de bästa sorbenterna (minskning med > 99,9 %) i vattenlösning. Baserat på dessa resultat utvärderades systematiskt en kommersiellt tillgänglig injicerbar kolloidal AK-produkt (PlumeStop®) för markstabilisering för PFAS. Den bästa behandlingseffektiviteten för 10 olika jordar (förstärkta med 17 PFAS) behandlade med kolloidal AC så observerades en ökad sorption av > 80 % för perfluoroktanoat (PFOA), 6:2 fluorotelomersulfonat (6:2 FTSA) och perfluorohexansulfonat (PFHxS). Dessutom utvärderades även stabiliserings och solidifiering (S/S), en teknik som använder cement eller cementliknande material för att både kemiskt stabilisera PFAS och förhårda marken för att minska den hydrauliska konduktiviteten och därigenom minska utlakningen av PFAS. S/S-tekniken testades på PFAS-förstärkt jord med användning av 10 % cementinblandning och 0,2 % pulveriserad AK inblandning. I konservativa lakningstester, särskilt med AC, minskade utlakningen med > 99,9 % för längre kedjade PFAS, såsom perfluoroktansulfonat (PFOS). För ytterligare utvärdering av S/S-tekniken sattes ett pilotskaleexperiment upp, där över sex ton fältförorenad jord behandlade med 15 % cement och 0,2 % granulerad AK. Genom att använda ett artificiellt bevattningssystem utvärderades PFAS-utlakningen på motsvarande 6 års nederbörd. Behandlingseffektiviteten var > 97% för fyra dominerande PFAS: PFHxA, PFOA, PFHxS respektive PFOS, men låg (3%) för den kortkedjiga perfluoropentanoat (PFPeA). I slutändan kan man, baserat på laboratorie- och pilotskalaförsök, dra slutsatsen att stabiliseringstekniker för marksanering av PFAS-kontaminerade jordar kan vara en effektiv teknik, särskilt de längre kedjade PFAS.

Mattias Söregård, SLU, Department of Aquatic Sciences and Assessment,
P.O. Box 7050, 750 07 Uppsala, Sweden

Dedication

There are many people I would like to thank for their support during production of this thesis.

First and foremost, I want to thank my main supervisor **Lutz Ahrens** for initiating and managing the project with his endless high-quality but pragmatic and liberal problem solving, nurturing a pleasant lab environment, and for his great assistance in the writing process. I would also thank my second supervisor, **Dan Berggren Kleja** from the Swedish Geotechnical Institute (SGI), who provided valuable insights into chemistry and facilitated collaborations with stakeholders and government institutions. And a big thank you to Professor **Karin Wiberg**, for hosting a well-functioning and high-quality analytical research laboratory and research group, where the research group and work environment is characterised by competence, quality, cheerfulness and helpful attitudes. Multiple administrative staff members supported my PhD: Heads of department **Willem Goedcoop** and **Lars Sonnesten**, head of section **Jenny Kreuger** and administrative staff **Katarina, Maria, Ronald** and **Herman**. Also assisting me in my work were my collaborators: **Fredrik** and **Ola** at SGI, **Igor** at Rangsells, and my Master's students **Erik** and **Anna-Stina**. For language review on the papers, I would like to thank **Mary McAfee**.

During my whole PhD experience, the research group provided invaluable support in fully introducing me, an environmental engineer, to the world of analytical chemistry: **Jacob** (*for hosting fika*), **Minh** (*for reminding me about fika*), **Anna-Karin** (*for answering all questions*), **Oksana** (*for the Czech mate*), **Foon** (*introducing the trouser theorem*), **Rickard** (*for his analytical dignity*), **Wiebke** (*for the perspectives*), **Jana** (*for the HINE concept*), **Frank** (*for the laughs*), **Malin** (*for the dog*), **Winnie** (*for all the joyful talks*), **Hugo** (*for the reflections*), **George** (*for the good talks*), **Laura** (*for pure dedication*) and **Alexander** (*for the vocals*) and **Pablo** (*for sleeping under the stairs*). A special thank you to my fellow henchwoman and former roommate, **Vera Franke**, who started swimming in the PFAS pond at the same time and has been an ally since

we first met and she saved me by pointing out my open zipper. Good luck with your defence.

I thank my other fellow PhD students at the institutions for socially accommodating me and endlessly listening to my business ideas at lunch: **Jasmina, Kristina, Bonnie, Oskar, Baolin, Hannah, Amelie, Sophia, PianPian, Jenny, Emma, Carlotta, Claudia.**

Thanks also to **Gustav, Joachim, Lisa, Svenja, Sara, Joachim, Laura, Ana, Anastasia, Emil,** the **OMK** section and the **VR** council.

Finally, my deepest thanks to my parents, partner, friends and all teachers who paved the way with support and walked by my side through the years.

Contents

List of publications	8
1 Introduction	11
2 Overall aim of the thesis and specific objectives	15
3. Background	17
3.1 A world of PFASs	17
3.2 PFAS analysis	19
3.2.1 Stabilization	21
3.2.2 Stabilization-solidification	22
3.2.3 Long-term treatment efficiency of soil stabilization techniques	
4 Materials and Methods	25
4.1 Candidate materials for stabilization treatment	
4.2 Target PFASs	
4.3 Experimental treatment techniques	27
4.4 PFAS analysis	27
4.5 Quality assurance and quality control (QA/QC) for PFAS analysis	28
4.6 Characterisation of other variables	28
5 Results and Discussion	29
5.1 Activated carbon stabilization	29
5.2 Stabilization-solidification	31
6 Conclusions and Future work	35
References	39
Popular science summary	47
Populärvetenskaplig sammanfattning	49

List of publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

- I Söregård, M., Östblom, E., Köhler, S. & Ahrens, L. (2020). Adsorption behavior of per- and polyfluoroalkyl substances (PFASs) to 44 inorganic and organic sorbents and use of dyes as proxies for PFAS sorption. *Journal of Environmental Chemical Engineering* 8, 103744.
- II Sorengard, M., Kleja, D.B. & Ahrens, L. (2019). Stabilization of per- and polyfluoroalkyl substances (PFASs) with colloidal activated carbon (PlumeStop®) as a function of soil clay and organic matter content. *Journal of Environmental Management* 249, 109345.
- III Söregård, M., Kleja, D.B. & Ahrens, L. (2019). Stabilization and solidification remediation of soil contaminated with poly- and perfluoroalkyl substances (PFASs). *Journal of Hazardous Materials* 367, 639-646.
- IV Söregård, M., Gago-Ferrero, P., Kleja Berggren, D. & Ahrens, L. (2020). Laboratory-scale and pilot-scale stabilization and solidification (S/S) remediation of soil contaminated with per- and polyfluoroalkyl substances (PFASs). *Journal of Hazardous Materials*, 123453.

Papers I-IV are reproduced with the permission of the publishers.

The contribution of Mattias Söregård to the papers I-IV included in the thesis was as follows:

- I Planned the study with the co-authors and had the main responsibility for research questions, networking, study designs, laboratory experiments, data analysis, synthesis, writing and submission.
- II Planned the study with the co-authors and had the main responsibility for research questions, networking, study designs, laboratory experiments, data analysis, synthesis, writing and submission.
- III Planned the study with the co-authors and had the main responsibility for research questions, networking, study designs, laboratory experiments, data analysis, synthesis, writing and submission.
- IV Planned the study with the co-authors and had the main responsibility for research questions, networking, study designs, laboratory experiments, data analysis, synthesis, writing and submission.

1 Introduction

Per- and polyfluoroalkyl substances (PFASs) were first developed in the 1940s, starting with the polytetrafluoroethylene (Teflon) industry (Kissa, 2001). Since then, their oil- and water-repellent properties have proven useful for numerous consumer products, including water-, dirt- and oil-repellent textiles, fat-repellent food packaging, paper products, and in paint production, metallurgy and as firefighting foams (Buck *et al.*, 2011; Lindstrom *et al.*, 2011). Over 4700 different PFASs are available on the global market (Organisation for Economic Co-operation and Development (OECD), 2018). A common definition of PFASs is that they are alkylated compounds in which all or some carbon-hydrogen bonds have been replaced with very stable carbon-fluorine bonds (Buck *et al.*, 2011). Concerns have been raised about this group of compounds during the past decade, since some PFASs show high bioaccumulation potential in humans and some have been associated with adverse health effects (Martin *et al.*, 2003; Conder *et al.*, 2008; Johansson *et al.*, 2008; Borg *et al.*, 2012; Domingo, 2012; Borg *et al.*, 2013). Considering their environmental persistence, large production volumes and uncontrolled release to the environment, regulators are now taking measures to prevent further exposure to legacy and alternative PFASs (Ritscher *et al.*, 2018).

High levels of PFASs in humans have been linked to exposure through food and contaminated drinking water (Gebbinck *et al.*, 2015; Gyllenhammar *et al.*, 2019; Glynn *et al.*, 2020). The PFAS problem in Sweden attracted attention when elevated PFAS blood levels were found in pregnant women living in areas with contaminated drinking water (Glynn *et al.*, 2012). This led to the implementation of drinking water guidelines (Gobelius *et al.*, 2018) and ultimately to closure of some drinking water sources (Li *et al.*, 2018). Similar high contamination levels of PFASs in drinking water have been identified globally, with PFAS contamination leading to restriction of drinking water sources in *e.g.* Japan (Murakami *et al.*, 2009) and in Germany (Gellrich *et al.*, 2013) and the USA (Sunderland *et al.*, 2019). As a result, a growing body of research is now focusing on advanced treatment techniques for PFASs in drinking water (España *et al.*, 2015; Franke *et al.*, 2019). However, PFASs are continuing to leach into the aquatic environment and drinking water sources,

from various sources such as air deposition, industries, wastewater effluent, landfill leachates and contaminated soils (Ahrens, 2011). Leaching from contaminated soils can be a hot-spot for groundwater pollution affecting drinking water sources, and has been associated with PFAS exposure in humans in Japan (Murakami *et al.*, 2009), Germany (Gellrich *et al.*, 2013) and Sweden (Li *et al.*, 2018).

Soil contamination with PFASs is often associated with extensive use of PFAS-containing aqueous firefighting foams (AFFFs), which in the past have been released in large quantities at firefighter training facilities and fire sites (Ahrens *et al.*, 2015; Baduel *et al.*, 2015; Filipovic *et al.*, 2015). Due to the negative environmental impact, the use of perfluorooctane sulfonate (PFOS)-containing AFFFs has been regulated and PFOS-free AFFFs have been developed. However, many AFFF products still contain a large number of alternative PFASs (*e.g.* Barzen-Hanson *et al.*, 2017). In addition, legacy PFASs from soil contamination continue to leach from soil to groundwater and the aquatic environment (Ahrens *et al.*, 2015). There is thus an urgent need for remediation of PFAS-contaminated soils, but to date limited research has been performed on this topic (Ross *et al.*, 2018; Mahinroosta & Senevirathna, 2020).

The aim of the work described in this thesis was to provide an in-depth understanding of possible soil treatments for protection of drinking water sources and the aqueous environment. The stabilization technique as a promising option for PFAS-contaminated soil remediation was investigated specifically, since previous studies have reported promising results (Das *et al.*, 2013; Kupryianchyk *et al.*, 2016; Hale *et al.*, 2017).

In a first study (Paper I), cost-efficient materials and their PFAS-stabilising properties were screened (Figure 1). Screening and assessment of PFAS-stabilising sorbents were performed in various soil matrices with varying properties and PFAS contamination profiles in two further studies, focusing on colloidal activated carbon (1-2 μm) and powdered activated carbon in a cementitious stabilization-solidification matrix (Papers II and III, respectively).

To assess the technique under more realistic conditions, a pilot-scale experiment was conducted (based on results from Paper III) where stabilization-solidification was tested using six tons of contaminated soil subjected to more than six years of simulated rainfall (Paper IV).

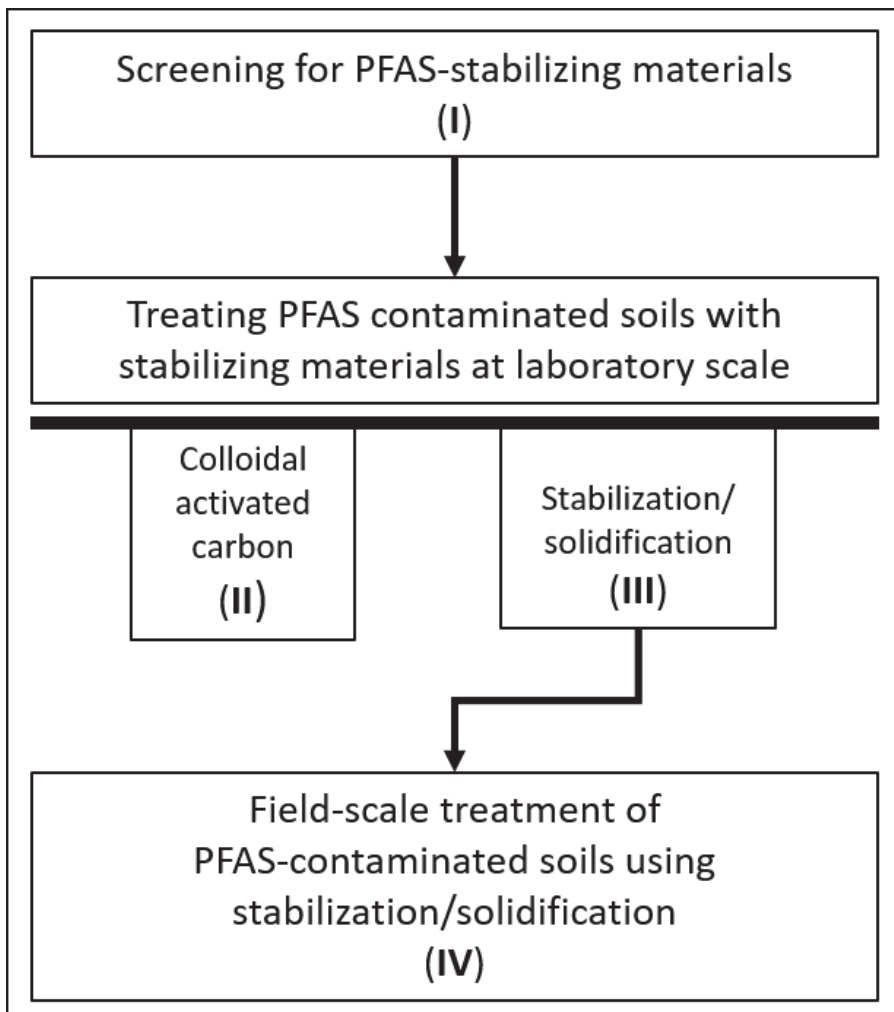


Figure 1. Overview of the work described in Papers I-IV in this thesis, including screening of materials, laboratory-scale experiments and pilot-scale testing on soils contaminated with per- and polyfluoroalkyl substances (PFASs).

2 Overall aim of the thesis and specific objectives

The overall aim of this thesis was to provide valuable novel information on stabilization technologies for remediation of soils contaminated with PFASs.

Specific objectives of the work described in Papers I-IV were to:

- Identify and assess 44 materials for their suitability in PFAS stabilization in soils, and determine the impact of perfluorocarbon chain length and functional group (Paper I).
- Assess colloidal activated carbon for stabilization of PFASs in soil, and determine the impact of organic carbon and clay content (Paper II)
- Evaluate the effect of solidification as a stabilization technology and the mechanical stability (strength) of the soil after solidification treatment (Paper III)
- Identify critical variables for successful long-term stabilization of PFASs in stabilization-solidification treatment under pilot-scale conditions (Paper IV)

3. Background

3.1 A world of PFASs

There are over 4700 different documented PFASs on the global market (OECD, 2018). The different PFASs vary in degree of fluorination, functional groups and perfluorocarbon chain length (Buck *et al.*, 2011) (Figure 2). The PFASs have either fully (*per-*) or partially (*poly-*) fluorinated carbon chains, and the strong carbon-fluorine bonds make them very stable compounds and thereby persistent in biotic and environmental systems (Lemal, 2004; Merino *et al.*, 2016).

PFASs are characterised by different functional groups, with carboxylic acids (PFCAs) and sulfonic acids (PFSAs) (including perfluorooctanoic acid (PFOA) and PFOS, respectively) being the most commonly reported. Other functional groups in PSASs are *e.g.* neutral, cationic, anionic or zwitterionic (Buck *et al.*, 2011; Barzen-Hanson *et al.*, 2017; Liu *et al.*, 2019; Martin *et al.*, 2019). PFASs with specific functional groups can naturally degrade into more stable forms such as PFCAs and PFSAs (Houtz & Sedlak, 2012; Harding-Marjanovic *et al.*, 2015). PFASs that naturally degrade to other more stable species in the environment are referred to PFAS precursors. Also, the perfluorocarbon chain length is critical for PFAS water solubility (Higgins & Luthy, 2006; Du *et al.*, 2014; Rostvall *et al.*, 2018), and thereby their environmental fate (Ahrens, 2011). For this reason, PFASs are often divided into short-chain PFASs (perfluorocarbon chain length <7 for PFCAs and <6 for PFSAs, respectively) and long-chain PFASs (perfluorocarbon chain length ≥ 7 for PFCAs and ≥ 6 for PFSAs, respectively) (Buck *et al.*, 2011).

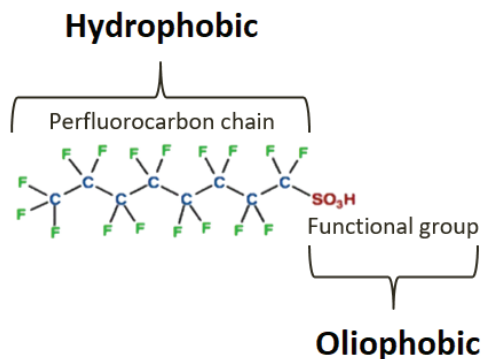


Figure 2. Chemical structure of perfluorooctane sulfonate (PFOS), a typical per- and polyfluoroalkyl substance (PFAS) with a hydrophobic perfluorinated chain and an oliophobic sulfonate functional group that is charged under environmental conditions.

Multiple PFASs have been found in human and biota samples (e.g. Borg *et al.*, 2013), in particular long-chain PFASs (Glynn *et al.*, 2012; Yeung *et al.*, 2013; Gyllenhammar *et al.*, 2019). Consequently, legislation globally regulates the usage of PFOSs and PFOAs and their precursors under the Stockholm Convention (Stockholm Convention on Persistent Organic Pollutants (POPS), 2018). Before legislative restrictions were introduced, PFOSs were voluntarily phased out by the global company 3M in 2001 (Paul *et al.*, 2009) and PFOAs were voluntarily phased out by the US EPA Stewardship Program in 2006 (US Environmental Protection Agency, 2006). The voluntary phasing out of PFOSs, PFOAs and other long-chain PFASs from consumer products has led to increased use of alternative PFASs (Land *et al.*, 2018; Cousins *et al.*, 2019; Yeung *et al.*, 2019).

Human exposure to PFASs has often been linked to consumption of PFAS-contaminated drinking water. The drinking water guideline values are often based on daily intake values, e.g. the European Food Safety Authority (EFSA) has set a tolerable daily intake (TDI) value of 150 ng kg⁻¹ body weight per day for PFOS and 1500 ng kg body weight per day for PFOA (EFSA, 2012). The drinking water guideline values for PFASs vary between countries, from e.g. 70 ng L⁻¹ for the sum of PFOA and PFOS in the USA (US EPA, 2016) to 530 ng L⁻¹ in the Netherlands (Gobelius *et al.*, 2018). The Swedish Food Agency has set a drinking water guideline value of 90 ng L⁻¹ for the sum of 11 PFASs (Gobelius *et al.*, 2018).

Furthermore, to protect drinking water sources and the environment, some countries have adopted guideline values for soil and groundwater. For example, Sweden has a guideline value of 45 ng L⁻¹ for PFOS in groundwater and 3000 ng kg⁻¹ and 20 000 ng kg⁻¹ for PFOS in soil for sensitive and less sensitive land use, respectively (SGI, 2015). Australia and New Zealand have guideline values of 0.009, 2 and 20 mg kg⁻¹ for PFOS, depending on soil usage (HEPA, 2018).

3.2 PFAS analysis

Initial environmental measurements of PFASs were performed in the early 2000s, using mass-electrometric instrumentation (Giesy & Kannan, 2001). During the past decade, analytical methods for PFASs have been expanded. However, the targeted methods currently available only cover a fraction of the over 4700 known PFASs, while a large proportion of PFASs in environmental samples remain unidentified (Koch *et al.*, 2020). There have been some analytical advances in quantifying the many unidentified PFASs (Pan *et al.*, 2020), including target screening using tandem mass spectrometry (Martin *et al.*, 2019), suspect screening using high-resolution mass spectrometry (Barzen-Hanson *et al.*, 2017), quantification of unknown fractions by assessing total extractable organic fluorine (TOF) (Yeung *et al.*, 2013) and total organic precursor (TOP) assay (Houtz & Sedlak, 2012). Many environmental matrices, such as consumer products (Schultes *et al.*, 2018), wastewater (Dauchy *et al.*, 2017) and river water (Koch *et al.*, 2019), can contain a large fraction of unidentified PFASs, while human plasma has been shown to contain 0-66% unidentified PFASs (Yeung *et al.*, 2019; Miaz *et al.*, 2020). Over time, there has been a shift in the use of PFASs (Ahrens, 2011). For this reason, and because of the analytical and regulatory challenges (Yeung *et al.*, 2019), the detection of all PFASs in the environment remains unresolved and new analytical methods are required in the future. In contaminated soil, PFASs and PFCAs are the dominant PFASs and are commonly included in targeted methods. The many 'unidentified' PFASs were outside of the scope of this thesis work, which focused on targeted analysis.

3.2 Soil remediation

Contamination of soil with PFASs is problematic, since PFASs can be harmful to soil organisms (Rich *et al.*, 2015), taken up by plants (Gobelius *et al.*, 2017) and/or leach into groundwater (Ahrens *et al.*, 2015; Filipovic *et al.*, 2015) (Figure 3). Regarding soil remediation, soils can either be treated *in situ*, *i.e.* on-site without excavation, or *ex situ*, *i.e.* where the soil is excavated for treatment on-site or at another location (Dermont *et al.*, 2008) (Figure 4).

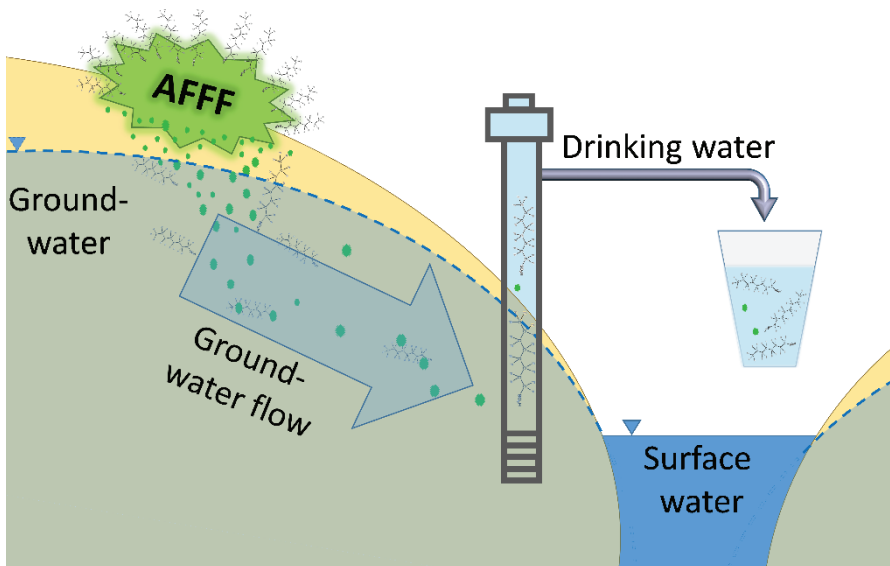


Figure 3. Drinking water exposure pathway in soils contaminated with per- and polyfluoroalkyl substances (PFASs) contained in aqueous film-forming foam (AFFF).

Ex situ treatment of soil containing organic contaminants, *e.g.* by landfilling or incineration, reduces the risk quickly but is also associated with practical difficulties, with high excavation and transportation costs. In addition, *ex situ* treatments for PFASs can be problematic since: (i) deposition in landfill could shift the problem to landfills, since they are known point sources of PFASs (Benskin *et al.*, 2012) and (ii) incineration is costly and has a high energy demand, with operating temperatures of >1000 °C required for degradation of PFASs (Loganathan *et al.*, 2007; Vecitis *et al.*, 2009; Wang *et al.*, 2013; Yamada *et al.*, 2005).

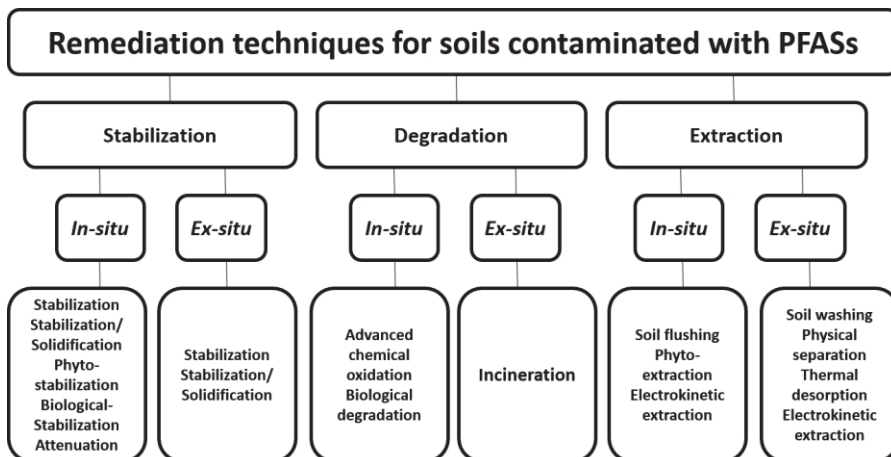


Figure 4. Possible remediation options for soils contaminated with per- and polyfluoroalkyl substances (PFASs).

In situ treatment techniques aim to treat the soil on-site, either by eliminating the contaminant or by preventing it from leaching into exposure pathways, e.g. by hindering polluted groundwater from reaching drinking water aquifers or surface water bodies in the aquatic environment. The latter can either be done through geohydrological interventions, i.e. physical barriers, or by chemical adsorption of the contaminants, which is often referred to as *stabilization* remediation (Kumpiene *et al.*, 2008).

This thesis focused entirely on *in situ* stabilization remediation techniques (also in combination with hydrogeological interventions), which aim to immobilise PFASs but not remove them. However, it is worth mentioning that other *in situ* soil removal remediation techniques for PFASs have been studied, with promising results. For example, laboratory studies have shown that it is possible to remove PFASs from contaminated soils by thermal desorption at high temperature (550 °C) (Söregård *et al.*, 2020), electrokinetic extraction (Söregård *et al.*, 2019), labour-intensive soil washing (Mahinroosta & Senevirathna, 2020) or cost-efficient, but slow, phytoremediation (Gobelius *et al.*, 2017). An alternative removal technique is ‘pump and treat’, a flushing technique where contaminated groundwater is treated aboveground with a suitable sorbent (Høisæter *et al.*, 2019).

3.2.1 Stabilization

Stabilization involves reducing the spread of contaminants by introducing different materials into the soil. Through chemical and physical processes, the treatment can hinder the leaching of contaminants to the groundwater and ultimately to drinking water and the environment. In general, two methods can be used: (i) altering the geohydrology of the soil profile to prevent water acting

as a vector of contaminant transport, often through capping or encapsulation of the contaminated soil; or (ii) increasing chemical partitioning of the contaminant to the soil, thereby reducing leaching to groundwater. For the latter, different sorbent materials may suit different contaminants and other factors also influence the stabilization process, such as pH, redox potential, ion exchange and precipitation (Kumpiene *et al.*, 2008). The aim is to reduce contaminant bioavailability, toxicity and leachability by different chemical reactions, precipitating them as salts or creating stable complexes with the added sorbent (Kumpiene *et al.*, 2008; Bolan *et al.*, 2014). Hydrophobic organic contaminants are often stabilised with adsorption processes on carbonaceous materials such as activated carbons (Rakowska *et al.*, 2012), zeolites (Misaelides, 2011) and clays (*e.g.* Khenifi *et al.*, 2009).

Bolan *et al.* (2014) conceptualised the stabilization efficiency achieved by binding with the contaminant. The stabilization efficiency generally increases with a stronger bond, in the order: precipitation > specific sorption > non-specific sorption > soil solution. Studies have shown that the binding strength of contaminants to soil constituents depends on time and temperature, in a process called soil ageing (Brennan *et al.*, 1984; Lothenbach *et al.*, 1999). The ageing process has been observed for hydrophobic organic contaminants (Cornelissen *et al.*, 1997; Kraaij *et al.*, 2002). In the current scientific literature on PFASs, many studies focus mainly on PFOA and PFOS adsorption to a variety of materials (Du *et al.*, 2014).

3.2.2 Stabilization-solidification

A popular stabilization strategy is the stabilization-solidification (S/S) method, which can be applied both *ex situ* (*e.g.* on landfill) and *in situ*. In the S/S strategy, a binding material, often a cementitious material, is mixed into the soil, where it hardens to a monolith (Wiles, 1987). The method dates back several decades and is one of the most popular soil remediation options in the USA, because of its high efficiency in contaminant retention, general applicability to contaminants and contaminated matrices, and relatively low costs (Brown *et al.*, 1992; Conner & Hoeffner, 1998). Stabilization-solidification treatment creates parallel levels of protection, where the addition of cementitious binders (i) chemically stabilises the contaminants and (ii) solidifies the contaminated matrix to a monolithic structure, which reduces the losses of contaminants to percolating water and groundwater flow, thus physically reducing contaminant leaching (Paria & Yuet, 2006). The technique is therefore a dual mitigation strategy hindering the spread of contaminants through altering groundwater flow as a vector of transport and through chemically increasing partitioning of the contaminant to the solid phase.

The S/S technique is a well-established method for different contaminants, such as heavy metals and other organic pollutants (*e.g.* tributyltin) (Dermont *et al.*, 2008; Shen *et al.*, 2019). Furthermore, field-scale *in situ* application methodologies and equipment are well developed for available off-the-shelf

usage, including high-pressure jet mixing (Xia *et al.*, 2019b; Ma *et al.*, 2020), deep auger mixing (McGregor, 2018) and surface solidification (Xia *et al.*, 2019a).

The workflow in establishing an appropriate S/S treatment design involves addressing both the physical solidification properties and chemical stabilization properties of the treated soil. In order to achieve satisfactory physical protection of the solidified structure, country-specific guidelines have been established for the properties of the solidified material. The most common tests performed on solidified materials involve measuring unconfined compressive strength (UCS) or measuring the hydraulic conductivity, or both. The UCS standard in the United States is 350 kPa to dispose of contaminated *ex situ* S/S material on risk waste landfill sites or the hydraulic conductivity should be $<1 \times 10^{-9} \text{ m s}^{-1}$ (United States Environmental Protection Agency, 1996). For *in situ* burial of S/S material, the UCS value can be as low as 140 kPa (Meegoda *et al.*, 2003), while for utilisation as a load-bearing concrete construction material the strength requirement can be up to 7 MPa (Tabbaa & Stegemann, 2005).

To the best of my knowledge, there are no general standardised targets for contaminant stabilization performance; rather, the outcome depends on the contaminant risk assessment and field site requirements. The target is therefore to design the S/S treatment so that contaminant leaching is minimised, by selection of an appropriate binder and other additives, as tested when the solidified structure is removed (monolith crushed to particles $<2 \text{ mm}$). Because of the wide variety in practice of contamination concentrations, matrices (soil, sediment, sludge, wastes *etc.*), binders (Portland cement, lime, fly ash, slag, MgO) and additives (activated carbon, zeolite, modified clay, bentonite, zero valent iron), it is recommended that S/S recipe evaluation and optimisation be performed for every new contamination situation (Hills *et al.*, 2015). Ultimately, before field application, the optimised S/S recipe must be tested to determine strength and leaching properties at laboratory scale.

3.2.3 Long-term treatment efficiency of soil stabilization techniques

A review by Kumpiene *et al.* (2008) indicated that there is high uncertainty as regards the long-term remediation efficiency of stabilization treatment, since prediction of future leaching is difficult. Over a long time, processes can occur in stabilised soil that are commonly not accounted for in laboratory-scale testing, such as changes in redox potential, microbial growth, freezing and thawing, degradation of amendment materials and competitive adsorption and ion exchange by naturally occurring chemical compounds. Despite these difficulties, stabilization techniques must rely on laboratory-scale optimisation approaches to identify the best available option. Because of the associated long-term

uncertainties, practitioners often prefer more costly contaminant removal alternatives, although stabilization techniques display high laboratory-scale treatment efficiencies.

There are many materials available that are known to adsorb PFASs, but a better mechanistic understanding is needed before stabilization can be recommended as a remediation strategy for PFAS-contaminated soils. Effective amendment materials for PFAS stabilization need to be evaluated in relation to natural soils, different PFASs and the chemical processes affecting possible long-term PFAS leaching behaviour. In addition, discrepancies between laboratory-scale and field-scale PFAS sorption behaviours have been observed (Li *et al.*, 2018), and these need to be understood before implementing stabilization as a treatment option for PFAS-contaminated soil.

4 Materials and Methods

4.1 Candidate materials for stabilization treatment

Prior to the work in this thesis, multiple natural and synthetic materials had been tested and evaluated for PFAS stabilization, in particular for PFOSs and PFOAs (Du *et al.*, 2014). However, because of differences in experimental conditions (*e.g.* pH, ion composition, liquid/solid ratio, equilibrium times *etc.*), the materials proved difficult to compare (Paper I). In the screening study described in Paper I, a total of 44 organic and inorganic sorbents (based on previous studies) were tested for PFAS sorption under comparable conditions in a water matrix. Promisingly high PFAS removal from leachate water was observed for activated carbons (by ACs) in Paper I, and therefore a novel colloidal (1-2 μm) AC product that can be injected into contamination plumes under high pressure was evaluated in Paper II. In the other two studies on which this thesis is based, a wide range of sorbents were tested for stabilization-solidification purposes, with the stabilising properties tested in soil and in varying cementitious matrices (Papers III and IV).

4.2 Target PFASs

In this thesis, the 11 PFASs covered by the Swedish Food Agency drinking water guidelines (PFBS, PFHxS, PFOS, 6:2 FTSA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA and PFDA; see Table 1) were included in the analyses. Up to sixteen additional PFASs of concern, including longer-chain PFCAs, PFASs, perfluorosulfonamides (FOSAs), perfluoro-sulfonamidoethanols (FOSEs), perfluorosulfonamidoacetic acids (FOSAAs) and fluorotelomersulfonates (FTSAs), representing PFASs of different chain length and functional groups, were also included in the analyses (Table 1). FOSAs, FOSEs, FOSAAs and FTSAs are considered to be PFAS precursors, since they are suspected to undergo transformation to the highly stable PFASs and PFCAs (Eriksson *et al.*, 2017).

Table 1. *Abbreviation, CAS No. and purity of the per- and polyfluoroalkyl substance (PFAS) standards used in this study and PFASs included in the Swedish drinking water guidelines (indicated by *)*

	PFAS	CAS No.	Abbreviation
PFSAs	Perfluorobutane sulfonic acid*	375-73-5	PFBS
	Perfluorohexane sulfonic acid*	355-46-4	PFHxS
	Perfluorooctane sulfonic acid*	1763-23-1	PFOS
	Perfluorodecane sulfonic acid	335-77-3	PFDS
PFCAs	Perfluorobutanoic acid*	375-22-4	PFBA
	Perfluoropentanoic acid*	2706-90-3	PFPeA
	Perfluoroheptanoic acid*	307-24-4	PFHxA
	Perfluorooctanoic acid*	375-85-9	PFHpA
	Perfluorooctanoic acid*	335-67-1	PFOA
	Perfluorononanoic acid*	375-95-1	PFNA
	Perfluorodecanoic acid*	335-76-2	PFDA
	Perfluoroundecanoic acid	2058-94-8	PFUnDA
FOSAs	Perfluorooctane sulfonamide	754-91-6	FOSA
	<i>N</i> -methyl perfluorooctane sulfonamide	31506-32-8	MeFOSA
	<i>N</i> -ethyl perfluorooctane sulfonamide	4151-50-2	EtFOSA
FOSEs	<i>N</i> -methyl perfluorooctane sulfonamidoethanol	24448-09-7	MeFOSE
	<i>N</i> -ethyl perfluorooctane sulfonamidoethanol	1691-99-2	EtFOSE
FOSAAs	Perfluorooctane sulfonamidoacetic acid	2806-24-8	FOSAA
	<i>N</i> -methylperfluorooctane sulfonamidoacetic acid	2355-31-9	MeFOSAA
	<i>N</i> -ethylperfluorooctane sulfonamidoacetic acid	2991-50-6	EtFOSAA
FTSAs	6:2 Fluorotelomersulfonate*	425670-753	6:2 FTSA
	8:2 Fluorotelomersulfonate	678-39-7	8:2 FTSA

4.3 Experimental treatment techniques

The stabilization performance of different materials was evaluated in laboratory-scale batch-test experiments (Papers I-IV). The solid sorbent and aqueous phase were shaken together for 24 hours or one week, until assumed equilibrium for PFAS partitioning between the two phases. Equilibrium conditions are often assumed to be representative of natural conditions for soil pore water, because of the normally low hydraulic velocity in groundwater and pore water. For sorbent screening (Paper I), the partitioning was tested for varying sorbents and pure water fortified with PFASs. For soil treatment (Paper II-IV), 4-15% (by dry weight (dw)) of sorbent was mixed with PFAS-contaminated soil, either artificially spiked soil (Papers II and III) or contaminated field soil (Paper IV). In the batch laboratory tests (Papers III-IV), the stabilization properties of the solidified soil were evaluated after crushing the material to 0.1-2 mm, a conservative standardised test step whereby the treatment effect of solidification is diminished.

To assess the S/S technology (Paper IV), a pilot-scale experiment was performed treating more than six tons of contaminated soil subjected to over six years of simulated rainfall in a lysimeter facility, where PFAS concentrations in leachate water were monitored.

4.4 PFAS analysis

In all PFAS analyses, representative internal standards (IS) were used to compensate for losses in sample preparation and for instrumental matrix effects. In general, three different sample preparation methods were used for PFAS analysis: (i) direct injection for high PFAS concentrations in water samples ($0.1-100 \text{ ng mL}^{-1}$), for which 0.5 mL samples were spiked with methanol and IS mixture; (ii) offline solid phase extraction (SPE) for low PFAS concentrations in water samples ($0.1-100 \text{ ng L}^{-1}$), for which 0.25 L water samples were spiked with IS and loaded on a 150 mg WAX SPE cartridge and eluted with 12 mL methanol with 0.1% sodium hydroxide. The methanol extract was concentrated to 0.5 mL under nitrogen gas and diluted with 0.5 mL MilliQ water before instrumental analysis; and (iii) solid-liquid extraction for solid samples, *i.e.* PFAS-contaminated soil. The extraction solvent for 3 g dry soil was 30 mL of a 80% methanol and 20% 1 M sodium hydroxide solution, spiked with an IS mixture. After equilibrating, 10 mL of the aliquot was concentrated to 0.5 mL under nitrogen gas and diluted with 0.5 mL MilliQ water. All samples were filtered through a $0.45 \text{ }\mu\text{m}$ recycled cellulose syringe filter before injection into the instrument.

Analysis of PFASs in all samples was performed using ultra-high performance liquid chromatography coupled with tandem mass spectroscopy (UHPLC-MS/MS) (Quantiva TSQ; Thermo Fisher). The analytes were separated using a

BEH-C18 column (1.7 μm , 50 mm, Waters) and an injection volume of 10 μL . The eluent gradient was 12 min, and the mobile phases were Millipore water and acetonitrile with 5 mM ammonium acetate. The isotope dilution method was used for quantification and for compensating for losses and matrix effects. An eight-point calibration curve (0.01-100 ng mL^{-1}) was used for quantification and the data were evaluated using TraceFinderTM software (Thermo Fisher).

4.5 Quality assurance and quality control (QA/QC) for PFAS analysis

Quality assurance and quality control (QA/QC) was performed on all individual experiments. The QA/QC included absolute recovery experiments based on losses of ISs and estimation of experimental replicate standard deviation. In general, all measurements were performed in either duplicate or triplicate, or by intense sampling over time to account for experimental and analytical variation. Recovery was assessed in each experiment and was always >50%. Laboratory blanks were included in each batch of experiments (typically every 10 samples). The instrument detection limit (IDL) was set to the lowest calibration point with either signal to noise threshold >3 or deviation <30% in the average response factor (ARF). The method detection limit (MDL) was set to the IDL or, if PFASs were detected in laboratory blanks, the MDL was set to the average blank PFAS concentration plus three times the standard deviation.

4.6 Characterisation of other variables

A wide variety of other parameters were determined in order to enable evaluation and analysis of the results. The parameters analysed were pressure (UCS), pH, conductivity, grain size distribution (soil characterisation), hydraulic conductivity, loss of ignition (soil carbon content), z-potential and particle size distribution. Other analyses performed included surface area measurement (BET), X-ray tomography, scanning electron microscopy (SEM) and high-resolution mass spectrometry (for details, see Papers I-IV).

5 Results and Discussion

5.1 Activated carbon stabilization

In the screening of 44 possible materials for PFAS sorption (Figure 5), it was found that only a few of the materials tested had a significant impact on sorption of PFASs compared with natural soil constituents (Paper I).



Figure 5. Images of (left) different sorption materials evaluated in Papers I and III, and (right) the colloidal activated carbon evaluated in Paper II.

Carbon-based materials, such as biochars and other organic-rich materials, *i.e.* peat and sewage sludge, showed increased PFAS sorption compared with untreated soil and water (Papers I and II). The dominant sorption mechanism was identified to be primarily hydrophobic sorption, followed by electrostatic sorption, with the latter being more important for compounds with shorter perfluorocarbon chain length. Hydrophobic sorption dependency was apparent as linearly increasing partitioning of PFASs to sorbents with increasing

perfluorocarbon chain length, while electrostatic sorption dependency was apparent from discrepancies in sorption of PFASs with the same perfluorocarbon chain length but different functional groups. This behaviour was observed in all experiments.

Comparisons of the sorption of PFASs to the different materials tested in the screening study (Paper I) showed that activated carbons had particularly good sorption capacity for PFASs. This has been reported previously for PFASs in laboratory-scale water treatment experiments (Ochoa-Herrera & Sierra-Alvarez, 2008; McCleaf *et al.*, 2017) and in full-scale water treatment plants using granulated activated carbon (GAC) (Belkouteb *et al.*, 2020). In addition, activated carbon material has been used for treating groundwater in *e.g.* soil washing and pump-and-treat systems for soil remediation purposes. Stabilization with 4% powdered activated carbon has previously been shown to reduce PFOS leaching from contaminated soils by >99% (Kupryianchyk *et al.*, 2016; Hale *et al.*, 2017).

However, the same high efficiency was not observed for a colloidal activated carbon product, PlumeStop[®], a commercially available sorbent for use in soil stabilization treatment for PFASs (and other contaminants) (Paper II). It was found to have a maximum treatment efficiency of around 80% for PFOS and no effect on short-chain PFASs, *i.e.* PFBA and PFBS. This result was contradictory to findings reported for field-scale colloidal activated carbon treatment, which reduced the PFOS groundwater concentration from 1500 ng L⁻¹ to below 20 ng L⁻¹ in downstream observation wells after 18 months (McGregor, 2018). It remains to be determined whether such treatment efficiency remains stable over a longer period of time, or whether field treatment efficiencies converge to laboratory-scale equilibrium results (Paper II).

Paper II showed an effect of soil type on treatment efficiency. It was found that the competitive properties of soil organic matter reduced the treatment efficiency of colloidal activated carbon, while an increasing proportion of clay increased the treatment efficiency, due to the higher surface area to which the sorbent can attach.

5.3 Stabilization-solidification

In the evaluation of S/S treatment as a stabilization technique (Paper III), high removal efficiencies (>99%) were achieved for *e.g.* PFOS at laboratory scale using 10% binder mixture. Even higher efficiencies (up to 99.7%) were observed on adding 0.2% powdered activated carbon (PAC), which involved considerably less material and was cheaper than the 4% activated carbon treatment tested in previous studies by Kupryianchyk *et al.* (2016) and Hale *et al.* (2017). The addition of 0.2% PAC in Paper III did not markedly affect the solidifying properties of the treated soil, a factor that determines the longevity of the physical monolithic structure (Figure 6). An additional laboratory-scale screening of different cement binders in Paper IV did not show any considerable difference in either PFAS leaching or strength performance. Hence, the commonly available (in Sweden) cement binder mixture of 50:50 CEM II/A-V 52.5 N Portland:fly ash (Bas cement, CEMENTA) was sufficient for successful S/S treatment for PFASs. However, treatment efficiencies for short-chain PFCAs (*i.e.* PFBA, PFPeA and PFHxA) were low (or even negative when not using 0.2% PAC additive) in the laboratory-scale trials (Papers III and IV) and in the pilot-scale study (Paper IV). This was explained by the relatively higher importance of the electrostatic sorption mechanism, which is not favourable in the basic matrix of cementitious binders due to competitive binding of hydroxide ions.

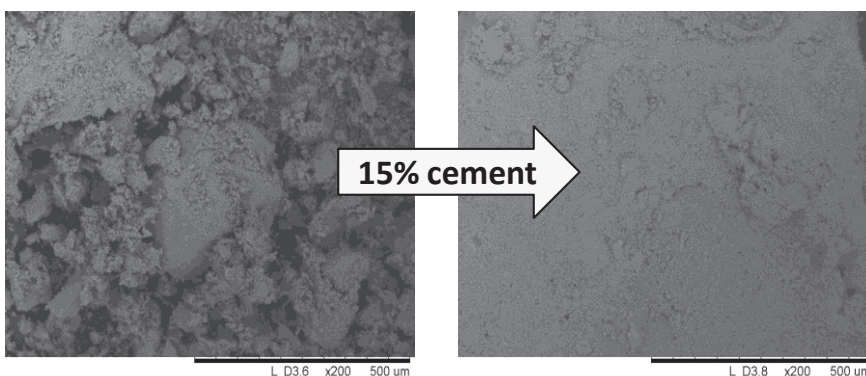
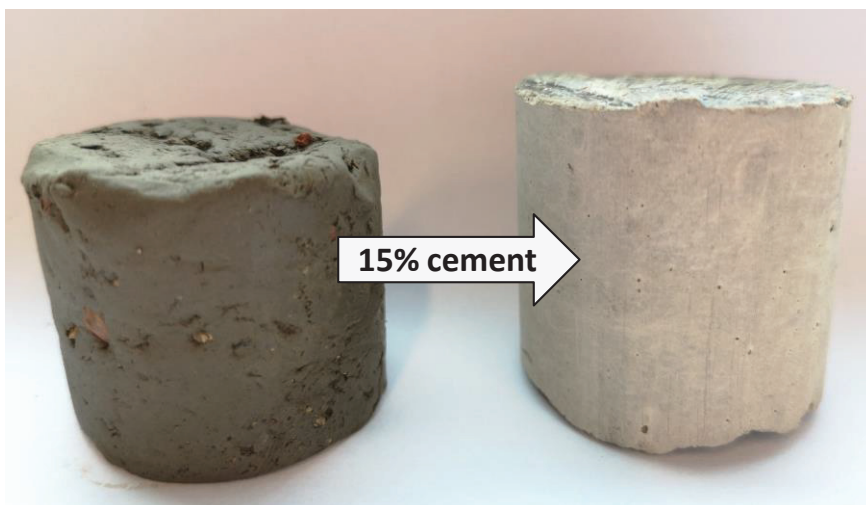


Figure 6. (Upper row) Images of soil monoliths following stabilization-solidification (S/S) treatment with 15% cement in pilot-scale experiments, and (lower row) the corresponding scanning electron microscope (SEM) images at 500 μm resolution.

The promising results obtained for the cost-efficient and commercially available S/S remediation technique encouraged further studies on a larger scale, leading to Paper IV. The scale is important in S/S testing, since the physical protection afforded by soil solidification limits the contact to water leachate by lowering the exposed surface area. The S/S-treated soil in Paper IV was treated with 15% cement and 0.2% GAC. The artificial rain applied (300 mm y^{-1}) infiltrated and percolated through S/S-treated ($n = 2$) and reference soils ($n = 2$). The treatment was performed over one year and leachate was collected every 2-3 weeks. In the leachate from the untreated soil, PFOS, PFHxS, PFHpS and PFOA dominated, comprising 62%, 12%, 9% and 4%, respectively, of the total concentration of the 17 PFASs analysed. The treatment efficiency for those PFASs was found to

be 97-99%. At the last sampling point for the S/S-treated soil, the short-chain PFPeA contributed almost 50% of the total PFAS concentration in leachate, although the homologue comprised a negligible proportion in the reference soil leachate. This is in accordance with the leaching behaviour of short-chain PFASs in the laboratory-scale tests (Papers III and IV). In general, the relative leaching behaviour in the laboratory-scale experiments was significantly correlated with that in the pilot-scale experiment. This is a promising finding, as laboratory-scale S/S recipe optimisation is still a critical and integral part of assuring the longevity of treatment.

Ultimately, the sum of PFASs (not including PFBA) concentration in leachate from the treated soil at the end of the experiment was around 300 ng L^{-1} , which exceeded the Swedish drinking water guideline of 90 ng L^{-1} for the sum of 11 PFASs (including PFBA). However, the PFAS leaching concentration was still decreasing at the end of experiment (as reported in Paper IV), and may continue to decrease as the experiment will continue for one more year (outside the time-scope of this thesis). A noteworthy observation when studying the leaching behaviour in the two systems was that the apparent ‘sorption strength’ (partitioning coefficient K_d) increased over time for both the reference soil and the leachate. The initial partitioning coefficient for the reference soil was of the same order of magnitude as in the laboratory-scale equilibrium batch tests, *e.g.* for PFOS in Papers II and IV, but was one order of magnitude higher at the end of the experiment. This discrepancy in K_d values between laboratory-scale and field-scale studies has previously been observed by Li *et al.* (2018), who found that field-scale partitioning was one order of magnitude higher than in laboratory-scale experiments. This process is often referred to as soil ageing, and can be due to limitations in mass transfer from soil pores to the mobile aqueous phase and/or differences in chemical sorption strength.

Overall, the efficiency of stabilization techniques in immobilising PFASs was found to vary greatly with soil type (organic matter and clay content), sorbent type and PFASs targeted by the treatment (long-chain, short-chain). Activated carbon materials proved to be most effective in soil remediation, as shown for the case of PFOS in Figure 7. Colloidal activated carbon was easily applied but was the least effective alternative investigated, although it still reduced PFOS leaching by over 80%. The highest soil treatment efficiency for PFOS was found for 10% cementitious S/S treatment with 0.2% PAC, which gave a >99% reduction in leaching. At pilot scale, 15% cementitious S/S treatment with 0.2% GAC gave the best long-term (<6 years) stabilization of PFOS (>97%). A pure 10% cementitious S/S treatment was also found to be a suitable option for PFOS stabilization (Figure 7).

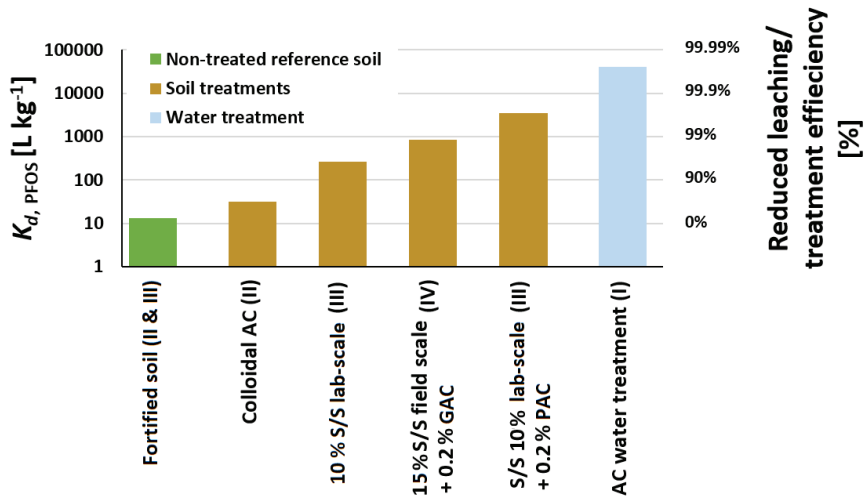


Figure 7. Comparison of treatment efficiencies and sorption coefficient (K_d) values for perfluorooctane sulfonate (PFOS), based on results obtained in Papers I-IV. AC = activated carbon, GAC = granulated activated carbon, PAC = powdered activated carbon

6 Conclusions and Future work

The aim of this thesis was to identify available and promising materials for efficient PFAS stabilization.

- Screening of 44 candidate sorption materials for soil stabilization and PFAS sorption showed that materials based on activated carbon performed significantly better in PFAS sorption than all other sorbents. The main sorption mechanism was hydrophobic binding, followed by electrostatic binding.
- A novel liquid colloidal activated carbon, which can be injected under high pressure into contaminated soil, was investigated for PFAS sorption in 10 different soils. The results showed that treatment efficiency in PFAS sorption was 1-2 orders of magnitude lower than in stabilization of PFAS-contaminated soils by mechanical mixing with powdered activated carbon.
- Stabilization-solidification (S/S) treatment of PFAS-contaminated soil showed promising results in laboratory-scale trials. Assessment of the long-term sorption of PFASs in pilot-scale S/S-treated soil, using artificial irrigation simulating six years of natural precipitation (300 mm y^{-1}), revealed a discrepancy between short- and long-term leaching of PFASs. Long-chain PFASs were better retained in the longer term, possibly due to stronger sorption.
- The efficiency of stabilization techniques in immobilising PFASs varied greatly with the type of sorbent material used. Activated carbon materials performed best. Colloidal activated carbon was easily applied, but was least effective in reducing PFOS leaching (~80% reduction).

- The highest stabilization effect for PFOS was obtained with 10% cementitious S/S treatment combined with 0.2% powdered activated carbon in the laboratory (>99% reduction in leaching). At pilot scale, 15% cementitious S/S treatment with 0.2% granulated activated carbon gave the best long-term (<6 years) stabilization of PFOS (>97% reduction in leaching), followed by 15% S/S cementitious treatment alone.

Future work

This thesis presents results for laboratory- and pilot-scale S/S treatment, a readily available technique that can prevent leaching of PFASs to groundwater in order to meet regulatory limits. S/S techniques can be used in full-scale field applications and are now sufficiently mature for field-scale testing, which is critical for evaluating the true treatment efficiency in reducing PFAS leaching to groundwater. Such experiments are very costly and practically challenging, but important due to the urgency of treating polluted soil before the contaminants have dispersed too far from the original contaminated site. Questions remain on appropriate design of field-scale trials, the role of soil ageing and the longevity of stabilization treatment. Assuming that the longevity of S/S treatment for PFASs is similar to that for other organic soil pollutants (*e.g.* polycyclic aromatic hydrocarbons), previous results for other pollutants in field-scale stabilization trials could help understand the efficiency of PFAS treatment, including long-term effects on sorbent weathering and sorbent degradation.

It was apparent from the results in this thesis that short-chain PFASs, which are considered less bioaccumulative than their longer-chain counterparts, are not retained well with stabilization techniques, either in soil or in water matrices. However, these more water-soluble homologues tend to leach faster than their longer counterparts do. Hence, alternative sorption materials are needed to complement activated carbon sorbents or other techniques are required. Colloidal activated carbon has the advantage of ease of application on-site and can be used as a complement in S/S treatment of a highly contaminated hotspot, but more work is needed (*e.g.* development of a sorbent with a higher capacity for short-chain PFASs). Other complementary removal remediation techniques have been shown to be more efficient for short-chain PFASs, such as phytoremediation and electrokinetic soil remediation, which can be combined with destructive treatment techniques such as incineration and advanced oxidation methods, respectively.

Overall, the S/S treatment technique has a rigorous history and available infrastructure for treating contaminated soils cost-efficiently, has the flexibility for remediation *in situ* but also *ex situ*, and can be used for different types of solid materials (*e.g.* soil, sediment, waste products). Politicians, regulatory institutions and practitioners are therefore encouraged to take action to mitigate PFAS contamination in polluted soils. However, few guideline values have been set for PFASs in soil and groundwater, and existing values are only limited to a few PFASs (*e.g.* PFOS, PFOA), so target remediation contaminant levels remain uncertain. Another important aspect of *in situ* stabilization methods is that the pollutants are not removed but retained, so guidelines should include limits on leaching of PFASs from stabilised soil. Setting guideline values for unknown PFASs is another important task for the future, possibly using analytical procedures such as total organic fluorine or TOP-assay approaches.

Be brave.

Take the lead.

References

- Ahrens, L., 2011. Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. *J. Environ. Monit.* 13, 20–31. <https://doi.org/10.1039/C0EM00373E>
- Ahrens, L., Norström, K., Viktor, T., Cousins, A.P., Josefsson, S., 2015. Stockholm Arlanda Airport as a source of per- and polyfluoroalkyl substances to water, sediment and fish. *Chemosphere* 129, 33–38. <https://doi.org/10.1016/j.chemosphere.2014.03.136>
- Arias Espana, V.A., Mallavarapu, M., Naidu, R., 2015. Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA): A critical review with an emphasis on field testing. *Environ. Technol. Innov.* 4, 168–181. <https://doi.org/10.1016/j.eti.2015.06.001>
- Baduel, C., Paxman, C.J., Mueller, J.F., 2015. Perfluoroalkyl substances in a firefighting training ground (FTG), distribution and potential future release. *J. Hazard. Mater.* 296, 46–53. <https://doi.org/10.1016/j.jhazmat.2015.03.007>
- Barzen-Hanson, K.A., Roberts, S.C., Choyke, S., Oetjen, K., McAlees, A., Riddell, N., McCrindle, R., Ferguson, P.L., Higgins, C.P., Field, J.A., 2017. Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater. *Environ. Sci. Technol.* 51, 2047–2057. <https://doi.org/10.1021/acs.est.6b05843>
- Belkouteb, N., Franke, V., McCleaf, P., Köhler, S., Ahrens, L., 2020. Removal of per- and polyfluoroalkyl substances (PFASs) in a full-scale drinking water treatment plant: Long-term performance of granular activated carbon (GAC) and influence of flow-rate. *Water Res.* 182, 115913. <https://doi.org/10.1016/j.watres.2020.115913>
- Benskin, J.P., Li, B., Ikonomou, M.G., Grace, J.R., Li, L.Y., 2012. Per- and polyfluoroalkyl substances in landfill leachate: Patterns, time trends, and sources. *Environ. Sci. Technol.* 46, 11532–11540. <https://doi.org/10.1021/es302471n>
- Bolan, N., Kunhikrishnan, A., Thangarajan, R., Kumpiene, J., Park, J., Makino, T., Kirkham, M.B., Scheckel, K., 2014. Remediation of heavy metal(loid)s contaminated soils - To mobilize or to immobilize? *J. Hazard. Mater.* 266, 141–166. <https://doi.org/10.1016/j.jhazmat.2013.12.018>
- Borg, D., Håkansson, H., Sverige, Naturvårdsverket, 2012. Environmental and health risk assessment of perfluoroalkylated and polyfluoroalkylated substances (PFASs) in Sweden. Swedish Environmental Protection Agency, Stockholm.
- Borg, D., Lund, B.-O., Lindquist, N.-G., Håkansson, H., 2013. Cumulative health risk assessment of 17 perfluoroalkylated and polyfluoroalkylated substances (PFASs) in the Swedish population. *Environ. Int.* 59, 112–123. <https://doi.org/10.1016/j.envint.2013.05.009>
- Brennan, R.F., Gartrell, J.W., Robson, A.D., 1984. Reactions of copper with soil affecting its availability to plants. III effect of incubation temperature. *Aust. J. Soil Res.* 22, 165–172. <https://doi.org/10.1071/SR9840165>

- Brown, R.E., Jindal, B.S., Bulzan, J.D., 1992. Critical review of the effectiveness of stabilization and solidification of hazardous organic wastes. Presented at the ASTM Special Technical Publication, pp. 43–60.
- Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., Voogt, P.D., Jensen, A.A., Kannan, K., Mabury, S.A., van, L., 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integr. Environ. Assess. Manag.* 7, 513–541. <https://doi.org/10.1002/ieam.258>
- Conder, J.M., Hoke, R.A., De Wolf, W., Russell, M.H., Buck, R.C., 2008. Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. *Environ. Sci. Technol.* 42, 995–1003. <https://doi.org/10.1021/es070895g>
- Conner, J.R., Hoeffner, S.L., 1998. A critical review of stabilization/solidification technology. *Crit. Rev. Environ. Sci. Technol.* 28, 397–462. <https://doi.org/10.1080/10643389891254250>
- Cornelissen, G., Van, N., Govers, H.A.J., 1997. Desorption kinetics of chlorobenzenes, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls: Sediment extraction with Tenax® and effects of contact time and solute hydrophobicity. *Environ. Toxicol. Chem.* 16, 1351–1357. [https://doi.org/10.1897/1551-5028\(1997\)016<1351:DKOCPA>2.3.CO;2](https://doi.org/10.1897/1551-5028(1997)016<1351:DKOCPA>2.3.CO;2)
- Cousins, E.M., Richter, L., Cordner, A., Brown, P., Diallo, S., 2019. Risky Business? Manufacturer and Retailer Action to Remove Per- and Polyfluorinated Chemicals From Consumer Products: *NEW Solut. J. Environ. Occup. Health Policy.* <https://doi.org/10.1177/1048291119852674>
- Das, P., Arias, E., Kambala, V., Mallavarapu, M., Naidu, R., 2013. Remediation of perfluorooctane sulfonate in contaminated soils by modified clay adsorbent - A risk-based approach topical collection on remediation of site contamination. *Water. Air. Soil Pollut.* 224. <https://doi.org/10.1007/s11270-013-1714-y>
- Dauchy, X., Boiteux, V., Bach, C., Colin, A., Hemard, J., Rosin, C., Munoz, J.-F., 2017. Mass flows and fate of per- and polyfluoroalkyl substances (PFASs) in the wastewater treatment plant of a fluorochemical manufacturing facility. *Sci. Total Environ.* 576, 549–558. <https://doi.org/10.1016/j.scitotenv.2016.10.130>
- Dermont, G., Bergeron, M., Mercier, G., Richer-Lafleche, M., 2008. Metal-Contaminated Soils: Remediation Practices and Treatment Technologies. *Pract. Period. Hazard. Toxic Radioact. Waste Manag.* 12, 188–209. [https://doi.org/10.1061/\(ASCE\)1090-025X\(2008\)12:3\(188\)](https://doi.org/10.1061/(ASCE)1090-025X(2008)12:3(188))
- Domingo, J.L., 2012. Health risks of dietary exposure to perfluorinated compounds. *Environ. Int.* 40, 187–195. <https://doi.org/10.1016/j.envint.2011.08.001>
- Du, Z., Deng, S., Bei, Y., Huang, Q., Wang, B., Huang, J., Yu, G., 2014. Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents—A review. *J. Hazard. Mater.* 274, 443–454. <https://doi.org/10.1016/j.jhazmat.2014.04.038>
- Eriksson, U., Haglund, P., Kärman, A., 2017. Contribution of precursor compounds to the release of per- and polyfluoroalkyl substances (PFASs) from waste water treatment plants (WWTPs). *J. Environ. Sci., Special Issue on Emerging chemicals of concern* 61, 80–90. <https://doi.org/10.1016/j.jes.2017.05.004>
- Filipovic, M., Woldegiorgis, A., Norström, K., Bibi, M., Lindberg, M., Österås, A.-H., 2015. Historical usage of aqueous film forming foam: A case study of the widespread distribution of perfluoroalkyl acids from a military airport to groundwater, lakes, soils and fish. *Chemosphere* 129, 39–45. <https://doi.org/10.1016/j.chemosphere.2014.09.005>
- Franke, V., Schäfers, M.D., Lindberg, J.J., Ahrens, L., 2019. Removal of per- And polyfluoroalkyl substances (PFASs) from tap water using heterogeneously catalyzed ozonation. *Environ. Sci. Water Res. Technol.* 5, 1887–1896. <https://doi.org/10.1039/c9ew00339h>
- Gebbink, W.A., Glynn, A., Berger, U., 2015. Temporal changes (1997–2012) of perfluoroalkyl acids and selected precursors (including isomers) in Swedish human serum. *Environ. Pollut.* 199, 166–173. <https://doi.org/10.1016/j.envpol.2015.01.024>

- Gellrich, V., Brunn, H., Stahl, T., 2013. Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in mineral water and tap water. *J. Environ. Sci. Health - Part Toxic/Hazardous Subst. Environ. Eng.* 48, 129–135. <https://doi.org/10.1080/10934529.2013.719431>
- Giesy, J.P., Kannan, K., 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environ. Sci. Technol.* 35, 1339–1342. <https://doi.org/10.1021/es001834k>
- Glynn, A., Berger, U., Bignert, A., Ullah, S., Aune, M., Lignell, S., Darnerud, P.O., 2012. Perfluorinated alkyl acids in blood serum from primiparous women in Sweden: Serial sampling during pregnancy and nursing, and temporal trends 1996-2010. *Environ. Sci. Technol.* 46, 9071–9079. <https://doi.org/10.1021/es301168c>
- Glynn, A., Kotova, N., Dahlgren, E., Lindh, C., Jakobsson, K., Gyllenhammar, I., Lignell, S., Nälsén, C., 2020. Determinants of serum concentrations of perfluoroalkyl acids (PFAAs) in school children and the contribution of low-level PFAA-contaminated drinking water. *Environ. Sci. Process. Impacts* 22, 930–944. <https://doi.org/10.1039/c9em00497a>
- Gobelius, L., Hedlund, J., Dürig, W., Tröger, R., Lilja, K., Wiberg, K., Ahrens, L., 2018. Per- and Polyfluoroalkyl Substances in Swedish Groundwater and Surface Water: Implications for Environmental Quality Standards and Drinking Water Guidelines. *Environ. Sci. Technol.* <https://doi.org/10.1021/acs.est.7b05718>
- Gobelius, L., Lewis, J., Ahrens, L., 2017. Plant Uptake of Per- and Polyfluoroalkyl Substances at a Contaminated Fire Training Facility to Evaluate the Phytoremediation Potential of Various Plant Species. *Environ. Sci. Technol.* 51, 12602–12610. <https://doi.org/10.1021/acs.est.7b02926>
- Gyllenhammar, I., irina.gyllenhammar@slv.se, Benskin, J.P., Sandblom, O., Berger, U., Ahrens, L., Lignell, S., Wiberg, K., Glynn, A., 2019. Perfluoroalkyl acids in children's serum and contribution from perfluoroalkyl acid-contaminated drinking water. *Environ. Sci. Technol.* 53. <https://doi.org/10.1021/acs.est.9b01746>
- Hale, S.E., Arp, H.P.H., Slinde, G.A., Wade, E.J., Bjørseth, K., Breedveld, G.D., Straith, B.F., Moe, K.G., Jartun, M., Høisæter, Å., 2017. Sorbent amendment as a remediation strategy to reduce PFAS mobility and leaching in a contaminated sandy soil from a Norwegian firefighting training facility. *Chemosphere* 171, 9–18. <https://doi.org/10.1016/j.chemosphere.2016.12.057>
- Harding-Marjanovic, K.C., Houtz, E.F., Yi, S., Field, J.A., Sedlak, D.L., Alvarez-Cohen, L., 2015. Aerobic Biotransformation of Fluorotelomer Thioether Amido Sulfonate (Lodyne) in AFFF-Amended Microcosms. *Environ. Sci. Technol.* 49, 7666–7674. <https://doi.org/10.1021/acs.est.5b01219>
- Heads of EPAs Australia and New Zealand (HEPA), 2018. PFAS National Environmental Management Plan.
- Higgins, C.P., Luthy, R.G., 2006. Sorption of Perfluorinated Surfactants on Sediments †. *Environ. Sci. Technol.* 40, 7251–7256. <https://doi.org/10.1021/es061000n>
- Hills, C., Gunning, P., Bates, E., 2015. Stabilisation-solidification of contaminated soil and waste. Hygge Media, Greenmount, Bury.
- Høisæter, Å., Pfaff, A., Breedveld, G.D., 2019. Leaching and transport of PFAS from aqueous film-forming foam (AFFF) in the unsaturated soil at a firefighting training facility under cold climatic conditions. *J. Contam. Hydrol.* 222, 112–122. <https://doi.org/10.1016/j.jconhyd.2019.02.010>
- Houtz, E.F., Sedlak, D.L., 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environ. Sci. Technol.* 46, 9342–9349. <https://doi.org/10.1021/es302274g>
- Johansson, N., Fredriksson, A., Eriksson, P., 2008. Neonatal exposure to perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) causes neurobehavioural defects in adult mice. *Neurotoxicology* 29, 160–169. <https://doi.org/10.1016/j.neuro.2007.10.008>
- Khenifi, A., Zohra, B., Kahina, B., Houari, H., Zoubir, D., 2009. Removal of 2,4-DCP from wastewater by CTAB/bentonite using one-step and two-step methods: A comparative study. *Chem. Eng. J.* 146, 345–354. <https://doi.org/10.1016/j.cej.2008.06.028>

- Kissa, E., Kissa, E., 2001. Fluorinated surfactants and repellents, 2nd ed., rev.expanded. ed, Surfactant science series. Marcel Dekker, New York.
- Koch, A., Aro, R., Wang, T., Yeung, L.W.Y., 2020. Towards a comprehensive analytical workflow for the chemical characterisation of organofluorine in consumer products and environmental samples. *TrAC Trends Anal. Chem.* 123, 115423. <https://doi.org/10.1016/j.trac.2019.02.024>
- Koch, A., Kärrman, A., Yeung, L.W.Y., Jonsson, M., Ahrens, L., Wang, T., 2019. Point source characterization of per- and polyfluoroalkyl substances (PFASs) and extractable organofluorine (EOF) in freshwater and aquatic invertebrates. *Environ. Sci. Process. Impacts* 21, 1887–1898. <https://doi.org/10.1039/C9EM00281B>
- Kraaij, R.H., Tolls, J., Sijm, D., Cornelissen, G., Heikens, A., Belfroid, A., 2002. Effects of contact time on the sequestration and bioavailability of different classes of hydrophobic organic chemicals to benthic oligochaetes (tubificidae). *Environ. Toxicol. Chem.* 21, 752–759. [https://doi.org/10.1897/1551-5028\(2002\)021<0752:EOCTOT>2.0.CO;2](https://doi.org/10.1897/1551-5028(2002)021<0752:EOCTOT>2.0.CO;2)
- Kumpiene, J., Lagerkvist, A., Maurice, C., 2008a. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments – A review. *Waste Manag.* 28, 215–225. <https://doi.org/10.1016/j.wasman.2006.12.012>
- Kumpiene, J., Lagerkvist, A., Maurice, C., 2008b. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments – A review. *Waste Manag.* 28, 215–225. <https://doi.org/10.1016/j.wasman.2006.12.012>
- Kupryianchyk, D., Hale, S.E., Breedveld, G.D., Cornelissen, G., 2016. Treatment of sites contaminated with perfluorinated compounds using biochar amendment. *Chemosphere, Biochars multifunctional role as a novel technology in the agricultural, environmental, and industrial sectors* 142, 35–40. <https://doi.org/10.1016/j.chemosphere.2015.04.085>
- Land, M., de Wit, C.A., Bignert, A., Cousins, I.T., Herzke, D., Johansson, J.H., Martin, J.W., 2018. What is the effect of phasing out long-chain per- and polyfluoroalkyl substances on the concentrations of perfluoroalkyl acids and their precursors in the environment? A systematic review. *Environ. Evid.* 7, 4. <https://doi.org/10.1186/s13750-017-0114-y>
- Lemal, D.M., 2004. Perspective on Fluorocarbon Chemistry. *J. Org. Chem.* 69, 1–11. <https://doi.org/10.1021/jo0302556>
- Li, Y., Fletcher, T., Mucs, D., Scott, K., Lindh, C.H., Tallving, P., Jakobsson, K., 2018. Half-lives of PFOS, PFHxS and PFOA after end of exposure to contaminated drinking water. *Occup. Environ. Med.* 75, 46–51. <https://doi.org/10.1136/oemed-2017-104651>
- Li, Yasong, Oliver, D.P., Kookana, R.S., 2018. A critical analysis of published data to discern the role of soil and sediment properties in determining sorption of per and polyfluoroalkyl substances (PFASs). *Sci. Total Environ.* 628–629, 110–120. <https://doi.org/10.1016/j.scitotenv.2018.01.167>
- Lindstrom, A.B., Strynar, M.J., Libelo, E.L., 2011. Polyfluorinated compounds: Past, present, and future. *Environ. Sci. Technol.* 45, 7954–7961. <https://doi.org/10.1021/es2011622>
- Liu, Y., D'Agostino, L.A., Qu, G., Jiang, G., Martin, J.W., 2019. High-resolution mass spectrometry (HRMS) methods for nontarget discovery and characterization of poly- and per-fluoroalkyl substances (PFASs) in environmental and human samples. *TrAC Trends Anal. Chem.* 121, 115420. <https://doi.org/10.1016/j.trac.2019.02.021>
- Loganathan, B.G., Sajwan, K.S., Sinclair, E., Senthil, K., Kannan, K., 2007. Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. *Water Res.* 41, 4611–4620. <https://doi.org/10.1016/j.watres.2007.06.045>
- Lothenbach, B., Furrer, G., Schärli, H., Schulin, R., 1999. Immobilization of zinc and cadmium by montmorillonite compounds: Effects of aging and subsequent acidification. *Environ. Sci. Technol.* 33, 2945–2952. <https://doi.org/10.1021/es981317q>
- Ma, B., Wang, Z., Yuan, X., Cen, K., Li, J., Yang, N., Zhu, X., 2020. In situ stabilization of heavy metals in a tailing pond with a new method for the addition of mineral stabilizers—high-pressure rotary jet technology. *Environ. Sci. Pollut. Res.* 27, 15388–15400. <https://doi.org/10.1007/s11356-020-07782-9>

- Mahinroosta, R., Senevirathna, L., 2020. A review of the emerging treatment technologies for PFAS contaminated soils. *J. Environ. Manage.* 255, 109896. <https://doi.org/10.1016/j.jenvman.2019.109896>
- Martin, D., Munoz, G., Mejia-Avenida, S., Duy, S.V., Yao, Y., Volchek, K., Brown, C.E., Liu, J., Sauvé, S., 2019. Zwitterionic, cationic, and anionic perfluoroalkyl and polyfluoroalkyl substances integrated into total oxidizable precursor assay of contaminated groundwater. *Talanta* 195, 533–542. <https://doi.org/10.1016/j.talanta.2018.11.093>
- Martin, J.W., Mabury, S.A., Solomon, K.R., Muir, D.C.G., 2003. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (*Oncorhynchus mykiss*). *Environ. Toxicol. Chem.* 22, 196–204.
- McCleaf, P., Englund, S., Östlund, A., Lindegren, K., Wiberg, K., Ahrens, L., 2017. Removal efficiency of multiple poly- and perfluoroalkyl substances (PFASs) in drinking water using granular activated carbon (GAC) and anion exchange (AE) column tests. *Water Res.* 120, 77–87. <https://doi.org/10.1016/j.watres.2017.04.057>
- McGregor, R., 2018. In Situ treatment of PFAS-impacted groundwater using colloidal activated Carbon. *Remediation* 28, 33–41. <https://doi.org/10.1002/rem.21558>
- Meegoda, J.N., Ezeldin, A.S., Fang, H.-Y., Inyang, H.I., 2003. Waste immobilization technologies. *Pract. Period. Hazard. Toxic Radioact. Waste Manag.* 7, 46–58. [https://doi.org/10.1061/\(ASCE\)1090-025X\(2003\)7:1\(46\)](https://doi.org/10.1061/(ASCE)1090-025X(2003)7:1(46))
- Merino, N., Qu, Y., Deeb, R.A., Hawley, E.L., Hoffmann, M.R., Mahendra, S., 2016. Degradation and Removal Methods for Perfluoroalkyl and Polyfluoroalkyl Substances in Water. *Environ. Eng. Sci.* 33, 615–649. <https://doi.org/10.1089/ees.2016.0233>
- Miaz, L.T., Plassmann, M.M., Gyllenhammar, I., Bignert, A., Sandblom, O., Lignell, S., Glynn, A., Benskin, J.P., 2020. Temporal trends of suspect- and target-per/polyfluoroalkyl substances (PFAS), extractable organic fluorine (EOF) and total fluorine (TF) in pooled serum from first-time mothers in Uppsala, Sweden, 1996–2017. *Environ. Sci. Process. Impacts* 22, 1071–1083. <https://doi.org/10.1039/C9EM00502A>
- Misaelides, P., 2011. Application of natural zeolites in environmental remediation: A short review. *Microporous Mesoporous Mater.* 144, 15–18. <https://doi.org/10.1016/j.micromeso.2011.03.024>
- Murakami, M., Kuroda, K., Sato, N., Fukushi, T., Takizawa, S., Takada, H., 2009. Groundwater Pollution by Perfluorinated Surfactants in Tokyo. *Environ. Sci. Technol.* 43, 3480–3486. <https://doi.org/10.1021/es803556w>
- Ochoa-Herrera, V., Sierra-Alvarez, R., 2008. Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge. *Chemosphere* 72, 1588–1593. <https://doi.org/10.1016/j.chemosphere.2008.04.029>
- Organisation for Economic Co-operation and Development (OECD), 2018. Toward a new comprehensive global database of per- and polyfluoroalkyl substances (PFASs): summary report on updating the oecd 2007 list of per- and polyfluoroalkyl substances (PFASs), Series on Risk Management. Organisation for Economic Co-operation and Development (OECD), Paris, France.
- Pan, Y., Wang, J., Yeung, L.W.Y., Wei, S., Dai, J., 2020. Analysis of emerging per- and polyfluoroalkyl substances: Progress and current issues. *TrAC - Trends Anal. Chem.* 124. <https://doi.org/10.1016/j.trac.2019.04.013>
- Paria, S., Yuet, P.K., 2006. Solidification-stabilization of organic and inorganic contaminants using portland cement: A literature review. *Environ. Rev.* 14, 217–255. <https://doi.org/10.1139/A06-004>
- Paul, A.G., Jones, K.C., Sweetman, A.J., 2009. A First Global Production, Emission, And Environmental Inventory For Perfluorooctane Sulfonate. *Environ. Sci. Technol.* 43, 386–392. <https://doi.org/10.1021/es802216n>
- Perfluoroalkylated substances in food: occurrence and dietary exposure, 2012. *EFSA J.* 10, 2743. <https://doi.org/10.2903/j.efsa.2012.2743>
- Rakowska, M.I., Kupryianchyk, D., Harmsen, J., Grotenhuis, T., Koelmans, A.A., 2012. In situ remediation of contaminated sediments using carbonaceous materials. *Environ. Toxicol. Chem.* 31, 693–704. <https://doi.org/10.1002/etc.1763>

- Rich, C.D., Blaine, A.C., Hundal, L., Higgins, C.P., 2015. Bioaccumulation of perfluoroalkyl acids by earthworms (*Eisenia fetida*) exposed to contaminated soils. *Environ. Sci. Technol.* 49, 881–888. <https://doi.org/10.1021/es504152d>
- Ritscher, A., Wang, Z., Scheringer, M., Boucher, J.M., Ahrens, L., Berger, U., Bintein, S., Bopp, S.K., Borg, D., Buser, A.M., Cousins, I., DeWitt, J., Fletcher, T., Green, C., Herzke, D., Higgins, C., Huang, J., Hung, H., Knepper, T., Lau, C.S., Leinala, E., Lindstrom, A.B., Liu, J., Miller, M., Ohno, K., Perkola, N., Shi, Y., Småstuen Haug, L., Trier, X., Valsecchi, S., van der Jagt, K., Vierke, L., 2018. Zürich Statement on Future Actions on Per- and Polyfluoroalkyl Substances (PFASs). *Environ. Health Perspect.* 126, 84502. <https://doi.org/10.1289/EHP4158>
- Ross, I., McDonough, J., Miles, J., Storch, P., Thelakkat Kochunarayanan, P., Kalve, E., Hurst, J., S. Dasgupta, S., Burdick, J., 2018. A review of emerging technologies for remediation of PFASs. *Remediat. J.* 28, 101–126. <https://doi.org/10.1002/rem.21553>
- Rostvall, A., Zhang, W., Dürig, W., Renman, G., Wiberg, K., Ahrens, L., Gago-Ferrero, P., 2018. Removal of pharmaceuticals, perfluoroalkyl substances and other micropollutants from wastewater using lignite, Xylit, sand, granular activated carbon (GAC) and GAC+Polonite® in column tests – Role of physicochemical properties. *Water Res.* 137, 97–106. <https://doi.org/10.1016/j.watres.2018.03.008>
- Schultes, L., Vestergren, R., Volkova, K., Westberg, E., Jacobson, T., Benskin, J.P., 2018. Per- and polyfluoroalkyl substances and fluorine mass balance in cosmetic products from the Swedish market: Implications for environmental emissions and human exposure. *Environ. Sci. Process. Impacts* 20, 1680–1690. <https://doi.org/10.1039/c8em00368h>
- Shen, Z., Jin, F., O'Connor, D., Hou, D., 2019. Solidification/Stabilization for Soil Remediation: An Old Technology with New Vitality. *Environ. Sci. Technol.* 53, 11615–11617. <https://doi.org/10.1021/acs.est.9b04990>
- Sörensngård, M., Lindh, A.-S., Ahrens, L., 2020. Thermal desorption as a high removal remediation technique for soils contaminated with per- and polyfluoroalkyl substances (PFASs). *PLOS ONE* 15, e0234476. <https://doi.org/10.1371/journal.pone.0234476>
- Sörensngård, M., Niarchos, G., Jensen, P.E., Ahrens, L., 2019. Electrodialytic per- and polyfluoroalkyl substances (PFASs) removal mechanism for contaminated soil. *Chemosphere* 232, 224–231. <https://doi.org/10.1016/j.chemosphere.2019.05.088>
- Stockholm convention on persistent organic pollutants (POPs), 2018. Stockholm convention on persistent organic pollutants (pops)- texts and annexes - revised in 2017 [WWW Document]. BRSMes. URL <http://chm.pops.int/?tabid=2511> (accessed 7.6.20).
- Sunderland, E.M., Hu, X.C., Dassuncao, C., Tokranov, A.K., Wagner, C.C., Allen, J.G., 2019. A Review of the Pathways of Human Exposure to Poly- and Perfluoroalkyl Substances (PFASs) and Present Understanding of Health Effects. *J. Expo. Sci. Environ. Epidemiol.* 29, 131–147. <https://doi.org/10.1038/s41370-018-0094-1>
- Tabbaa, A.A., Stegemann, J.A., 2005. *Stabilisation/Solidification Treatment and Remediation: Proceedings of the International Conference on Stabilisation/Solidification Treatment and Remediation*, 12-13 April 2005, Cambridge, UK. CRC Press.
- United States Environmental Protection Agency, 1996. *Prohibition on the Disposal of Bulk Liquid Hazardous Waste in Landfills – Statutory Interpretive Guidance*. Washington D.C.
- US Environmental Protection Agency., 2006. PFOA Stewardship Program (No. EPA HQ/OPPT/2006/0621). Washington, DC.
- US EPA, O., 2016. *Drinking Water Health Advisories for PFOA and PFOS* [WWW Document]. USEPA. URL <https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos> (accessed 7.6.20).
- Vecitis, C.D., Park, H., Cheng, J., Mader, B.T., Hoffmann, M.R., 2009. Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA). *Front. Environ. Sci. Eng. China* 3, 129–151. <https://doi.org/10.1007/s11783-009-0022-7>
- Wang, F., Shih, K., Lu, X., Liu, C., 2013. Mineralization Behavior of Fluorine in Perfluorooctanesulfonate (PFOS) during Thermal Treatment of Lime-Conditioned Sludge. *Environ. Sci. Technol.* 47, 2621–2627. <https://doi.org/10.1021/es305352p>

- Wiles, C.C., 1987. A review of solidification/stabilization technology. *J. Hazard. Mater.* 14, 5–21. [https://doi.org/10.1016/0304-3894\(87\)87002-4](https://doi.org/10.1016/0304-3894(87)87002-4)
- Xia, W.-Y., Du, Y.-J., Li, F.-S., Guo, G.-L., Yan, X.-L., Li, C.-P., Arulrajah, A., Wang, F., Wang, S., 2019a. Field evaluation of a new hydroxyapatite based binder for ex-situ solidification/stabilization of a heavy metal contaminated site soil around a Pb-Zn smelter. *Constr. Build. Mater.* 210, 278–288. <https://doi.org/10.1016/j.conbuildmat.2019.03.195>
- Xia, W.-Y., Du, Y.-J., Li, F.-S., Li, C.-P., Yan, X.-L., Arulrajah, A., Wang, F., Song, D.-J., 2019b. In-situ solidification/stabilization of heavy metals contaminated site soil using a dry jet mixing method and new hydroxyapatite based binder. *J. Hazard. Mater.* 369, 353–361. <https://doi.org/10.1016/j.jhazmat.2019.02.031>
- Yamada, T., Taylor, P.H., Buck, R.C., Kaiser, M.A., Giraud, R.J., 2005. Thermal degradation of fluorotelomer treated articles and related materials. *Chemosphere* 61, 974–984. <https://doi.org/10.1016/j.chemosphere.2005.03.025>
- Yeung, L.W.Y., De, S., Loi, E.I.H., Marvin, C.H., Taniyasu, S., Yamashita, N., Mabury, S.A., Muir, D.C.G., Lam, P.K.S., 2013. Perfluoroalkyl substances and extractable organic fluorine in surface sediments and cores from Lake Ontario. *Environ. Int.* 59, 389–397. <https://doi.org/10.1016/j.envint.2013.06.026>
- Yeung, Leo W. Y., Robinson, S.J., Koschorreck, J., Mabury, S.A., 2013. Part I. A Temporal Study of PFCAs and Their Precursors in Human Plasma from Two German Cities 1982–2009. *Environ. Sci. Technol.* 47, 3865–3874. <https://doi.org/10.1021/es303716k>
- Yeung, L.W.Y., Yamashita, N., Falandysz, J., 2019. Legacy and emerging perfluorinated and polyfluorinated compounds: An update. *Chemosphere* 237, 124506. <https://doi.org/10.1016/j.chemosphere.2019.124506>

Popular science summary

It is claimed that per- and polyfluoroalkyl substances (PFASs) are the new polychlorinated biphenyls (PCBs) of this century. Their chemical properties, such as dirt and water repellence, make them very useful in many everyday products, such as textiles for outdoor jackets, paper products like microwave popcorn bags and make-up products. These chemicals can even save lives, as they are used in aqueous firefighting foams (AFFFs). However, while PFASs have ‘useful’ properties for consumer products, these properties also make them extremely persistent, with the potential to accumulate in the environment. They are also potentially toxic. Previous studies have shown that drinking water is an important source of human exposure to PFASs. The presence of PFASs in drinking water is often tracked back to unregulated use of PFAS-containing AFFFs at firefighter training facilities, where PFASs can be released directly into the natural soil. Due to the high mobility of many PFASs, they can contaminate local drinking water source areas and pose a risk of human exposure.

This thesis evaluated innovative techniques to remediate PFAS-contaminated soils, in order to protect drinking water source areas and ecosystems. There are two principal techniques for treating contaminated soil: (i) removing the contaminant or (ii) immobilising the contaminant within the soil to prevent it being transported to the groundwater. This thesis focused on the immobilisation approach, which is often referred to as soil stabilization. A total of 44 materials were screened for their sorption of PFASs. Activated carbons showed the highest sorption capacity for PFASs among the materials tested, due to their high surface area and sorption capacity. Based on these findings, a novel liquid activated carbon, which can be injected *in situ* from the soil surface without intrusive and expensive excavation and mixing, was tested in further studies. The results showed that for some PFASs, leaching was reduced by about 80%. Laboratory-scale evaluation of the cost-efficient stabilization-solidification (S/S) method, which involves mixing cement into the soil to trap contaminants, showed that most PFASs were retained from 93%, or to more than 99.9% when a small portion of activated carbon was added to the cement. Pilot-scale evaluation of S/S treatment using around six tons of PFAS-

contaminated soil subjected to more than six years of artificial rainfall revealed treatment efficiency of more than 97% for the sum of PFASs, indicating that S/S treatment can be an efficient long-term treatment. These novel findings can help researchers, politicians and practitioners make well-informed decisions on use of stabilization treatment for remediation of PFAS-contaminated soils.

Populärvetenskaplig sammanfattning

Det är sagt att PFAS (per- och polyfluorerade alkylämnen) är detta århundrades nya PCBer. Deras kemiska egenskaper, så som smuts- och vattenavstötande, gör att de är väldigt användbara i allehanda vardagsprodukter så som jackor, pappersförpackningar t.ex. popcornförpackningar och smink. PFAS-kemikalierna har även livsavgörande egenskaper då de används i effektiva brandskum vid svåra bränder. Men även om PFAS har mångsidiga nyttoegenskaper för vardagslivet, så har de även egenskaper som är oroande då det har visat sig att de inte bryts ned över lång tid, ackumuleras i människor och miljön, samt att vissa PFAS har hälsofarliga effekter.

Tidigare studier har visat att dricksvatten är en viktig källa för människors dagliga intag av PFASs. Ursprunget av PFAS i dricksvatten har visat sig ofta komma från intilliggande förorenad mark där just PFAS-brandskum obegränsat har använts i stora mängder, så som brandövningsplatser. Stora mängder PFAS har då fastnat i marken som sedan kontinuerligt läcker ner till grundvattnet som i vissa fall används till dricksvatten. För att skydda dricksvattnet från att förorenas måste den kontaminerade marken saneras, och hittills har endast ett fåtal studier utvärderat olika tekniker för att effektivt sanera PFAS-förorenad mark.

Syftet med denna avhandling är att utvärdera saneringstekniker för att sanera PFAS-förorenad mark för att skydda dricksvattentäkter och därmed exponering för människor. Sanering av mark sker ofta genom två huvudprinciper: (1) ta bort från föroreningen eller (2) att immobilisera föroreningarna i marken och därmed skydda mot utlakning till dricksvattnet. Den här avhandlingen handlar om immobiliseringstekniken, vilken också kallas för stabilisering.

Den första studien ämnade hitta material som adsorberar och fastlägger PFAS. 44 olika material testades, och en grupp material, nämligen aktiverat kol, visade sig konsekvent ha extra bra sorptionsförmåga. Att aktivt kol fungerar bra för att stabilisera föroreningar är tidigare känt då materialet har hög ytareal där de kan fastna.

Baserad på dessa resultat gjordes en vidare studie på ett kolloidalt rinnande aktivt kol som kan högtrycksinjiceras från marknivå utan omblandning. Resultatet visade sig minska utlakningen av vissa PFAS med upp till 80 % för vissa PFAS.

I en tredje studie testades en teknik som heter stabilisering och solidifiering. Det är en välbeprövad och kostnadseffektiv teknik för många andra föroreningar, och baseras på att blanda cement ner i marker. Marken blir då hårt och impermeabel, vilket går att regnvatten inte kan rinna igenom den kontaminerade men förhårdnade marken och därmed transporteras inte heller föroreningarna vidare till vattentäkten. Resultaten visade att denna teknik minskade utlakningen med 99.9% om också en liten del aktiverad kol användes med cement.

Då stabilisering och solidifiering studien visade på mycket lovande resultat utfördes et pilotskaleexperiment där över sex ton jord behandlades med cement och aktivt kol. För att se hur utlakningen av PFAS skedde över en längre tid, bevattnades den behandlade jorden med motsvarande sex årsnederbörder. Resultaten visade att PFAS minskade med mer än 97 %, vilket är en god effektivitet över en sådan lång tid.

Med ny kunskap från denna forskning kan politiker och problemägare göra bestämma om en stabiliseringsmetod av PFAS-förorenad mark är en lämplig metod att använda i framtiden.

Acknowledgements

This work was supported by the project PFAS-PURE from VINNOVA (2015-03561).

ACTA UNIVERSITATIS AGRICULTURAE SUECIAE

DOCTORAL THESIS NO. 2020:39

Per- and polyfluoroalkyl substances (PFASs) are used in many products and an important pollution pathway to the environment comes from historical use of PFAS-containing aqueous foams used at firefighting training sites. Because of continuous leakage, PFAS-contaminated soils is a major concern for drinking water sources and the aquatic environment. This thesis addresses possible stabilization remediation technologies to prevent PFASs in soil to spread and thereby protect the environment.

Mattias Sörengård received his graduate education at the Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences (SLU), Uppsala. He received his M.Sc. degree in Aquatic and Environmental Engineering from Uppsala University.

Acta Universitatis Agriculturae Sueciae presents doctoral theses from the Swedish University of Agricultural Sciences (SLU).

SLU generates knowledge for the sustainable use of biological natural resources. Research, education, extension, as well as environmental monitoring and assessment are used to achieve this goal.

Online publication of thesis summary: <http://pub.epsilon.slu.se/>

ISSN 1652-6880

ISBN (print version) 978-91-7760-596-6

ISBN (electronic version) 978-91-7760-597-3