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Effect of organic carbon, active carbon,
calcium ions and aging on the sorption of
per- and polyfluoroalkylated substances
(PFASs) to soil.

Erika Schedin

Abstract

Effect of organic carbon, active carbon, calcium ions and aging on the sorption of per- and polyfluoroalkylated substances (PFASs) to soil.

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Per- and polyfluoroalkylated substances (PFASs) are a large group of organic chemicals that have gained an increased attention during recent years. Many of the compounds have shown to be persistent, toxic and bioaccumulating and they are found in water, soils, sediments, biota, animals and humans across the globe. The effects of PFASs to humans and animals are still being debated. It is suspected that the compounds can be carcinogenic, disrupt different hormone systems and have other severe effects.

The main transport pathways of PFASs to soil are applied PFAS based firefighting foam, soil improvers and waste from industries producing PFASs or PFAS based products. Once the PFASs find their way to the soil the risk for leaching to drinking water supplies and aquatic ecosystems becomes some of the issues of great concern. In order to be able to evaluate the potential leakage of PFASs from different contaminated soils it is important to know how the PFASs interact with the soil matrix and what parameters that affects these interactions.

The objective of this study was to investigate the influence of organic carbon (OC), Ca²⁺ ions and active carbon (AC) on the sorption of PFCAs and PFASs to soil. The PFCAs examined were PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFOcDA, PFHxDA and PFOcDA and the PFASs examined were PFBS, PFHxS, PFOS and PFDS. Batch experiments were performed on soils with varying concentrations of TOC, Ca²⁺ and AC. The samples were spiked with PFAS native standard solution containing the 12 target PFASs. All studied parameters showed a positive influence on the sorption of PFASs to soil. The AC was found to have the highest influence on the sorption. The OC was however found to be the most important soil parameter influencing the sorption of PFASs to soil. In order to investigate the influence of aging on the sorption of PFASs, batch experiments were also conducted on soils from four different PFAS contaminated sites. The results showed that the aging positively influenced the strength of the interactions between PFASs and soil.

The organic carbon normalized distribution coefficients (K_{oc}) showed a positive correlation with the carbon chain length of the PFAS molecules and also with the substitution of a carboxylic group with a sulfonic group. The log K_{oc} values calculated in this study decreased in the following order PFDS (log K_{oc} 3.8±0.3) > PFOS > (log K_{oc} 2.8±0.3) > PFUnDA (log K_{oc} 3.2±0.2) > PFDA (log K_{oc} 2.7±0.1) > PFNA (log K_{oc} 2.0±0.1) > PFHxS (log K_{oc} 1.9±0.1) > PFOA (log K_{oc} 1.8±0.3) > PFHxA (log K_{oc} 1.6 ±0.3) > PFBS (log K_{oc} 1.5±0.2). The log K_{oc} values found in this study were within the range of previously reported log K_{oc} values.

Keywords: PFAS, sorption, soil, calcium, active carbon, organic carbon, aging.

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Referat

Effekt av organiskt kol, aktivt kol, kalcium joner och åldring på sorptionen av per- och polyfluoroalkylerade substanser (PFASer) till mark.

Erika Schedin

Per- och polyfluoroalkylerade ämnen (PFASer) är en bred grupp av organiska föreningar som har uppmärksamats under senare år. Många av ämnena har visat sig vara persistenta, toxiska och bioackumulerande och de återfinns i vatten, jordar, sediment, biota, djur och människor över hela jorden. Effekterna av PFASer på människor debatteras fortfarande. Ämnena misstänks vara carcinogena, hormonstörande och ha andra allvarliga effekter.

De främsta transportvägarna för PFASer till mark är PFAS baserade brandsläckningskum, jordförbättringsmedel och avfall från industrier som producerar PFASer eller PFAS baserade produkter. När PFASerna väl har hittat sin väg till marken blir spridning till dricksvatten täkter och akvatiska system några av riskerna att beakta. För att kunna utvärdera det potentiella läckaget av PFASer från olika förorenade jordar är det viktigt att veta hur PFASerna interagerar med jordmatrisen och vilka parametrar som påverkar dessa interaktioner.

Syftet med studien var att undersöka påverkan av totalt organiskt kol (TOC), Ca^{2+} joner och aktivt kol (AC) på sorptionen av PFCAer och PFSAer till jord. De studerade PFCAerna var PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFOcDA, PFHxDA och PFOcDA. De PFSAer som ingick i studien var PFBS, PFHxS, PFOS och PFDS. Skakexperiment utfördes på jordar med varierande koncentrationer av TOC, Ca^{2+} och AC. Proven spikades med PFAS standardlösning som innehöll de 12 studerade PFASerna. Alla undersökta parametrar uppvisade en positiv inverkan på sorptionen av PFASerna till jord. AC uppvisade den högsta påverkan på sorptionen, dock konstaterades TOC generellt vara den viktigaste jordparametern för sorption av PFASer till jord. För att undersöka inverkan av åldring på PFASer utfördes även skakexperiment på fyra olika jordar från PFAS förorenade områden. Åldring visade sig ha en positiv effekt på interaktionsstyrkan mellan PFASer och jord.

Fördelningskoefficienter normaliserade för organiskt kol (K_{oc}) uppvisade en positiv korrelation med kolkedjelängd hos PFAS molekylerna. Även utbytet av en karboxylgrupp mot en sulfonatgrupp visade sig ha en positiv inverkan på K_{oc} värdet. Log K_{oc} värdena minskade i följande ordning PFDS ($\log K_{oc} 3.8 \pm 0.3$) > PFOS > ($\log K_{oc} 2.8 \pm 0.3$) > PFUnDA ($\log K_{oc} 3.2 \pm 0.2$) > PFDA ($\log K_{oc} 2.7 \pm 0.1$) > PFNA ($\log K_{oc} 2.0 \pm 0.1$) > PFHxS ($\log K_{oc} 1.9 \pm 0.1$) > PFOA ($\log K_{oc} 1.8 \pm 0.3$) > PFHxA ($\log K_{oc} 1.6 \pm 0.3$) > PFBS ($\log K_{oc} 1.5 \pm 0.2$). Log K_{oc} värden beräknade för PFASerna i denna studie låg inom samma spann som tidigare rapporterade log K_{oc} värden.

Nyckelord: PFAS, sorption, jord, kalcium, aktivt kol, organiskt kol, åldring.

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Populärvetenskaplig sammanfattning

Effekt av organiskt kol, aktivt kol, kalciumjoner samt åldring på bindningen av per- och polyfluoroalkylerade substanser (PFASer) till jord.

Erika Schedin

Per- och polyfluoroalkylerade ämnen (PFASer) är en bred grupp av organiska föreningar som har blivit uppmärksammade under senare år. Många av ämnena har visat sig vara persistenta, toxiska och bioackumulerande, det vill säga de bryts ned mycket långsamt samt är giftiga och har potential att ansamlas i levande organismer och växter. Oro uppstod då PFASer upptäcktes i mänskligt serum år 2001. Sedan dess har forskningsinsatserna kring PFASer ökat. Effekterna av PFASer på människor debatteras fortfarande. Ämnena misstänks vara cancerframkallande, hormonstörande och ge andra allvarliga effekter.

På grund av PFASernas unika ytaktiva egenskaper har de använts över hela världen i brandsläckningsskum, matförpackningar, ytbeläggningar och beläggningstillsatser, hydrauliska vätskor i flygindustrin med fler. Det finns idag regulationer mot vissa PFASer. PFOS, en av de mest kända PFASerna, lades år 2009 till Stockholmskonventionens lista över persistenta organiska föroreningar (POPs). Detta innebär att det från och med år 2009 finns regler som begränsar produktion och användande av PFOS i de 179 länder som lyder under konventionen.

Den här studien har fokuserat på att undersöka PFASers beteende i mark. Få studier har genomförts med fokus på detta ämne. Det finns därmed ett behov att skaffa fram data som kan täcka vissa av de kunskapsluckor som idag existerar kring PFASers beteende i miljön. PFASer tillförs främst jord genom applicerat brandsläckningsskum, jordförbättringsmedel och avfall från industrier som producerar PFASer eller PFAS baserade produkter. När PFASerna väl har hittat sin väg till jorden blir spridning till dricksvattentäkter, vattendrag, sjöar och hav några av de stora problemen som måste beaktas. För att kunna utvärdera det potentiella läckaget av PFASer från olika förorenade jordar är det viktigt att veta hur PFASerna interagerar med jorden och vilka parametrar som påverkar dessa interaktioner. Olika jordar är olika bra på att binda organiska föreningar. Bindningsförmågan påverkas av olika parametrar i jorden såsom organiskt kol-innehåll, ytladdning hos jordpartiklarna, innehåll av olika positiva och negativa joner med mera. Den påverkas även av egenskaperna hos de organiska föreningarna. De interaktioner som studerades i den här studien kallas sorption och är en typ av bindningar som sker mellan organiska eller oorganiska föreningar och jordpartiklar samt organiskt material.

Syftet med den här studien var att undersöka hur innehåll av organiskt kol, aktivt kol och kalciumjoner påverkar bindningsförmågan av PFASer till jorden. Aktivt kol är ett konstgjort kol som påminner om det svarta kol som kan återfinnas i jordar. Det svarta kolet tillkommer främst jordar genom bränder eller via förbränningsrester som transporteras till jorden via luften. De 12 PFASer som undersöktes tillhörde två undergrupper inom PFAS-familjen, PFCAer och PFSAer. Den stora skillnaden mellan PFCAer och PFSAer är att PFCAer innehåller en karboxylgrupp (COOH) medan PFSAerna innehåller en sulfonatgrupp (SO₃). De

PFCAer som undersöktes var PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFOcDA, PFHxDA och PFOcDA. De PFSAer som undersöktes var PFBS, PFHxS, PFOS och PFDS.

Jordens bindningsförmåga undersöktes genom skaktest för jordprover i vatten vilka tillsatts PFASer till en koncentration av 100 ng/L. Proverna tillfördes olika koncentrationer av organiskt kol, aktivt kol och kalciumjoner. Efter 48 timmars skakning analyserades koncentrationerna av PFASer i jorden samt i vattnet. Resultaten visade att alla undersökta parametrar hade en positiv inverkan på bindningen av PFASerna. Aktivt kol visade sig ha den största effekten på bindningsförmågan. Det organiska kolet konstaterades dock vara den viktigaste parametern i jorden som påverkade bindningsförmågan. Detta då koncentrationen av organiskt kol oftast är betydligt högre än koncentrationen av svart kol (jämförbart med aktivt kol). Ökad kolkedjelängd hos PFASerna samt utbyte av karboxylgruppen mot en sulfonatgrupp visade sig även ge en starkare bindning. Dessa resultat stämde väl överens med tidigare rapporterade resultat.

För att undersöka inverkan av åldring på PFASer utfördes även skakexperiment på fyra olika jordar från PFAS förorenade områden. Åldring är en process som kan ske då organiska föreningar får interagera med jorden under en längre tid. Föreningarna kan då krypa in i porer och sprickor och därmed bilda starka bindningar till jordpartiklarna. Resultaten från experimenten visade att åldring hade en positiv effekt på styrkan hos bindningarna mellan PFASer och jord. Åldring kan därigenom utgöra en potentiell källa till långsiktig förorening av mark samt bidra till en minskad biotillgänglighet av PFASs till växter och annan biota.

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1 Introduction

1.1 Per- and polyfluoroalkylated substances (PFASs)

Per- and polyfluoroalkylated substances (PFASs) are a group of substances that have earned an increasing public attention in recent years due to their environmental persistence, bioaccumulation properties, toxicity and global distribution (Scheutze et al., 2010; Giesy and Kannan 2002; Conder et al., 2007). Although PFASs do not occur naturally in the environment, they are found in biota, animals, soils, sediments, water and air across the globe (Ahrens et al., 2011; Butt et al., 2010; Giesy and Kannan, 2002). Several studies have also documented the occurrence of different PFASs in human serum from populations all over the world (Eriksen et al., 2013; Midasch et al., 2012; Giesy and Kannan, 2002).

The PFASs consist of a hydrophobic carbon chain of different length and a hydrophilic group consisting of, for example, sulfonic or carboxylic acid (Labadie and Chevreuil, 2011; Scheutze et al., 2010). As a result, PFASs repel dust, water, fat and oil. The substances have also been found to have good chemical, thermal, biological and UV stability (Zhao et al; 2012; Yu et al., 2009; Yamashita et al., 2005). Due to these properties PFASs have been used widely in both industrial processes and products such as firefighting foam, food packaging, floor polishing, denture cleansers, shampoos, coating and coating additives, hydraulic fluids in the aviation industry and many other products for more than fifty years (Giesy and Kannan, 2001; Martin et al., 2004; Paul et al., 2009; Kannan et al., 2001).

There are several different PFAS groups within the PFAS family. This study has focused on the two groups perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) and their behavior in soil. These groups have been shown to be very persistent and their longer chained compounds ($> C_6$ for PFSAs and $> C_8$ for PFCAs) have shown to bioaccumulate and biomagnify in food webs (Buck et al., 2011; Butt et al., 2010). Perfluorooctane sulfonic acid (PFOS), member of the PFSAs, and perfluorooctanoic acid (PFOA), member of the PFCAs, are the most frequently detected PFASs in environmental samples across the globe, even in samples from more remote areas such as the Antarctic, the Arctic and the open Oceans (Butt et al., 2010; Giesy and Kannan, 2001; Kannan et al., 2001; Martin et al., 2004).

1.2 Production and release

Manufacturing and usage of PFAS-based products, discharges from wastewater treatment plants and application of firefighting foam are the dominating pathways for the direct release of PFCAs and PFSAs to the environment (Labadie and Chevreuil, 2011; Kwadik, 2010; Butt et al., 2010). The indirect release of PFCAs and PFSAs are dominated by the abiotic and biotic degradation of precursors that can form PFCAs and PFSAs (Buck et al., 2011; Labadie and Chevreuil, 2011; Yu et al., 2009). Many of these precursors are volatile and contribute to the spreading of the stable non-volatile PFAS to distant regions far from pollution sources (Buck et al., 2011; Pan and You 2010; Butt et al. 2010).

The 3M Company was the largest global producer of PFOS until they started the phase out of PFOS and PFOS-related products in 2000. The phase-out of PFOS was completed in 2002

(3M 2012, de Solla et al., 2012; ATSDR 2009). The production was instead shifted towards shorter chain PFASs which has proven to have shorter half-life in the human body (Butt et al., 2010; Ochoa-Herrera 2008). PFOS are, however, still produced in unknown quantities in China (Buck et al., 2011; Oliaei et al., 2012) and other South Asian countries (Butt et al., 2010; Karrman et al., 2011; Paul et al., 2008). Other PFASs, often with limited toxicity data, are increasingly being used as a replacement for PFOS (Oliaei et al., 2012).

1.3 Regulations

In 2009 PFOS and PFOS-related compounds were added to the Annex B list of the Stockholm convention of persistent organic pollutants (POPs). As a result of this the production and use of these compounds are now restricted within the 179 countries which fall under the convention (Vierke et al., 2012; European Union, 2010). Restrictions towards production and use of different PFCAs and PFSAAs have also been introduced by national and international regulatory agencies, such as the US Environmental Protection Agency (USEPA) and Environment Canada. In addition, PFOS has been added both to the OSPAR Commission's list of chemicals for priority action and to the list of 'new contaminants' being monitored by the Arctic Monitoring and Assessment Program (Butt et al., 2010).

In 2009 restrictions towards the use of PFOS were implemented in the REACH directive (EG) nr 1907/2006. Sweden is subordinate the REACH regulation. Thereby the regulations are directly applicable and do not need to be implemented in Swedish law in order to apply. According to REACH PFOS and PFOS-precursors are not allowed to be used in products or to be released to the market. However, there are some exceptions for applications within the photolithographic industry and the photoindustry, some types of chrome plating and hydraulic fluids within the aviation industry (Swedish Chemicals Agency, 2009).

1.4 Exposure and toxicity

POPs and other hydrophobic contaminants usually accumulate in lipid-rich tissues in biota. PFASs, on the other hand, are proteinophilic and are found in protein-rich tissues such as liver, blood and kidney (de Solla et al., 2012; Labadie and Chevreuil, 2011; Butt et al., 2010). PFOS was discovered in wildlife and human blood plasma in 2001 (Hansen et al., 2001; Buck et al., 2011). Since then more studies have confirmed the frequent occurrence of different PFASs in blood plasma from populations all over the world (Eriksen et al., 2013; Midasch et al. 2012; Halldorson et al., 2012; Maisonet et al., 2012; Hansen et al., 2001).

PFASs have been shown to bioaccumulate and biomagnify in the food chains. For example, the PFAS concentrations detected in polar bears, whales and other top-predators have shown to be higher than the levels of individuals further down in the food chain (Sonne, 2010; Giesy and Kannan, 2001; Butt et al., 2007). Studies have also shown correlations between increased PFAS concentrations in water living organisms and distance to point sources of PFASs (de Solla, 2012). Data from animal studies indicate that PFOA and PFOS can have toxic effects on the liver, the endocrine system and the immune system. The studies have also shown that the contaminants can cause neonatal death and different tumors (Halldorson et al., 2012; Stahl et al. 2011; Steenland et al., 2010).

Food and beverages, either primarily contaminated or secondarily contaminated through food packages, are the main exposure pathways for PFASs to humans (Skutlarek et al., 2006; Felizeter et al., 2012). Dust and air have also been suggested to form important exposure pathways (Felizeter et al., 2012; Stahl et al., 2011; Haug et al., 2011). Different PFASs have been detected in human sera, breast milk of pregnant women and in newborns, indicating both placental transfer from mother to fetus and postnatal transfer through breast milk (Maisonet et al., 2012; Halldorsson et al., 2012; Stahl et al., 2011).

The effects from PFAS on humans have not yet been clearly established. Lower birth weights have been reported for newborns to mothers with high PFOS concentrations in the blood serum. Similar patterns have been shown for PFOA and perfluorohexane sulfonic acid (PFHxS) (Maisonet et al., 2012). Also, a positive correlation have been shown between PFOA concentrations in blood serum of pregnant women and body mass index (BMI), waist circumference and serum insulin and leptin levels of their female offspring's at 20 years of age (Halldorson et al., 2012).

1.5 PFASs in soil

As seen in Figure 1 PFAS-based firefighting foam is one of the main sources for release of PFASs to soil (Moody et al., 2002; Karrman et al., 2011). Other important sources are sludge and biosolids from waste water treatment plants applied on fields (Felizeter et al., 2012; Sepulvado et al., 2011) and industrial sites where PFAS based products have been or are produced (Oliaei, 2013) . Precipitation has also been found to form a transport pathway for PFASs to soil (Kwok et al., 2010) as well as landfills that contains products such as PFAS-impregnated carpets, papers and textiles (Oliaei et al., 2012).

Once the PFASs have been released to the soil they can sorb to the soil particles, leach to the groundwater or bioaccumulate in worms (Joung et al., 2010), plants and other biota (Felizeter et al., 2012). The PFASs released to the groundwater can be transported to drinking water supplies, lakes, rivers, seas and other recipients. Drinking water is, as mentioned above, one of the main exposure pathways for PFASs to humans (Felizeter et al., 2012; Stahl et al., 2011; Skutlarek et al., 2006) and leaching of PFASs from soil to drinking water supplies is therefore of major concern (Skutlarek et al., 2006). Another concern is the damage that the PFASs can have on aquatic ecosystems once they reach lakes, rivers, seas and other surface waters.

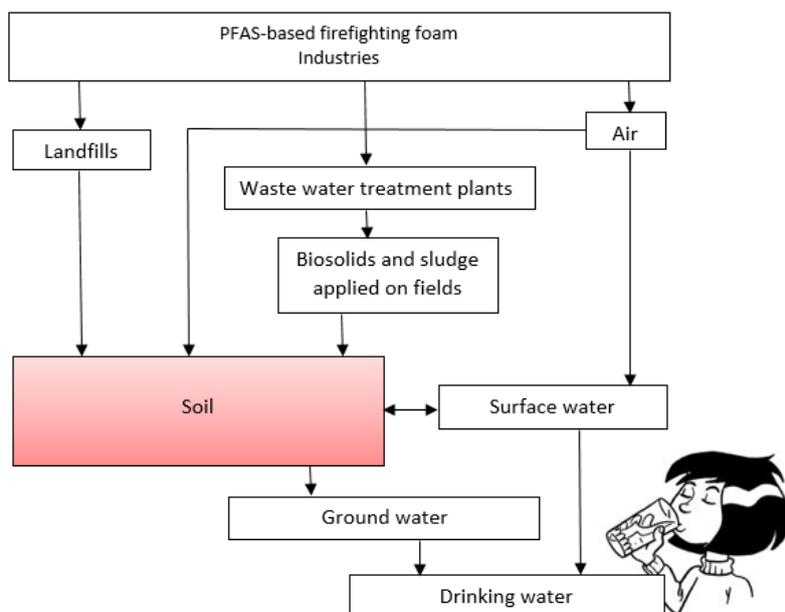


Figure 1. Conceptual model over main PFAS-transport pathways to and from soil.

1.6 Objectives and hypotheses

In order to prevent risk of exposure of PFASs to humans, animals, fish and other organisms it is important to understand the sorption processes taking place between the PFASs and the soil particles. This knowledge is also of great importance in order to understand and predict the leaching potential, distribution and release of PFASs into the environment.

The objective of this study was to examine the partitioning of PFASs between soil and water and parameters which can have an influence on this process. Only a handful studies have so far investigated the sorption of PFASs to soil (Tang et al., 2010). There is thereby a lack of knowledge on PFASs behavior in soil. The aim of the study was to produce data that can contribute to increased understanding of PFAS behavior in soil and thereby also in the environment. The study has focused on the PFCAs and PFSAAs.

A literature study was conducted in order to gain a better understanding of PFAS properties. The aim of the study was also to investigate the outcome of previous studies on PFASs in order to form the experiment design and method. Based on previous results hypotheses were set as follows:

The sorption of PFASs will increase with:

- Increased content of organic carbon.
- Increased concentration of calcium ions.
- Increased concentration of active carbon.
- Increased chain length.

Further, aging was expected to positively influence the strength of the interactions between PFASs and soil.

2 Literature study

The experiment method and design were formed based on information presented in the sections 2.2 *PFAS Properties* and 2.3 *Previous studies*. The information in these two sections were gathered in order to gain a better understanding of PFASs and their behaviors and to form hypotheses about the outcome of the experiments in the study. The solid-water distribution coefficient, K_d , and the organic carbon normalized distribution coefficient, K_{oc} , were used throughout the study in order to describe the sorption of PFASs to soil. These coefficients, calculated from PFAS-concentrations detected in soil and water in the different experiments, are described in the section 2.1 *Partitioning*.

2.1 Partitioning

The partitioning of a compound between different phases is an important process to understand when trying to predict the behavior of a compound in the environment. This thesis focuses on the partitioning of PFAS between soil and water and how it is affected by different external parameters. This information is very important when, for example, planning sampling and remediation strategies and also for modeling transport and distribution of PFASs.

The partitioning of organic compounds between two different phases can be considered as chemical reactions where bonds are broken or formed. However, in the partitioning process the bonds are formed of intermolecular attraction energies which are much weaker than the covalent bonds involved in a chemical reaction. When bonds are formed in such a way that a compound is found *within* a specific phase it is called *absorption*. If the bonds are instead formed between a compound and the *interface* of a specific phase it is called *adsorption* (Schwarzenbach et al., 2003). In this thesis the common term *sorption* is used when both sorption processes are involved. The process when bonds are broken and a compound moves between different phases is called *desorption* (Schwarzenbach et al., 2003).

The potential intermolecular attractions involved in the partitioning process are Van der Waals interactions and electron donor-acceptor interactions, also known as hydrogen donor-acceptor interactions. Example of Van Der Waals interactions are hydrophobic interactions and interactions between permanent dipoles and induced dipoles. The permanent dipoles have permanent sites where the electric charge is more negative. The negative sites of a dipole will attract the positive sites of another dipole or induced dipole. The induced dipoles are a result of time varying, uneven electron distributions within a molecule which induces parts of molecules to become more or less negatively charged (Schwarzenbach et al., 2003).

The electron donor-acceptor interactions occur between permanently electron-poor parts (e.g. the hydrogen attached to an oxygen atom) and permanently more electron-rich parts (e.g. the non-bonded electrons of for example oxygen or nitrogen atoms). An electron-rich moiety of a molecule will then act as an electron donor (also referred to as hydrogen acceptor) while an electron-poor moiety of another molecule will act as an electron acceptor (also referred to as hydrogen donor) (Schwarzenbach et al., 2003).

The partitioning of a compound between different phases is controlled by the total free energy (or Gibbs free energy (G)), which depends on many different parameters such as temperature, pressure, chemical composition of the system and chemical potential of the compounds involved in the partitioning process. Equilibrium has been reached when the occurrence of the compounds is balanced between the different phases and as long as the external factors such as temperature and pressure remain unchanged (Schwarzenbach et al., 2003).

The equilibrium case can be described with the *equilibrium partitioning constant*, K_{i12} , which is defined as shown in equation 1

$$K_{i12} = \frac{c_{i\text{phase } 1}}{c_{i\text{phase } 2}} \quad (1)$$

where $c_{i\text{phase } 1}$ represents the concentration of compound i in phase 1 and $c_{i\text{phase } 2}$ represents the concentration of compound i in phase 2. Partitioning constants are often reported at 25 °C and atmospheric pressure (101 325 Pa). The constants can be extrapolated in order to cover other temperatures. For most cases in environmental organic chemistry environmentally realistic changes in pressure does not have a big influence on the partitioning constant, why the extrapolation is focused on change in temperature and not in pressure (Schwarzenbach et al., 2003).

In this thesis, the solid-water distribution coefficient, K_{id} , or just K_d , is investigated which is calculated as shown in equation 2

$$K_{id} = \frac{c_{is}}{c_{iw}} \quad (2)$$

where c_{is} is the concentration of compound i in solid phase (mol kg⁻¹) and c_{iw} is the concentration of compound i in water phase (mol L⁻¹) (Schwarzenbach et al., 2003). A higher K_{id} value means that a greater part of the compounds will sorb to the solid phase and vice versa.

Since the content of organic carbon has proven to have a significant influence on the sorption of many organic chemicals an organic carbon normalized solid-water distribution coefficient, K_{oc} , has been developed. This coefficient is frequently used to describe the sorption of a compound to the organic carbon in the solid phase (Schwarzenbach et al., 2003). Different solid phases differ a lot between different sites. Therefore it is not possible to calculate a K_{id} value that would represent all different types of solid phases. The organic carbon content of the solid phase is quite easy to determine, why the K_{oc} value is very useful for making an approximation of the expected partitioning behavior. The K_{oc} value is calculated from the K_{id} value as described in equation 3

$$K_{oc} = \frac{K_{id}}{f_{oc}} = \frac{c_{ioc}}{c_{iw}} \quad (3)$$

where K_{id} is the solid-water distribution coefficient, f_{oc} is the fraction organic carbon, calculated as described in equation 4, c_{ioc} is the concentration of compound i sorbed to the

organic carbon (mol kg^{-1}) and c_{iw} is the concentration of compound i in water phase (mol L^{-1}).

$$f_{oc} = \frac{m_{oc}}{m_{sorbant}} \quad (4)$$

where m_{oc} is the mass of organic carbon (kg) and $m_{sorbant}$ is the total mass of sorbent (kg) (Schwarzenbach et al., 2003).

2.2 PFAS properties

2.2.1 Structure

PFAS consist of *per*- and *poly*fluoroalkyl substances. The carbon chains of the perfluoroalkyl substances are fully fluorinated, and can be linear or branched. The chemical formulas for the perfluoroalkyl substances are written on the form $\text{C}_n\text{F}_{2n+1}\text{-R}$, where n is the number of carbon atoms and R is the functional group consisting of, for example, a carboxylic acid (COOH) or a sulfonic acid (SO_3H). The polyfluoroalkyl substances have the same structure but contain at least one hydrogen atom in the tail. However, at least one fluorine atom must be attached to each carbon in the tail for the compound to be classified as a polyfluorinated compound. Under the right conditions the polyfluoroalkyl substances have the potential to be abiotically or biotically transformed to perfluoroalkyl substances. The *per*- and *poly*fluoroalkyl substances are non polymeric. There are also some polymeric compounds in the PFAS family, which are formed of many monomers attached to each other. However, in this study all examined PFASs were non polymeric.

The covalent bonds between the carbon and fluorine atoms are very strong. The fluorine atoms shield the carbon chain from being degraded by other substances or microorganisms. For example, the PFCAs and PFSA resist degradation through heat, photooxidation, biological activities, photolysis and hydrolysis. The degradation processes in the environment is generally not strong enough to break the fluor-carbon bond (Zhao et al., 2012; Stahl et al., 2011; Butt et al., 2010; Yu et al., 2009).

2.2.2 PFAS families

There are several different subfamilies within the PFAS family, containing different substances with different properties (Buck et al., 2011). In this section the largest families of significance for this study are accounted for.

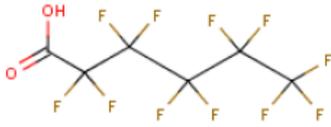
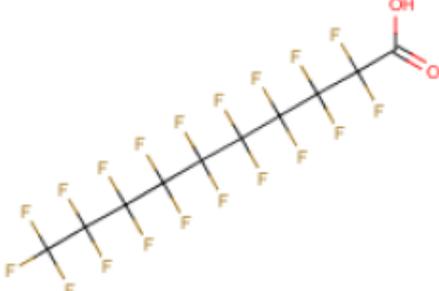
The PFCAs and PFASs are members of the perfluoroalkyl acids, PFAAs. PFASs from this subfamily occupy a substantial part of the literature on PFASs, due to their highly persistent properties, their global use in industrial and consumer applications and their widespread emissions to the environment. The compounds are released both through direct sources and through biotic and abiotic degradation of precursors in the environment. The PFAAs family consists of the carboxylic, sulfonic, sulfinic, phosphonic and phosphinic acids. The different PFAAs have very different physiochemical properties. For example, the perfluorooctanoate anion has high water solubility and a negligible vapor pressure whereas the perfluorooctanoic acid has low water solubility and vapor pressure high enough to partition from water to air.

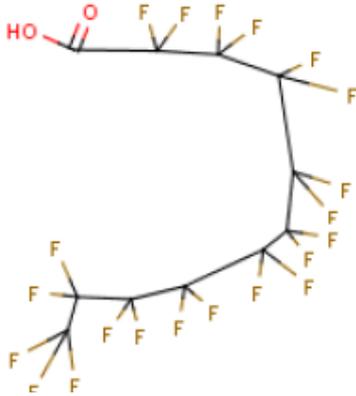
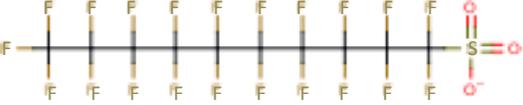
The PFCAs and PFSA are the two largest PFAA families of significance. The PFSA contain a sulfonic group and are written on the form $C_nF_{2n+1}SO_3H$ while the PFCAs contain a carboxylic acid and are written on the form $C_nF_{2n+1}COOH$. The most known member of PFSA is PFOS and the most known member of the PFCAs is PFOA (Buck et al., 2011; Butt et al., 2010).

Another PFAS family that has gained attention during recent years are the fluorotelomer based products. Many of the PFASs from this group can degrade to PFCAs (Buck et al., 2011, Butt et al., 2010; Prevedouros et al., 2006). Members from this group are, for example, the fluorotelomer alcohols (FTOHs), written on the form $C_nF_{2n+1}CH_2CH_2OH$ and the fluorotelomer sulfonic acids (FTSAs), written on the form $C_nF_{2n+1}CH_2CH_2SO_3H$ (Buck et al., 2011).

Important precursors of PFSA are found within the group perfluoroalkane sulfonyl fluorides (PASFs) written on the form $C_nF_{2n+1}SO_2F$. The PASFs are used as starting chemicals for, for example, PFSA, *N*-ethyl and *N*-methyl perfluoroalkane sulfonamides (EtFASAs and MeFASAs) and *N*-ethyl and *N*-methyl perfluoroalkane sulfonamido ethanols (EtFASEs and MeFASEs). All four of the latter named groups can be degraded to PFSA. The fluorotelomer based products belongs to the polyfluoroalkyl substances while the PFAAs belongs to the perfluoroalkyl substances (Buck et al., 2011, Prevedouros et al., 2006). This study focused on the 12 different PFASs within the PFCA and PFSA groups listed in Table 1.

Table 1. List over PFCAs and PFSA examined in this study (Bioforsk, Norwegian Institute for Agricultural and Environmental Research, 2012).

Compound	Acronym	Chemical formula	Molecular formula
PFCAs			
Perfluorohexanoic acid	PFHxA	$C_5F_{11}COOH$	
Perfluorooctanoic acid	PFOA	$C_7F_{15}COOH$	
Perfluorononanoic acid	PFNA	$C_8F_{17}COOH$	
Perfluorodecanoic acid	PFDA	$C_9F_{19}COOH$	

Perfluoroundecanoic acid	PFUnDA	$C_{10}F_{21}COOH$	
Perfluorododecanoic acid	PFDoDA	$C_{11}F_{23}COOH$	
Perfluorohexadecanoic acid	PFHxDA	$C_{15}F_{31}COOH$	Not available
Perfluorooctadecanoic acid	PFOcDA	$C_{17}F_{35}COOH$	Not available
PFSAs			
Perfluorobutane sulfonic acid	PFBS	$C_4F_9SO_3H$	
Perfluorohexane sulfonic acid	PFHxS	$C_6F_{13}SO_3H$	Not available
Perfluorooctane sulfonic acid	PFOS	$C_8F_{17}SO_3H$	
Perfluorodecane sulfonic acid	PFDS	$C_{10}F_{21}SO_3H$	

2.2.3 Water solubility and acid dissociation constants, pK_a

Water has been suggested to form an important transport pathway for PFASs. This is because PFASs generally have high water solubilities (Yamashita et al., 2008; Prevedouros et al., 2006; Yamashita, 2005). The water solubility of the fluorotelomer alcohols (FTOHs), PFCAs and PFSAs increases with decreasing carbon chain length (Rayne and Forest, 2009; Aastrup Jenssen et al., 2008; Niva 2007). Various water solubilities have been reported for different PFASs. The water solubility values for PFOS in freshwater have for example been estimated in the range 370-680 $mg L^{-1}$ (Jeon, 2011; You et al., 2010; Pan et al., 2009; Rayne and Forest 2009; Niva 2007; Yamashita et al., 2005). The corresponding value for PFOA has been estimated to 3400 $mg L^{-1}$ (Rayne and Forest 2009).

Both PFCAs and PFSAAs are relatively strong acids and thereby dissociate to their anionic form in most environmentally realistic pH (de Solla et al., 2012; Rayne and Forest 2009). The PFSAAs are stronger acids than their PFCA analogs. Several different pK_a values have been suggested for different PFASs in the literature (Rayne and Forest, 2009). The pK_a value describes the tendency of an acid to dissociate to its conjugate acid-base pair. A low pK_a means that the compound has a stronger tendency to dissociate to its conjugate ions (Nelson and Cox, 2008). Goss predicted the pK_a of 21 PFCAs to range between -0.1 and 4.2 (Goss, 2008). For PFOS the reported pK_a values are found to range from -5 to -3.3 (Brooke et al., 2004; Campbell et al., 2009; Tang et al., 2010). Corresponding values for PFOA ranges from -0.5 to 3.8 has been estimated (Campbell et al., 2009; Burns et al., 2008; Goss, 2008; Prevedouros et al., 2006).

2.2.4 Volatility

Because of the low pK_a values of PFSAAs and PFCAs they mostly exist in their anionic form in the environment. As an effect of this, most compounds of these groups have low volatility. Other PFAS groups such as FTOHs, perfluorooctane sulfonamidoethanols (FOSEs) and perfluorooctane sulfonamides (FOSAs) are much more volatile (Muller et al., 2012; Environment Canada, 2012; Butt et al., 2010; ATSDR 2009). The substances from these groups can be transported in the atmosphere and be degraded by photo oxidation to form PFSAAs and PFCAs (Muller et al., 2012; Butt et al., 2010; ATSDR, 2009).

2.2.5 Micelles

As a result of the surfactant properties of the PFAS molecules with one hydrophilic end group and one hydrophobic tail the molecules can form micelles when dissolved in water. The micelles are aggregates of molecules formed as a result of hydrophobic moieties of the surfactants seeking to avoid contact with water. The hydrophilic end groups then form a shell that protects the hydrophobic tails inside the micelle. The process is reversible and occurs when the concentration of surfactants exceeds the critical micelle concentration, CMC (Liu et al., 1996). The CMC value was accounted for when PFAS concentrations for the experiments in this study was decided. It was important to use PFAS concentrations under the CMC in order to prevent PFASs micelles to disrupt the partitioning of PFASs between soil and water.

The CMC for PFSAAs and PFCAs depend on the carbon chain length, chain branching and the presence of counter ions in the solution. For example, CMC for several different C7 through C11 PFASs has been reported to range between 0.1 to 30 mM. For PFOA the CMC was reported to range between 8 and 9 mM (Shinoda et al., 1972 cited by Rayne and Forest, 2009). The CMC for PFOS has been reported to 6.3 mM (Xiao et al., 2012).

2.2.6 Partitioning between octanol and water, K_{ow}

Since the PFAS are both hydrophobic and hydrophilic it is not possible to empirically determine the water-octanol partitioning constant, K_{ow} . The substances form aggregates at the interface instead of dissolving in either octanol or water (de Vos et al., 2008; Swedish Chemical Agency, 2009).

2.3 Previous studies

2.3.1 Organic carbon

The organic carbon (OC) content of a soil plays an important role for the sorption of many organic chemicals (Schwarzenbach et al., 2003). Previous studies have shown the PFASs to be among the chemicals strongly influenced by the OC concentration of the solid matrix (Nordskog, 2012; Ahrens et al., 2011; Jeon et al., 2011; Ahrens et al., 2010; You et al., 2010; Higgins and Luthy, 2006).

In a recent study by Nordskog (2012), the partitioning of different PFASs between soil and water was investigated both through batch experiments and column tests. The result showed that the fraction of OC (f_{oc}) in the soils had a positive influence on the sorption of perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA) and PFOS. These results were in good agreement with the results of Higgins and Luthy (2006), who showed that the organic matter was the most important parameter influencing the sorption of PFOS, PFOA, PFNA, PFDA, perfluoroundecanoic acid (PFUnDA) and perfluorodecane sulfonic acid (PFDS) to sediments. These results were supported by You et al. (2010) Ahrens et al. (2009) and Jeon et al. (2011).

Additionally, Ahrens et al. (2010) showed that the organic carbon content had a greater influence on the sorption of PFOS and PFUnDA than on PFNA and PFDoDA. In a field-based study by Kwadijk et al. (2010), a positive correlation between f_{oc} and sorption of PFOS and PFOA was reported. However, for other PFASs found in the sediment samples (PFBS and PFNA) no such correlation was found.

Several different $\log K_{oc}$ values have been estimated for the different PFASs. A selection of $\log K_{oc}$ values derived from water-sediment partitioning experiments is shown in Table 2.

Table 2. Log K_{oc} values ($\text{cm}^3 \text{g}^{-1}$) reported for PFOS, PFOA, PFNA, PFDA, PFUnDA, PFHxS and PFDS from previous studies on water-sediment partitioning.

Chemical	Log K_{oc} ($\text{cm}^3 \text{g}^{-1}$)	Author
PFOS	3.7±0.6	Ahrens et al., 2011
	3.8±0.1	Ahrens et al., 2010
	3.2±0.3	Kwadjik et al., 2010
	2.6	Higgins and Luthy, 2006
	2.4-2.8	Johnson et al., 2007
PFOA	2.4±0.1	Ahrens et al., 2011
	1.9±0.1	Ahrens et al., 2010
	2.6±0.3	Kwadjik et al., 2010
	2.1	Higgins and Luthy, 2006
PFNA	2.4±0.1	Ahrens et al., 2010
	2.4±0.09	Higgins and Luthy, 2006
PFDA	3.6±0.1	Ahrens et al., 2010
	2.8±0.1	Higgins and Luthy, 2006
PFUnDA	4.8±0.2	Ahrens et al., 2010
	3.3±0.1	Higgins and Luthy, 2006
PFHxS	3.6±0.1	Ahrens et al., 2010
PFDS	3.5±0.1	Higgins and Luthy, 2006

The log K_{oc} reported by Ahrens et al. (2011) Johnson et al. (2007) and Higgins and Luthy (2006) were derived from experiments conducted on samples spiked with PFASs, whereas the experiments performed by Kwadjik et al. (2010) and Ahrens et al. (2010) were conducted on naturally contaminated sediments. The PFASs concentrations in the experiments performed by Ahrens et al. (2011) Ahrens et al. (2010) and Kwadjik et al. (2010) were similar while the concentrations in the experiments performed by Higgins and Luthy (2006) and Johnson et al. (2007) were three orders of magnitude higher. Further Johnson et al. (2007) reported log K_{oc} values for PFOS on kaolinit (AlSi_2O_5), clay loam and sandy loam to range from 2.4 (kaolinit) to 2.6 (clay loam) and 3.1 (sandy loam).

2.3.2 Influence of chain length and functional group

Previous studies that have investigated PFAS partitioning between water and sediments/soils have found the carbon chain length as well as the functional group of the PFAS molecules to influence the sorption (Nordskog, 2012; Ahrens et al., 2011; Ahrens et al., 2010; Ahrens et al., 2009; Kwadjik et al. 2010; Higgins and Luthy, 2006).

Nordskog (2012) found the fluorinated carbon chain length to be the most important structural feature affecting PFASs sorption to different soils (Nordskog, 2012). This result was in good agreement with a previous study by Johnson et al. (2007) which showed that the fluorinated carbon chain length positively affected the sorption of PFASs to different mineral surfaces (Johnson et al., 2007).

Similar results have been reported from studies investigating PFAS partitioning between sediments and water (Ahrens et al., 2011; Ahrens et al., 2010; Ahrens et al., 2009; Kwadjik et al., 2010; Higgins and Luthy, 2006). Ahrens et al. (2010) showed that the sorption of PFASs to

sediment increased with 0.52 to 0.75 log units for each additional CF₂ moiety in the carbon chain. Also, the sorption of PFASs was found to be 0.71 to 0.76 log units higher compared to PFCA analogs (Ahrens et al., 2010). These results were in good agreement with the results reported by Higgins and Luthy (2006) who found the fluorinated carbon chain length to be the dominant structural parameter influencing the sorption of PFASs to sediment. Each CF₂ moiety was found to contribute to an increase in the measured distribution coefficients of 0.50 to 0.60 log units. Also, the sulfonate moiety was found to contribute an additional 0.23 log units (Higgins and Luthy, 2006). These findings were supported by the results reported by Ahrens et al. (2011) Kwadjik et al. (2010) and Ahrens et al. (2009).

In addition, Ochoa-Herrera and Sierra-Alvarez (2008) reported the fluorinated carbon chain length as well as the functional group to positively influence the sorption of PFASs to activated carbon (Ochoa-Herrera and Sierra-Alvarez, 2008).

2.3.3 Active carbon

Black carbon (BC) is a product of incomplete combustion of biomass or fossil fuels that can be found in different concentrations in soils. The largest sources of BC in soils are air emissions and fires (Brodowski et al., 2007; Laser et al., 1998). In order to get an indication of how the BC influence the partitioning of PFASs in soil the influence of active carbon (AC) on the PFASs was investigated. The AC has similar sorption properties as the BC (Brändli et al., 2008).

Active carbon is a manufactured type of charcoal with strong sorbing properties and a large surface area, up to 1000 m²/g AC. The AC has been shown to be an effective water cleaning agent for different pollutants. Recent studies have also documented its remediation capacity for soil and sediment (Hansen et al., 2009). Several studies have proven the sorptive capacity of AC to different PFASs. Most studies have been performed on PFASs dissolved in water, in the absence of sediment and soil (Carter and Farell, 2010; Senevirathna et al. 2010; Yu et al., 2009; Ochoa-Herrera and Sierra-Alvarez, 2008).

Ochoa-Herrera and Sierra-Alvarez (2008) compared the sorption of PFOS, PFOA and PFBS to granular active carbon (GAC), zeolites (microporous crystalline hydrated aluminosilicates) and waste water treatment sludge. The study showed that GAC was the best sorbent for all three PFASs. The sorption was stronger for PFOS than for PFOA and PFBS, reflecting the influence of an increasing carbon chain length and the substitution of a carboxylic group by a sulfonic group. The sorption of PFOS to the different sorbents decreased as follows: GAC > hydrophobic zeolite > anaerobic granular sludge > activated sludge (Ochoa-Herrera & Sierra-Alvarez, 2008).

Studies comparing the sorption of PFAS to GAC and powder active carbon (PAC) have shown PAC to be a better sorbent of PFASs than GAC (Yu et al., 2009; Hansen et al., 2010). In a study by Carter and Farell (2010) comparing the sorption of PFOS and PFBS to GAC and an ion exchange resin, the equilibrium time between the PFASs and the GAC was found to be approximately 50 hours (Carter and Farell, 2010).

2.3.4 Calcium ions

Because of weathering of minerals in the soil all natural soils contain different concentrations of cat ions such as Ca^{2+} ions (Nilsson et al., 2005). Most studies that have investigated the influence of calcium ions on the sorption of PFASs to solids have focused on the partitioning of PFOS between sediments and water (You et al. 2010; Higgins and Luthy, 2006; Pan and You, 2010; Kwadik, 2010).

You et al. (2010) showed that the sorption of PFOS to sediment increased with increasing concentrations of Ca^{2+} in the water. One reason for this was suspected to be due to the salting-out effect (You et al., 2010), that is, the decrease of aqueous solubility that different kind of compounds shows in the increasing presence of inorganic salts (Görgényi et al. 2006; Turner & Rawling 2001). Another reason for the increased sorption of PFOS was proposed to be due to changes in electrostatic sorption. The positively charged Ca^{2+} ions can act as neutralizers of the electrostatic repulsion between the negatively charged sediment particles and the PFOS anions. Thereby the sorption of PFOS through electrostatic attraction will potentially increase as the concentration of Ca^{2+} ions increases (You et al., 2010).

You et al. further discovered that the sorption of PFOS increased by a factor 3 when increasing the calcium chloride (CaCl_2) concentration from 5 mM to 500 mM at pH 7, while corresponding increase in CaCl_2 concentration at pH 8 resulted in a sorption increase with almost a factor of 6. This was believed to be due to formation of more basic surface sites such as carboxyl, alcoholic, phenolic and quinone groups, where more Ca^{2+} ions could attach (You et al., 2010).

The effect of Ca^{2+} ions on the sorption of PFOS to sediments was further investigated by Higgins and Luthy (2006) who noticed that an increase of Ca^{2+} concentration resulted in an average increase in $\log K_d$ per log unit $[\text{Ca}^{2+}]$ of 0.36 (Higgins and Luthy, 2006). These results were in contrast with the results of Kwadik et al. (2010) who found no correlation between Ca^{2+} concentrations and sorption of PFAS when examining the partitioning of different PFAS between water and sediment under field conditions. However, according to the authors, the results in this study might have been influenced by the limited range in Ca^{2+} concentrations or by occasional non equilibrium between overlying water and bed sediment (Kwadik et al., 2010).

In a study by Tang et al. (2010) the sorption of PFOS to goethite was found to increase significantly at high concentrations of H^+ and Ca^{2+} . Goethite colloids are positively charged at a pH under the pH of zero point charge (pH_{pzc}), that is the pH at which no exchange of H^+ between solid and water phase occurs, and negatively charged at pH above pH_{pzc} . In this study the pH_{pzc} was 9.4. This explains why the sorption of PFOS increased at lower pH. Ca^{2+} ions can interact with the goethite surfaces in a similar way as with the organic matter, promoting the electrostatic PFOS-surface adsorption. This in combination with the pH influence on the surface charge of the goethite explains the increased PFOS adsorption observed for low pH and high concentrations of Ca^{2+} ions. The sorption of PFOS to silica, on the other hand, was only marginally affected by pH and Ca^{2+} concentrations. This was believed to reflect the non-electrostatic interactions, such as hydrophobic interactions, dominating the adsorption of PFOS to silica (Tang et al., 2010).

The effect of Ca^{2+} ions on the sorption of PFASs to soil particles was further investigated by Nordskog (2012). The study showed an increased sorption of PFDA, PFNA and PFOS to soil with increasing Ca^{2+} concentrations in the soil. The shorter chained PFASs, perfluorohexanoic acid (PFHxA) and PFBS, showed the opposite behavior with a decreased sorption at higher concentrations of Ca^{2+} ions (Nordskog 2012).

2.3.5 Aging

Sorption of organic chemicals to soil and sediments is often initially a fast and reversible process. With time the chemicals slowly diffuse into small pores of the soil aggregates where they become harder to extract. Also, the strength of some intermolecular interactions with organic matter in the soil increases with time. The aging process can thereby influence the partitioning of a chemical between soil or sediment and water (Loibner et al., 2006). No studies were found which investigate the influence of aging on the partitioning of PFASs in soil or sediment. However, aging has been proven to have an influence on the partitioning of other organic chemicals in soils and sediments (Loibner et al., 2006; Northcott and Jones, 2001; Hatzinger and Alexander, 1995).

3 Materials and methods

3.1 Experiment design

The experiment design was created in accordance with previous studies mentioned above. In order to find suitable soils for the experiments, ten different soils were characterized. Three of the soils, all silty sands with varying content of organic carbon, were chosen for spiked batch experiments (i.e. batch experiments where PFASs were added to the soils). Also, one artificial soil (made according to OECDs guidelines nr 207, 1984) was included in the spiked experiments. The artificial soil was used in order to facilitate the repeatability and comparisons with future experiments. The aim of the spiked experiments was to investigate the influence of organic carbon content, PFAS carbon chain length, calcium ions and AC on the sorption of PFAS to soil. In order to examine the influence of aging four different soil samples from PFAS contaminated sites were chosen for non-spiked batch experiments. These soils were among the ten characterized soils.

3.2 Soil samples

The soils chosen for spiked experiments were collected from F18 former airport in Riksten, south of Stockholm. Three of the field contaminated soil samples were chosen from soil samples collected by Sweco at a PFAS-contaminated firefighting training site. The PFAS concentrations of these soils were determined at IVL's special laboratory in Stockholm. One of the field contaminated soil samples was chosen from soils collected from Riksten. The PFAS concentration for this soil was determined at the POP laboratory, Department of Aquatic Sciences and Assessment, SLU. All soil samples were sieved and stored at -20 °C before the start of the experiment in order to decrease potential biological activity.

3.3 Artificial soil

The artificial soil (soil AS) was created according to OECD's guidelines nr 207, 1984. Approximately 200 g was created through the mixing of 148 g air-dried industrial sand (50-70 mm mesh particle size, Sigma Aldrich, Germany), 40 g kaolinit clay (Halloysite nanoclay, Sigma Aldrich, USA) and 10 g of peat (dry spagnum moss, mixed to a size less than 2 mm). The pH was adjusted with calcium carbonate (CaCO₃) to 6.2.

3.4 Characterization

Characterization of the soil samples was conducted at Swecos geo lab according to standard procedures. The characterization procedure is described in Appendix A. Swecos soil characterization program GeoSiktNET was used in order to create sieving curves for all characterized soils. The sieving curves were based on data from sedimentation and dry sieving. The sieving curves are presented in A2 through A5, Appendix A.

The soils used in the Ca²⁺ experiments, soil AS and soil 1 (Table 3), were sent for analysis of cation exchange capacity, CEC. Organic matter (OM), total organic carbon (TOC) and CEC for each soil are presented in Table 3.

Table 3. Results from the soil characterization. Particle size fractions, organic matter (OM) and total organic carbon (TOC) are presented in %. CEC (cmol(+)/kg) was only determined for soil AS and soil 1 which was used in the experiments for Ca²⁺ ions. Each soil was mixed with tap water (liquid to solid ratio (L/S) = 5/100) and pH was determined using a pH meter.

Soil	Particle size fractions (%)				OM (%)	TOC (%)	pH	CEC
	Clay	Silt	Sand	Gravel/stones				
AS	7	15	78	0	7	4	6.2	9.9
1	18	26	55	1	1	1	9.0	7.0
2	3	40	57	0	6	3	8.0	
3	2	35	63	0	16	9	7.4	
C1	30	59	10	1	8	5	8.5	
C2	31	55	14	0	4	2	8.5	
C3	34	54	10	2	6	3	8.3	
C4	4	20	63	13	2	1	9.3	

3.5 Chemicals and materials

Native standard (80 pg μ L⁻¹, Wellington laboratories, Ontario, Canada) containing 12 different PFASs was used for all spiked experiments. Mass-labeled internal standard (20 pg μ L⁻¹, Wellington laboratories, Ontario, Canada) was used for all extractions. For all analyzes PFAS injection standard (200 pg μ L⁻¹, Wellington laboratories, Ontario, Canada) was used. The injection standard contained the same mass labeled PFASs as the internal standard. Methanol (> 99.9%, LiChrosolv) was used for all rinsing, solutions and experiments involving methanol. Ultra pure Millipore water was used for all solutions, rinsing and experiments involving water. Other chemicals used for the soil and water extraction were sodium hydroxide (NaOH) (99.9%, Merck, Darmstadt, Germany), hydrochloric acid (HCl) (30%, Merck, Darmstadt, Germany), acetic acid (100%, Merck, Darmstadt, Germany), ammonium acetate (\geq 99%, Sigma Aldrich, Netherlands) and ammonium hydroxide (28-30 %, Sigma Aldrich, Spain)

3.6 Batch sorption tests

Soil samples were freeze-dried for 48 h before the experiment. Duplicates were used for all batch experiments. A liquid to solid ratio (L/S) of 8 was achieved through the mixing of 5 g of soil with 40 mL of Millipore water in 50 mL polypropylene (PP) tubes. This water/soil ratio was used for all experiments (Higgins and Luthy, 2006; You et al., 2010; Pan et al., 2009). For the spiked samples 50 μ L of native standard PFAS solution (80 pg μ L⁻¹) was added in order to achieve a concentration of 100 ng L⁻¹. This concentration was used for the spiked samples throughout the experiments. The relatively low concentration was chosen in order to achieve environmentally realistic concentrations and to avoid the formation of micelles (Ahrens et al., 2011). Both spiked and non-spiked samples were shaken until equilibrium of PFASs between soil and water had been reached. The PFASs were then extracted and the concentrations detected in soil and water were studied.

3.6.1 Equilibrium tests

In order to determine the sorption equilibrium time for the different PFASs, an equilibrium test was conducted. Soils selected for the test was the artificial soil (soil AS), soil number 1

and the contaminated soil C1. Soil AS and soil number 1 (5 g) was mixed with 40 mL Millipore water in 50 mL PP tubes and spiked with a native standard PFAS solution (50 μL of 80 $\text{pg } \mu\text{L}^{-1}$). The samples were placed on a wrist-action shaker at 200 rpm (Figure 2) and shaken for 8.5 h, 24 h, 48 h and 72 h. Duplicates were prepared for each time step ($n = 24$). The non-spiked field contaminated samples were prepared in the exact same way as the spiked samples but without addition of native standards. The samples were placed on a wrist-action shaker at 200 rpm. Since the equilibrium time for the contaminated samples was expected to be longer than for the spiked samples, the contaminated samples were removed after 48 h, 196 h, 240 h and 360 h. Duplicates were prepared for each time step ($n = 8$). In addition, reference samples consisting of soil number 1 and soil AS (5 g soil, 40 mL Millipore water) were prepared ($n = 2$). Blanks consisting of 40 mL Millipore water were prepared in duplicates ($n = 2$). The blanks were treated in the exact same way as the other samples and were removed from the action-wrist shaker after 240 h. In order to investigate PFAS-losses during the process, recovery tests consisting of 40 mL Millipore water and 50 μL of PFAS native standard solution were shaken for 48 h and treated in the exact same way as the other samples ($n = 2$).



Figure 2. The samples were shaken on a 2D shaker at 200 rpm. The samples were removed from the shaker after 8, 24, 48, and 72 hours (spiked samples) and 48, 196, 240 and 360 hours (contaminated samples).

3.6.1.1 Separation

Directly after the shaking, the samples were centrifuged at 3000 rpm for 30 minutes. The supernatant was then transferred, using a 5 mL syringe (Omnifix, B. Braun, Melsungen, Germany), and filtered through a syringe filter (Minisart, RC 25, 0.45 μm , Goettingen, Germany) into a new 50 mL PP tube (Figure 3A). In order to release potential PFASs adsorbed to the syringe filter, 1 mL of methanol was pushed through the filters and into the water sample before the filter was discharged. Syringes, syringe filters and beakers were rinsed with approximately 1 mL methanol three times before use. After separation the water samples were stored at -20°C . Soils were freeze-dried for 48 hours (Figure 3B) and then stored at -20°C before extraction.

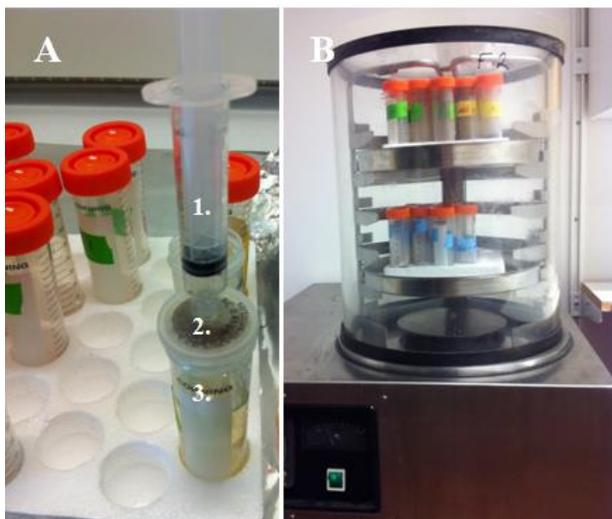


Figure 3. Figure A shows the separation of soil and water. The water was transferred with a 5 ml syringe (1.) and filtered through a 45 μL syringe filter (2.) into a new 50 ml PP tube (3.). The water was then stored at -20°C before extraction. The soil was freeze dried for 48 hours, Figure B.

3.6.1.2 Extraction

Each water sample was spiked with 100 μL of PFAS internal standard ($20 \text{ pg } \mu\text{L}^{-1}$). The spiking was done in order to correct for PFAS losses during the analysis. The samples were extracted through solid phase extraction (SPE) using Oasis Wax Cartridges (Waters, 6 cc, 150 mg, 30 μm , Ireland) as described previously (Ahrens et al., 2009). The setup is illustrated in Figure 4A. The cartridges were preconditioned with 4 mL ammonium hydroxide in methanol followed by 4 mL methanol and finally 4 mL Millipore water. The cartridges were then loaded with $\sim 20 \text{ mL}$ water sample at a rate of one drop per second. Finally the cartridges were washed with 4 mL 25 mM ammonium acetate buffer (pH 4) in Millipore water and dried through vacuum for 2 minutes. The elution was then carried out with 4 mL methanol followed by 4 mL 0.1 % ammonium hydroxide in methanol. The extract was then reduced to 1 mL under nitrogen stream (Figure 4B) and an injection standard ($10 \text{ } \mu\text{L}$ of $200 \text{ pg } \mu\text{L}^{-1}$) was added. Finally the samples were analyzed for PFASs using HPLC MS/MS.

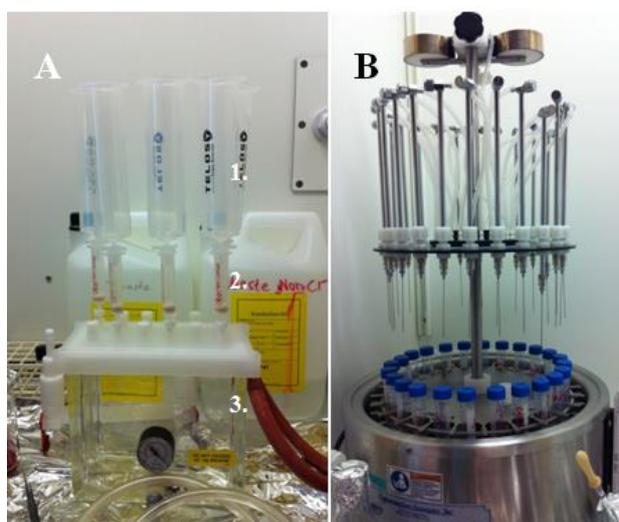


Figure 4. Figure A shows the water extraction setup. Approximately 20 ml of water sample was poured into the reservoir (1). The SPE cartridges (2) were then loaded with the water samples at a rate of approximately one drop per second. The water was then collected in the SPE manifold (3) while the PFASs sorbed to the cartridges. The PFASs were then extracted with methanol and ammonium hydroxide in methanol which was collected in 15 ml PP tubes. The samples were then reduced to 1 ml under nitrogen stream, Figure B.

The extraction of soil was carried out using solid-liquid extraction as described previously (Ahrens et al., 2009). Briefly, 2.5 g of soil was added to a 50 mL PP tube and 2 mL of 50 mM NaOH (20/80, Millipore water/methanol) was added. The mix was soaked for 30 minutes and then 20 mL of methanol and 100 μL of PFAS internal standard ($20 \text{ pg } \mu\text{L}^{-1}$) was added to the tube. The samples were then placed on an action-wrist shaker for 30 minutes followed by centrifugation at 3000 rpm for 15 minutes. The supernant was decanted into a new 50 mL PP tube (Figure 5). The extraction was repeated using 1 mL of 50 mM NaOH (20/80, Millipore water/methanol) followed by 30 minutes of soaking and then addition of 10 mL of methanol. The sample was again shaken for 30 minutes and centrifuged for 15 minutes. The supernant was decanted and mixed with the previously decanted supernant. The extract was then centrifuged at 3000 rpm for 5 minutes and 1/8 of the extract (4.15 mL) was transferred into a 15 mL PP tube. The sample was reduced to 1 mL under a nitrogen stream.

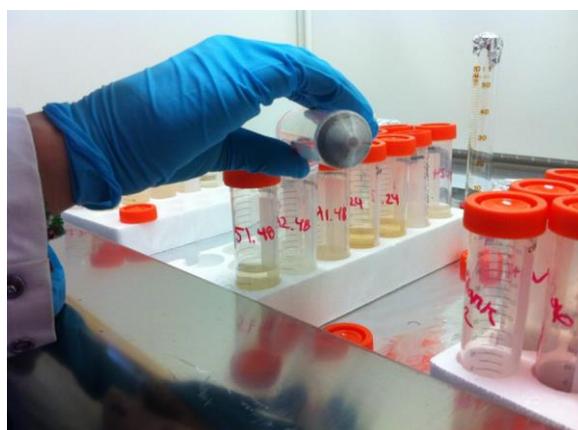


Figure 5. Decanting of soil extract after 30 minutes of shaking with methanol and 50 mM NaOH. The procedure was repeated twice. An aliquot of 1/8 of the extract was then transferred to 15 ml PP tubes and reduced to 1 ml under nitrogen stream as shown in Figure 3B.

The sample extract was transferred into a 1.7 mL Eppendorf centrifuge tube and acidified with 50 μL of 4 M HCl. For the clean-up, 25 mg of ENVI-carb (Supelco, mesh 120/400, Bellafonte, PA, USA) was used as described previously (Powley, 2005). The extract was vortexed for 30 seconds and centrifuged at 4000 rpm for 10 minutes. Finally, 0.5 mL of the extract was transferred into an auto-injector vial and an injection standard ($10 \mu\text{L}$ of $200 \text{ pg } \mu\text{L}^{-1}$) was added. The samples were analyzed with HPLC MS/MS. All tubes used during the extraction were rinsed three times with approximately 1 mL of methanol.

3.6.2 Organic carbon

In order to investigate the influence of organic carbon content on the sorption of PFASs to soil four different soils with varying organic carbon contents were chosen for batch experiments. These soils are listed in Table 4. The soils were prepared and treated in the same way as the soils for the spiked equilibrium test ($n = 12$). The samples were shaken for 48 h since the results from the equilibrium test indicated that equilibrium would have been reached after this time. Blanks were also prepared and treated in the same way as for the equilibrium test ($n = 2$).

Table 4. Soils chosen for organic carbon experiments. Soil AS and soil 1 were also used in experiments with AC and Ca²⁺ experiments.

Soil	Particle size fractions (%)				OM (%)	TOC (%)	pH	CEC
	Clay	Silt	Sand	Gravel/stones				
AS	7	15	78	0	7	4	6.2	9.9
1	18	26	55	1	1	1	9.0	7.0
2	3	40	57	0	6	3	8.0	
3	2	35	63	0	16	9	7.4	

3.6.3 Active carbon

For the batch experiments investigating the influence of powder active carbon, PAC, on sorption of PFASs to soil, the same soils were used as for the experiments with Ca²⁺-ions (soil 1 and soil AS). Three different amounts of PAC (100 mm mesh, DARIO, Sigma Aldrich, Netherlands) were mixed with the soils (0.1 g, 0.5 g and 1 g, to 5 g soil). The combination of water and soil used in this study required a larger amount of PAC compared to previous studies which used water only (Senevirathna et al., 2010; Yu et al., 2009; Occhoa-Herrera and Sierra-Alvarez, 2008). The soils were then prepared and treated in the same way as the samples for the equilibrium test ($n = 12$). Recovery tests were prepared and treated in the exact same way as for the equilibrium test ($n = 2$). The samples were removed from the shaker after 48 h.

3.6.4 Calcium ions

Soil AS and soil 1 (Table 4) were used for the batch experiments investigating the influence of Ca²⁺-ion concentrations on the sorption of PFASs to soil. Aqueous solutions with four different concentrations of Ca²⁺, 5 mM, 25 mM, 50 mM and 200 mM were created through the mixing of appropriate amounts of CaCl₂ and Millipore water. The different concentrations chosen for the experiment are in the same range as previous studies (You et al., 2010; Higgins and Luthy, 2006). Samples were prepared in duplicates for each soil and each Ca²⁺ concentration in the same liquid to solid ratio as the samples for the spiked equilibrium test ($n = 16$). The samples were then spiked and treated in the same way as the samples in the equilibrium test. Recovery tests were prepared and treated in the same way as for the equilibrium test ($n = 2$). The samples were removed from the shaker after 48 hours.

3.6.5 Field contaminated samples

The experiments investigating the influence of aging on the sorption of PFASs to soil were conducted on field contaminated soils C1, C2, C3 and C4 (Table 3). The samples were prepared and treated in the same way as the samples for the equilibrium test ($n = 8$). Blanks consisting of 40 mL of Millipore water were prepared and treated in the same way as the contaminate samples ($n = 2$). The samples were removed from the shaker after 240 hours since the results from the equilibrium tests indicated that equilibrium for the contaminated samples would have been reached after this time.

3.6.6 Instrumental analysis

All extracts were analyzed for PFASs in their ionic form using high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS) as was described

elsewhere (Ahrens et al, 2009). The analysis was performed by personnel from the POP laboratory, Department of Aquatic Sciences and Assessment, SLU.

4 Results

4.1 Quality assurance/quality control (QA/QC)

In order to avoid contamination of the samples during the experiments all fluorinated materials that could come in contact with the samples were removed. PP tubes were used in order to avoid adsorption of PFASs to tube walls. The method detection limit (MDL) was calculated as the sum of the average concentration in all blanks plus the standard deviation multiplied by three. Recoveries of PFASs for the water samples ranged between 61 ± 35 % for PFDODA, PFHxDA and PFOcDA to 103 ± 17 % for PFNA. The recoveries for the soil samples ranged between 79 ± 16 % for PFHxA and 122 ± 18 % for PFOA, PFBS, PFHxS, PFOS and PFDS.

The mass balance for individual PFASs was calculated considering the concentration measured in water, soil (i.e. non-spiked and spiked), and spiked amount added before the equilibration experiments (Table B5, Appendix B). The average mass balance for AC experiments was lower (55 ± 11 %) than the average mass balances in OC and Ca^{2+} experiments (i.e. 102 ± 21 % for OC and 88 ± 16 % for Ca^{2+}). Standard deviation for duplicate samples (precision) were generally low for all compounds. The average standard deviation (precision), MDL, instrumental detection limit (IDL) and the average recovery for PFASs in soil and water samples are listed in Table 5.

Table 5. Average concentration (ng absolute) measured in blanks, method detection limit (MDL) (ng absolute), precision (average standard deviation (%)), average recovery of PFASs for soil samples (%) and average recovery of PFASs for water samples (%).

	Concentration blanks (ng)	MDL (ng)	IDL (ng)	Precision (%)	Recovery water (%)	Recovery soil (%)
PFHxA	0.34	1.32	0.01	6	83 ± 14	79 ± 16
PFOA	0.03	0.30	0.01	4	103 ± 19	122 ± 18
PFNA	0.10	1.21	0.01	6	103 ± 17	94 ± 21
PFDA	0.02	0.22	0.01	8	93 ± 21	91 ± 21
PFUnDA	0.00	0.01	0.01	8	74 ± 28	89 ± 22
PFDODA	0.03	0.37	0.01	9	61 ± 35	93 ± 23
PFHxDA	0.00	0.00	0.01	16	61 ± 35	93 ± 23
PFOcDA	0.01	0.07	0.01	14	61 ± 35	93 ± 23
PFBS	0.00	0.02	0.01	10	103 ± 19	122 ± 18
PFHxS	0.00	0.01	0.01	6	103 ± 19	122 ± 18
PFOS	0.01	0.12	0.01	8	103 ± 19	122 ± 18
PFDS	0.00	0.00	0.01	12	103 ± 19	122 ± 18

4.2 Equilibrium test, spiked samples

As shown in Figure 6 48 hours of shaking was sufficient for all PFASs to reach equilibrium both for soil 1 and soil AS. The concentrations plotted in the figure were detected in soil. The concentrations of PFNA in soil were below the MDL for both investigated soils.

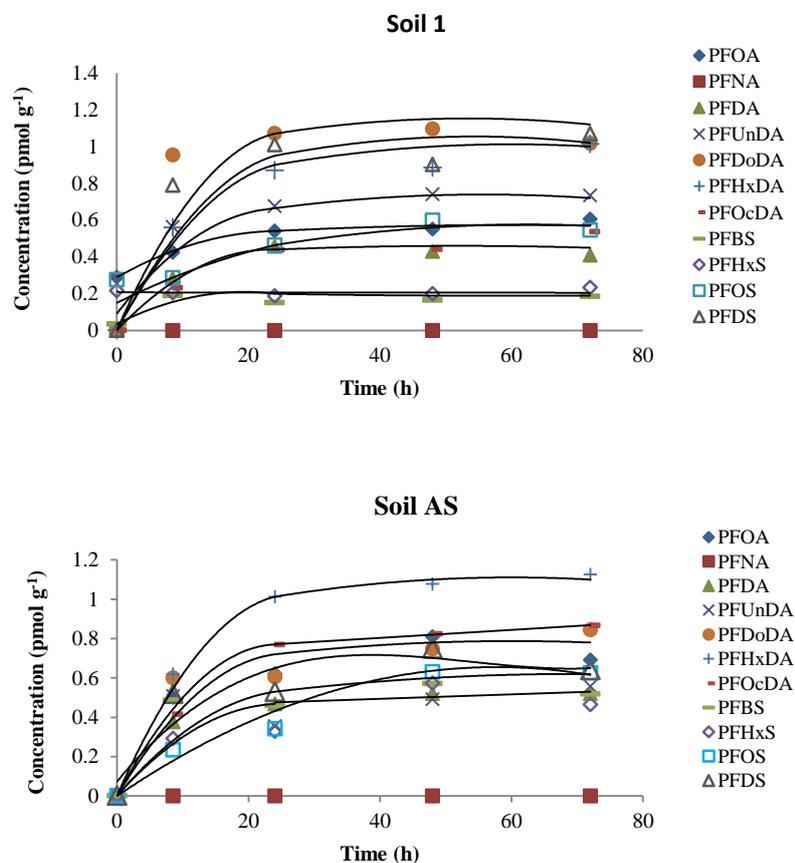


Figure 6. The plots illustrate the concentrations (pmol g⁻¹) of different PFASs detected in soil 1 (upper plot) and soil AS (lower plot) in the equilibrium test after different times of shaking (h).

Since the concentration for PFHxA was several times higher than for the other PFASs in both soils this compound is plotted on its own in Figure B1, Appendix B. Just as for the other spiked PFASs PFHxA was equilibrated after 48 hours.

4.3 Equilibrium test, field contaminated samples

For the field contaminated samples equilibrium was reached for all samples after 240 hours. The PFAS concentrations measured in the water phase at different time points for the equilibrium test with contaminated soil C1 are shown in Figure 67.

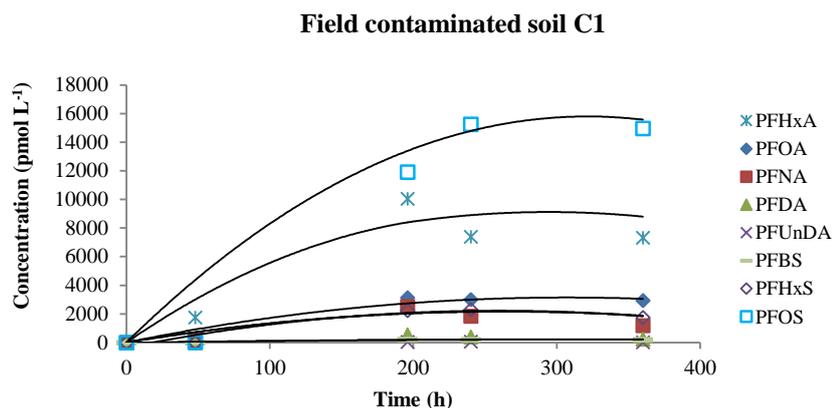


Figure 7. Plot over concentrations (pmol L⁻¹) of different PFASs detected in the water phase after different time of shaking during the equilibrium test for field contaminated soil C1.

4.4 Distribution coefficients, K_d and K_{oc}

Log K_d and log K_{oc} values were calculated from equation 2 and 3 described in Section 2.1 *Partitioning*. The calculations were based on concentrations detected in soil and water in the organic carbon experiments and in the experiments with contaminated samples. The values were calculated based on triplicates for soil 1 and soil 3. For soil 2 the values were based on duplicates since one sample was defect. The log K_d and log K_{oc} values calculated for the field contaminated samples (i.e. C1, C2, C3 and C4) were based on duplicates. Average log K_d and log K_{oc} values for the spiked experiments and the experiments conducted on contaminated samples ($n=8$) are presented in Table 6 and Table 7. Also the overall average ($n=16$) is presented. Log K_d and log K_{oc} values calculated for each soil are presented in Table. Since the partitioning of PFASs between soil AS and water showed a deviant behavior compared to the other soils the distribution coefficients calculated for soil AS is not included in the average log K_d and log K_{oc} values.

No K_d and K_{oc} values could be calculated for PFNA, PFDoDA, PFHxDA and PFOcDA for the spiked samples and for PFDoDA, PFHxDA, PFOcDA and PFDS for the contaminated samples since no concentrations of compound was detected in the water phase after equilibrium.

Table 6. Average log K_d values ($\text{cm}^3 \text{g}^{-1}$) calculated for the different soils in the spiked experiments (i.e. soil 1, 2 and 3) ($n=8$) and non-spiked experiments with contaminated soils (i.e. C1, C2, C3 and C4) ($n=8$). The average log K_d for spiked and field contaminated samples are listed in the column average ($n=16$). The log K_d values for soil AS ($n=2$) were not included in the average values and is presented on its own.

	Soil 1, 2, 3 ($n=8$)	Soil C1, C2, C3, C4 ($n=8$)	Average ($n=16$)	Soil AS ($n=2$)
PFHxA	1.0	-0.1±0.1	0.2±0.5	
PFOA	0.5±0.4	0.1±0.2	0.3±0.4	0.2±0.04
PFNA		0.5±0.1	0.5±0.1	
PFDA	1.1±0.6	1.2±0.1	1.1±0.5	0.2±0.1
PFUnDA	1.5±0.5	1.8±0.5	1.6±0.5	0.5±0.05
PFDoDA				1.3±0.1
PFHxDA				
PFOcDA				
PFBS	-0.2±0.4	0.0±0.1	-0.1±0.3	0.2±0.02
PFHxS	0.5±0.5	0.2±0.2	0.3±0.4	0.1±0.1
PFOS	1.4±0.9	1.1±0.3	1.2±0.6	0.3±0.03
PFDS	2.2±0.4		2.2±0.4	1.3±0.01

Table 7. Average log K_{oc} values ($\text{cm}^3 \text{g}^{-1}$) calculated for the different soils in the spiked experiments (i.e. soil 1, 2 and 3) ($n=8$) and non-spiked experiments with field contaminated soils (i.e. C1, C2, C3 and C4) ($n=8$). The average log K_{oc} for both spiked and contaminated samples are listed in the column average ($n=16$). The log K_{oc} values for soil AS ($n=2$) were not included in the average values and is presented on its own.

	Soil 1, 2, 3 ($n=8$)	Soil C1, C2, C3, C4 ($n=8$)	Average ($n=16$)	Soil AS ($n=2$)
PFHxA	2.0	1.4±0.2	1.6±0.3	
PFOA	2.0±0.2	1.7±0.3	1.8±0.3	1.6±0.04
PFNA		2.0±0.1	2.0±0.1	
PFDA	2.7±0.2	2.6±0.2	2.7±0.1	1.6±0.1
PFUnDA	3.1±0.2	3.4±0.02	3.2±0.2	1.9±0.05
PFDoDA				2.7±0.1
PFHxDA				
PFOcDA				
PFBS	1.4±0.1	1.6±0.2	1.5±0.2	1.6±0.02
PFHxS	2.0±0.1	1.8±0.2	1.9±0.1	1.5±0.1
PFOS	2.9±0.4	2.7±0.2	2.8±0.3	1.6±0.03
PFDS	3.8±0.3		3.8±0.3	2.7±0.01

4.5 Influence of chain length and functional group

In order to examine the influence of chain length and structure of the PFAS molecules on the partitioning between water and soil, the average $\log K_{oc}$ values for PFCAs and PFSAAs were plotted as a function of CF_2 chain length (Figure 8). The $\log K_{oc}$ value increased with increased carbon chain length for both PFCAs ($R^2 = 0.99$ for PFCAs with $\text{CF}_2 \geq 6$ and $R^2 = 0.89$ for PFCAs with $\text{CF}_2 \geq 5$) and PFSAAs ($R^2 = 0.99$). The values were generally higher for the PFSAAs. No $\log K_{oc}$ values could be calculated for PFASs with more than 10 CF_2 moieties in the tail since all detected concentration of these compounds were found in the soil. The $\log K_{oc}$ values calculated from soil AS did not correlate with the $\log K_{oc}$ values calculated from the natural soils (Figure 8 compared to Figure B2, Appendix B) and is therefore not included in the average values plotted in Figure 8.

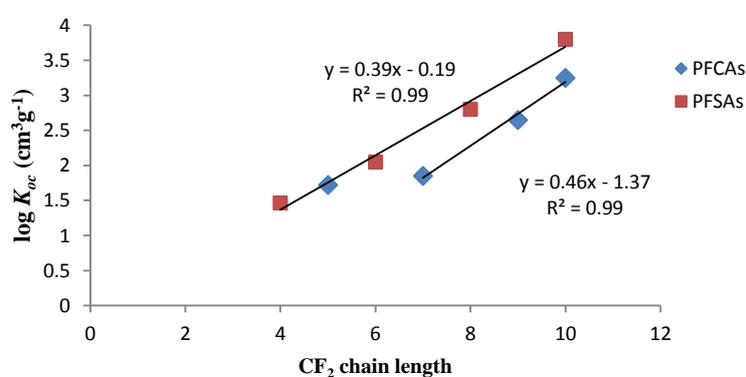


Figure 8. Average $\log K_{oc}$ values (cm^3g^{-1}) for PFCAs and PFSAAs plotted as a function of CF_2 chain length. The average $\log K_{oc}$ values were calculated from concentrations of PFASs detected in soil and water for spiked soils 1, 2 and 3 and field contaminated soils C1, C2, C3 and C4 ($n = 16$).

4.6 Organic carbon

In order to investigate the influence of OC on the partitioning of PFASs between soil and water the $\log K_d$ values calculated for soil 1, 2 and 3 (TOC = 0.6 %, 3.5 % and 9.2 % respectively) were plotted as a function of [TOC] (Figure 9). The results for some PFASs (i.e. PFOcDA, PFBS, PFUnDA, PFDoDA and PFDS) in soil AS (TOC = 4.2 %) did not correlate with the natural soil samples. The $\log K_d$ values calculated for this soil are therefore not included in Figure 9.

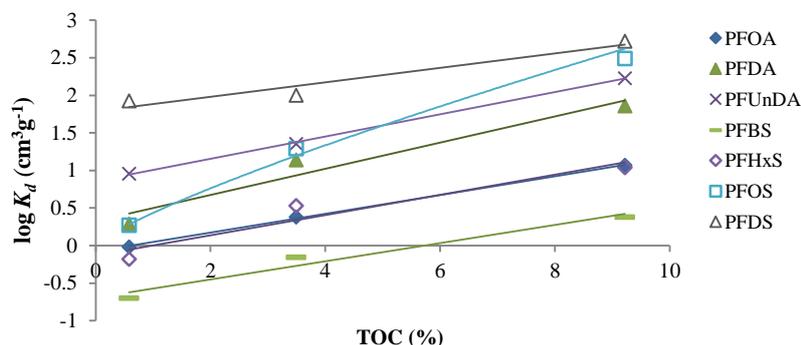


Figure 9. Scatter plot over calculated $\log K_d$ values (cm^3g^{-1}) for different TOC concentrations (%) ($n=3$ for $\log K_d(3.5\%)$ and $\log K_d(9.2\%)$, $n = 2$ for $\log K_d(0.6\%)$).

As illustrated in Figure 9 the sorption of all PFCAs and PFSAs increased with increased TOC concentration. The highest $\log K_d$ values were observed for PFDS followed by PFOS and PFUnDA. The lowest values were observed for PFBS, PFOA and PFHxA. The R^2 values ranged between 0.94 (PFDA) and 1.0 (PFOA and PFUnDA) for the PFCAs. R^2 values for the PFSAs ranged from 0.92 (PFHxS) to 1.0 (PFOS).

Since no K_d values could be calculated for PFNA, PFDoDA, PFHxDA and PFOcDA the concentrations of PFASs detected in soil were also investigated. The correlation of TOC against the PFAS concentration are shown in Figure 10 for soils 1, 2 and 3 (TOC = 0.6 %, 3.5 % and 9.2 % respectively). The PFAS concentrations detected in soil AS (TOC = 4.2 %) did not correlate with the natural soil samples and are therefore presented in Figure B3, Appendix B. The concentrations of all PFASs increased with increased TOC concentration except PFHxA and PFNA for which the concentrations detected in soil were below the MDL for the two lowest TOC concentrations (i.e TOC = 0.6 % and 3.5 %). High concentrations of the two compounds were however detected for the highest TOC concentration (9.2 %). The R^2 values ranged from 0.74 (PFOA) to 0.90 (PFOcDA) for all PFCAs except PFHxDA (0.23). The R^2 values for PFSAs ranged from 0.58 (PFHxS) to 0.91 (PFOS). The concentrations of PFASs detected in water are presented in Figure B4 Appendix B.

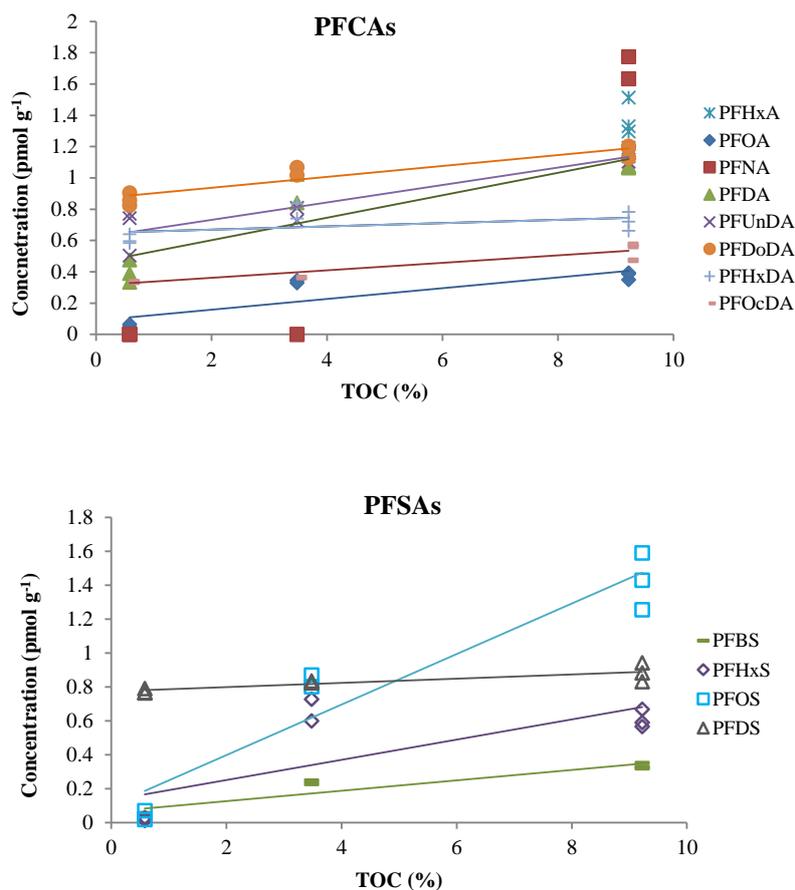


Figure 10. Scatter plot of the concentrations (pmol g^{-1}) of PFCAs (upper plot) and PFSA (lower plot) detected in soil for different TOC concentrations (i.e. soil 1 (TOC = 0.6 %), soil 2 (TOC = 3.5 %) and soil 3 (TOC = 9.2 %)).

4.7 Active carbon

Since the concentrations detected in water were below the MDL for all PFASs in all AC samples no K_d values could be calculated for the AC experiments. The PFAS concentrations detected in soil were therefore studied in order to get an indication of how the sorption was influenced by the AC concentration. As illustrated in Figure 11 the concentrations of all PFCAs detected in soil 1 (except PFDoDA, and PFOcDA) were higher for an AC concentration of 2.5 g L^{-1} compared to 0 g L^{-1} AC. Slightly decreasing concentrations were observed for soil 1 with an $[\text{AC}] 25 \text{ g L}^{-1}$. The decrease was greatest for the longer chained PFCAs ($C > 10$). PFUnDA and PFHxDA decreased for $[\text{AC}] > 2.5 \text{ g L}^{-1}$. The concentration of PFOcDA was highest for $[\text{AC}] 0 \text{ g L}^{-1}$; the concentration then decreased with increasing $[\text{AC}]$. The concentrations of PFHxA was higher than the other PFCAs, this compound is therefore plotted separately in Figure B6, Appendix B. As for the PFCAs, the concentrations of PFSA in soil 1 were highest for $[\text{AC}] 2.5 \text{ g L}^{-1}$; the concentrations then decreased with increased concentrations of AC.

The PFAS concentrations in soil AS showed a similar trend, however the decrease in concentrations for $[\text{AC}] 25 \text{ g L}^{-1}$ was not as distinct as for soil 1. The concentrations detected in soil AS are presented in Figure B5, Appendix B.

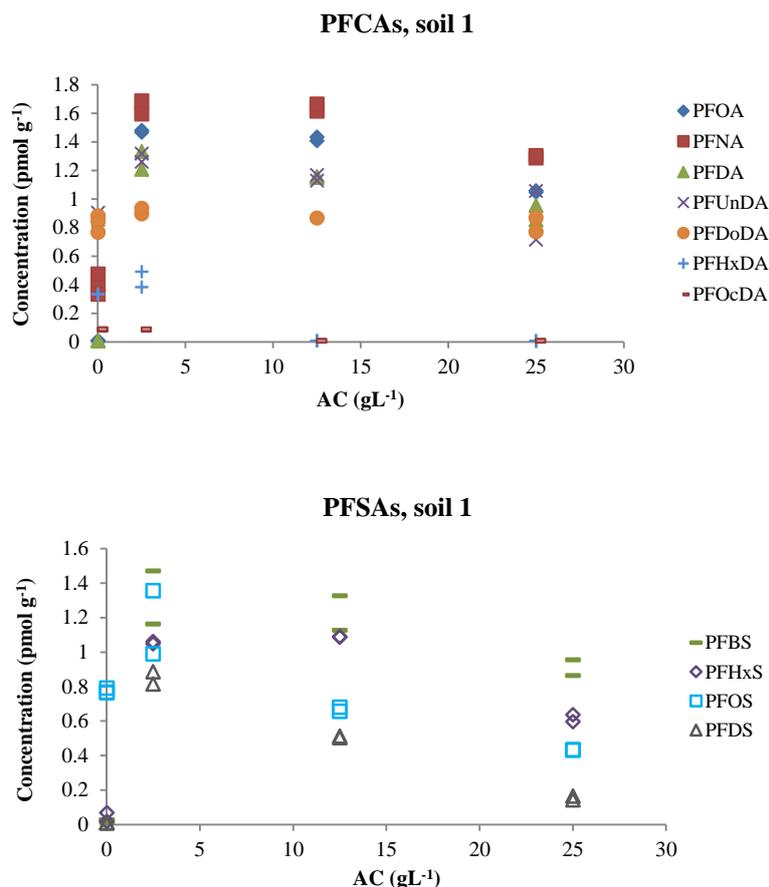


Figure 11. Scatter plot over concentrations (pmol L⁻¹) of PFCAs (upper plot) and PFASAs (lower plot) detected in soil 1 at different concentrations of AC (g L⁻¹) (i.e. 0, 2.5, 12.5 and 25 g L⁻¹).

The mass balances of PFASs in the AC experiments decreased with increased concentrations of AC (Figure B7 and Figure B8, Appendix B) reflecting the decrease in concentrations of PFASs detected in soil.

4.8 Calcium ions

In order to investigate the influence of Ca²⁺ ions on the sorption of PFASs to soil the log K_d values calculated for PFASs in the Ca²⁺ experiments were plotted as a function of log [Ca²⁺] (Figure 12). In soil 1 the log K_d values of all PFASs increased to a log [Ca²⁺] of -2.3 M ([Ca²⁺] 5 mM) above which the values stagnated. The same trend was observed for the PFASs in soil AS except for PFDS who showed a constant increase from the lowest Ca²⁺ concentration to the highest (i.e. from [Ca²⁺] 0 mM to [Ca²⁺] 200 mM). Also, the log K_d values for PFBS and PFHxS did not change with varying Ca²⁺ concentrations. No log K_d values could be calculated for PFHxDA, PFNA, PFDoDA, PFHxDA, PFOcDA and PFDS for soil 1. For soil AS no values could be calculated for PFNA, PFDoDA, PFHxDA and PFOcDA.

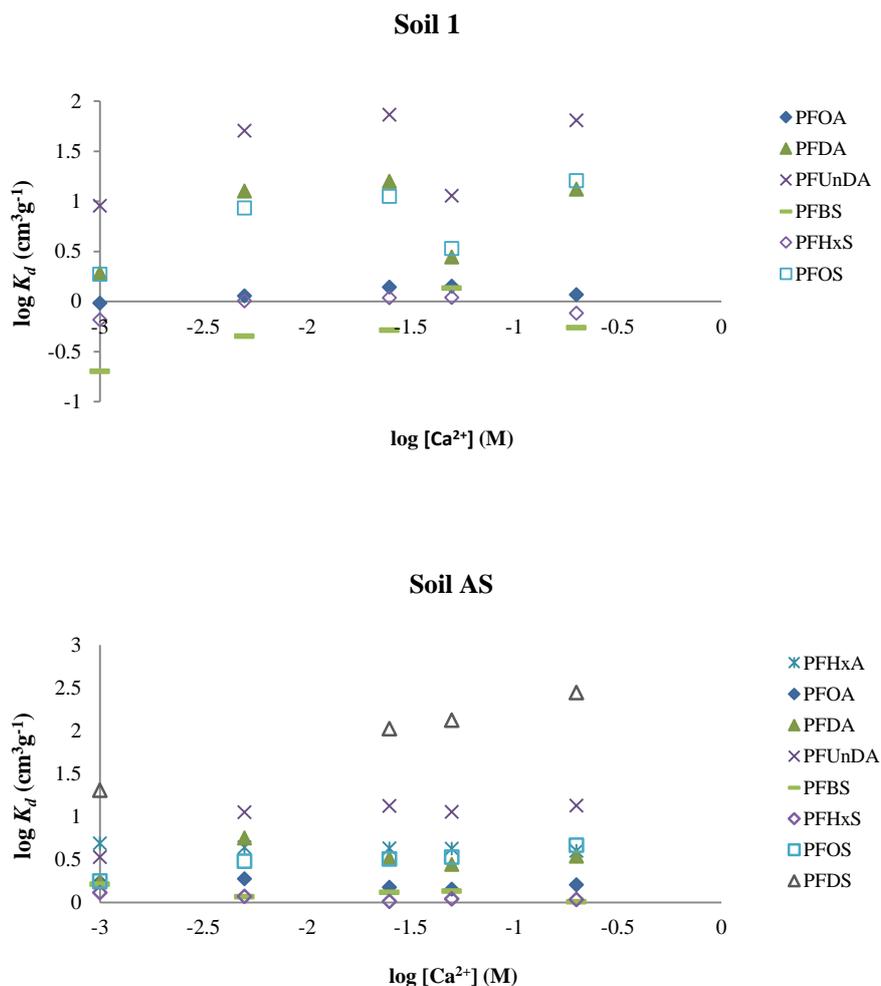


Figure 12. The upper scatter plot illustrates the correlation between $\log K_d$ (cm^3g^{-1}) and $\log [\text{Ca}^{2+}]$ (M) in soil 1. The lower plot shows the same correlation in soil AS.

Since no $\log K_d$ values could be calculated for PFHxDA, PFNA, PFDoDA, PFHxDA, PFOcDA and PFDS in soil 1 and for PFNA, PFDoDA, PFHxDA and PFOcDA in soil AS the concentrations of PFASs in soil were also investigated. As illustrated in Figure 13 the concentration of all PFASs except PFDoDA and PFHxS increased until a Ca^{2+} concentration of 50 mM, above which the concentrations stagnated. The increase in soil PFAS concentrations were substantially higher from $[\text{Ca}^{2+}]$ 0 mM to $[\text{Ca}^{2+}]$ 5mM than for $[\text{Ca}^{2+}] > 5$ mM. For PFOA, PFDA and PFUnDA the concentrations decreased for $[\text{Ca}^{2+}]$ 200 mM. The concentration of PFDoDA increased to the highest $[\text{Ca}^{2+}]$ (i.e. $[\text{Ca}^{2+}]$ 200 mM). The concentration of PFHxS showed a slight decrease from the lowest $[\text{Ca}^{2+}]$ to the highest. A similar trend was observed for the PFASs in soil AS (Figure B9, Appendix B). The concentrations of PFASs detected in water are presented in Figure B11, Appendix B.

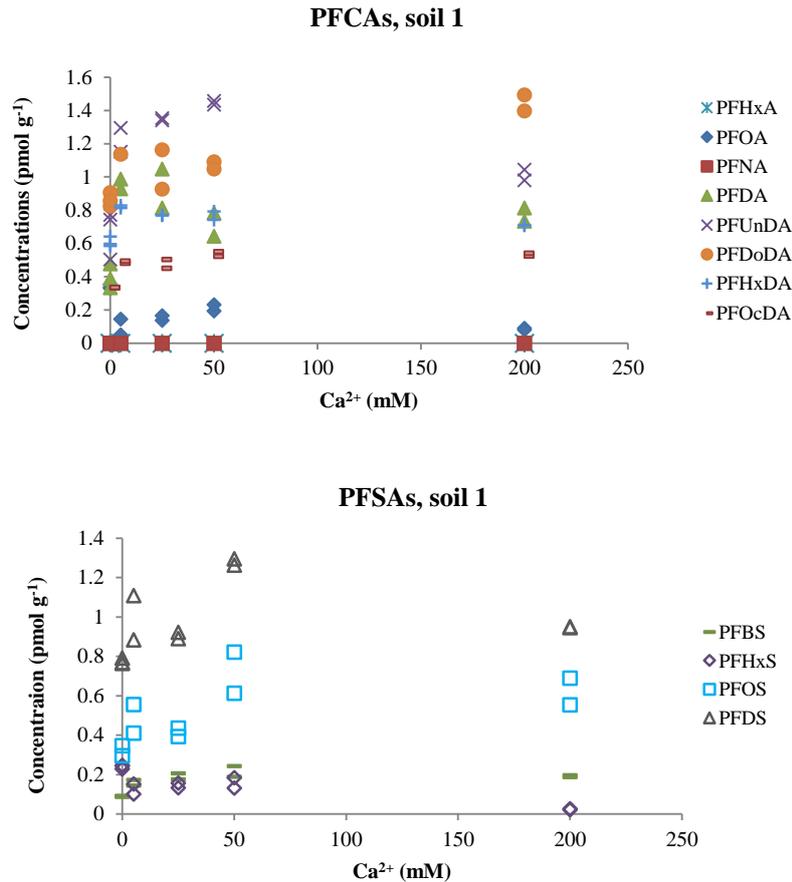


Figure 13. Scatter plot over concentrations (pmol g^{-1}) of PFCAs (upper plot) and PFSA (lower plot) detected in soil 1 at different concentrations of Ca^{2+} ions (mM) (i.e. 0, 5, 25, 50 and 200 mM).

4.9 Field contaminated samples

The sum of PFAS concentrations detected in water (C_w) and in soil (C_s) for the field contaminated samples shaken using Millipore water for 240 hours were compared with the concentrations detected from the directly extracted samples (Table 8). The directly extracted samples were extracted without shaking with Millipore water. Therefore all concentrations for these samples were detected in the soil extract. The concentrations in the shaken samples were generally higher than the concentrations detected in the directly extracted samples. For the samples with $[\text{PFAS}] > 20 \text{ pmol L}^{-1}$ the concentrations detected in shaken samples were a factor 1.2 (PFOS) to 2.2 (PFOA) higher than the concentrations detected in the directly extracted samples.

Table 8. Difference between total concentrations detected in contaminated samples (pmol g^{-1}) for samples extracted directly without shaking with Millipore water and for samples extracted after 240 hours of shaking with Millipore water.

	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFBS	PFHxS	PFOS
C_s in Directly extracted samples (pmol g^{-1})								
C1	35	14	10	6	3	1	11	423
C2	24	17	3	1	0	1	14	167
C3	10	3	2	0	0	1	11	30
C4	4	1	0	0	0	1	17	159
C_s + C_w after 240 h shaking using Millipore water (pmol g^{-1})								
C1	60	28	15	6	3	2	18	512
C2	43	37	6	1	1	2	22	204
C3	16	6	0	0	0	1	15	26
C4	6	3	0	0	0	2	26	214

4.10 Uncertainties

PFASs are very inclined to stick to surfaces. To avoid losses of PFASs to tube walls PP tubes were used for all steps in the experiment. However, the mass balances showed that the recovery was not 100 % for all samples. Based on the mass balances, the longer chained PFCAs ($C > 10$) and PFSAs ($C = 10$) seemed to be more sensitive to losses during the experiment process. The losses might have been caused by adsorption to tube walls, syringes, syringe filters or other surfaces that the PFASs came in contact with.

Figure 14 illustrates the losses of suspended solids that took place in the filtration process. This might have been a source of PFAS losses. However these potential losses were not measured.

Additionally, each instrument used in the method contributed to an extra potential error source due to the accuracy range of each instrument. Also, the human factor, for example difficulties to apply the same pressure to all pipettings and difficulties for the eye to measure exact levels of liquids in measuring cylinders and tubes adds another important factor to the error sources.



Figure 14. Syringe filters before (left) and after (right) filtration of one sample. Some suspended solids were stuck in the syringe filters. This might have act as a source for PFASs losses in the experiment method. These potential losses were however not measured.

5 Discussion

5.1 Equilibrium tests

The time for individual PFASs to reach equilibrium (Figure 6 and Figure 7) in the equilibrium test was in good agreement with previous results both for the spiked samples (Ahrens et al., 2011; You et al., 2010; Pan et al., 2009; Johnson et al., 2007) and the non-spiked samples (Nordskog, 2012; Navarro et al., 2008; Higgins and Luthy., 2006). Some previous studies have suggested 8 (Pan et al., 2010) and 24 (You et al., 2010) hours to be sufficient time to reach equilibrium for PFOS-contaminated sediments. This study, however, indicated that the equilibrium time for PFOS in field contaminated soil is much longer (i.e. 240 hours).

5.2 Distribution coefficients, K_d and K_{oc}

The log K_d values differed between the different soils (Table B1 through B4, Appendix B). This was expected since the TOC concentrations of the soils differed. According to the hypothesis, the TOC concentration would have a positive effect on the sorption of PFASs to soil. Thereby, soils with higher TOC concentrations were expected to have higher K_d values than soils with lower TOC contents. The standard deviations for the log K_d values ranged between 0.1 to 0.6 log units or 30 % to 602 % (PFDS being the exception with a standard deviation of 16%). When normalizing the log K_d values for organic carbon, the standard deviations decreased substantially (i.e. 0.1 to 0.3 log units or 4 % to 19 %). This indicated that the TOC concentration was the most important parameter in soil 1, 2, 3, C1, C2, C3 and C4 to influence the sorption of PFASs to soil. This assumption was strengthened by the linear correlation observed between log K_d and TOC in soil 1, 2 and 3 (Figure 9).

The average log K_{oc} value for PFOA observed in this study (i.e. 1.8 ± 0.3) was lower than reported in previous studies (i.e. 1.9 ± 0.1 (Ahrens et al., 2010) 2.1 Higgins and Luthy, 2006), 2.4 ± 0.1 (Ahrens et al., 2010) and 2.6 ± 0.3 (Kwadjik et al., 2010)) However, these values were all calculated from partitioning experiments performed on sediments. The average log K_{oc} value for PFOS in this study (2.8 ± 0.3) was in good agreement with the results reported for PFOS in kaolinit, clay loam and sandy loam reported by Johnson et al. (2007), i.e. 2.4 for kaolinit, 2.6 for clay loam and 3.1 for sandy loam. Also, the log K_{oc} value in this study was within the range reported in previous studies on PFOS in sediment (2.4 to 2.8 (Johnson et al., 2007), 2.6 (Higgins and Luthy, 2006), 3.2 ± 0.3 (Kwadjik et al., 2010), 3.6 ± 0.1 (Ahrens et al., 2010) and 3.7 ± 0.6 (Ahrens et al., 2011)).

The average log K_{oc} values for PFDA (2.7 ± 0.1) and PFUnDA (3.2 ± 0.2) agreed better with the values reported by Higgins and Luthy, 2006, (i.e. 2.8 ± 0.1 (PFDA) and 3.3 ± 0.1 (PFUnDA)) than with the values reported by Ahrens et al., 2010, (i.e. 3.6 ± 0.1 (PFDA) and 4.8 ± 0.2 (PFUnDA)). The values calculated for PFNA and PFHxS was lower than previously reported results (i.e. 2.0 ± 0.1 (PFNA) and 1.9 ± 0.1 (PFHxS) vs 2.4 ± 0.1 (PFNA) and 3.6 ± 0.1 (PFHxS) (Ahrens et al., 2010) and 2.4 ± 0.09 (PFNA) (Higgins and Luthy, 2006)). Further, the log K_{oc} value for PFDS (3.8 ± 0.3) was in good agreement with the log K_{oc} reported by Higgins and Luthy (2006) (i.e. 3.5 ± 0.1). All log K_{oc} values reported by Ahrens et al. (2010) and Higgins and Luthy (2006) were determined from partitioning experiments performed on sediments.

Both the log K_d values and the log K_{oc} values were generally lower for all PFASs in the artificial soil (soil AS), which means that the sorption of all PFASs was lower in soil AS than in the natural soils. Further, the influence of carbon chain length and functional group did not show as strong influence on the sorption of PFASs in soil AS as in the natural soils (Figure 8 compared to Figure B2, Appendix B). The PFASs obviously behaved differently in the artificial soil than in the natural soils. The reason for this was however not clear.

5.3 Influence of chain length and functional group

A positive correlation was observed between carbon chain length and sorption of PFASs to soil. The sulfonic group was also found to positively influence the sorption (Figure 8). These results were in good agreement with previous results (Nordskog, 2012; Ahrens et al., 2011; Ahrens et al., 2010; Kwadjik et al., 2010, Ahrens et al., 2009, Johnson et al., 2007; Higgins and Luthy, 2006). Each CF_2 moiety was found to contribute to an increase of the log K_{oc} with 0.4 to 0.6 log units for the longer chained PFASs ($C \geq 8$). Additionally, each sulfonate moiety was found to contribute with an extra increase of 0.5 to 0.6 log units.

These values were in good agreement with the results found by Higgins et Luthy (2006) (0.50 to 0.60 log units increase per CF_2 moiety and an extra 0.23 log units increase per sulfonate moiety) and Ahrens et al. (2010) (0.52 to 0.75 log units increase for each additional CF_2 moiety and an extra 0.71 to 0.76 log units increase per sulfonate moiety). However, in this study the influence of the chain length on the log K_{oc} value was substantially lower for the shorter chained PFASs ($C < 7$) (0.1 log units increase per CF_2 moiety for the PFCAs and 0.3 log units increase per CF_2 moiety for the PFASs).

5.4 Organic carbon

The log K_d values give a good picture of the sorption processes of PFASs in soil. However, the concentrations of some PFASs were under the MDL for either soil or water, and thus the log K_d values could not be calculated for these compounds (Figure 10 and Figure 11). Thereby, the PFAS concentrations in soil were also studied in order to investigate the influence of OC concentration on the sorption of PFASs.

The positive correlation between TOC concentration and sorption of PFASs found in the organic carbon experiments agreed well with results from previous studies (Jeon et al., 2011; Ahrens et al., 2010; You et al., 2010; Ahrens et al., 2009; Higgins and Luthy 2006). For all PFASs except PFOS and PFDA the log K_d value was found to increase with 0.1 log units per % increase of TOC. The corresponding values for PFOS and PFDA were 0.3 and 0.2 log units respectively (Figure 9).

Ahrens et al. (2010) found OC to have a greater influence on the sorption of PFUnDA and PFOS than on PFNA and PFDoDA. In agreement, this study showed that the TOC had a stronger influence on the sorption of PFUnDA and PFOS than on PFDoDA ($slope=0.15 \text{ pmol g}^{-1} \%^{-1}$ for PFOS ($R^2=0.91$), $slope=0.06 \text{ pmol g}^{-1} \%^{-1}$ for PFUnDA ($R^2=0.94$) and $slope=0.03 \text{ pmol g}^{-1} \%^{-1}$ for PFDoDA ($R^2=0.89$) (Figure 10)). No correlation was found between the sorption of PFNA and TOC concentration in any of the soils (Figure 10).

5.5 Active carbon

Since the concentration of most PFASs in the aqueous phase was under the MDL for the AC experiments, no log K_d values could be calculated. The concentrations in soil were therefore studied in order to investigate the influence of AC concentration on the partitioning of PFASs.

According to the hypothesis the sorption of PFASs would increase with increased concentrations of AC. The results presented in Figure 11 and Figure 12 however, showed a somewhat different behavior. The concentrations detected in soil increased to a level of [AC] 2.5 gL^{-1} above which the concentrations either stagnated or decreased with further addition of AC (i.e. [AC] 12.5 gL^{-1} and 25 gL^{-1}). The sorption of PFOcDA, however, decreased for [AC] $> 0 \text{ gL}^{-1}$. The PFASs detected in soil AS showed a similar trend as the PFASs in soil 1. However the decrease in PFAS concentrations for [AC] 25 gL^{-1} was not as distinct as for soil 1 (Figure B5, Appendix B).

Previous studies have shown that PFASs adsorb strongly to AC (Carter and Farrell, 2010; Senevirathna et al. 2010; Yu et al., 2009; Ochoa-Herrera and Sierra-Alvarez, 2008). This might be the reason for the decrease in PFAS concentrations observed for higher concentrations of AC. The extraction method does not seem to have been sufficient to break some of the strong bonds between the PFASs and the AC. As the AC concentration increased, more strong interactions seem to have been formed between the AC and the PFASs, limiting the efficiency of the soil extraction method. This would explain the decrease in PFAS concentrations detected for higher AC concentrations.

This theory was strengthened by the mass balances which decreased for most PFASs as the AC concentration increased (Figure B7 and Figure B8, Appendix B). The mass balances of all PFASs generally decreased with increased carbon chain length, indicating that the CF_2 chain length had a positive influence on the sorption of PFASs to AC. These results were in good agreement with the results reported by Ochoa-Herrera and Sierra-Alvarez, 2008.

The decrease in PFAS soil-concentrations observed for higher AC concentrations was more significant for the PFASs in soil 1 than in soil AS (Figure 11 and Figure 12 compared to Figure B5, Appendix B). The reason for this could be that the TOC concentration of soil AS was higher than that of soil 1 (4.2 % for soil AS vs 0.6 % for soil 1). Results from previous studies have shown the OC to be the most important natural soil parameter influencing the sorption of PFASs to sediments and soils (Ahrens et al., 2011; Ahrens et al., 2010; Higgins and Luthy, 2006). Thus in a soil with a higher OC content the strong interactions between the PFASs and the AC might be weakened by the counter forces from the OC. The soil extraction would thereby be more efficient for soils with higher concentrations of OC.

The increase in PFAS soil-concentrations observed for both soils from [AC] 0 g L^{-1} to [AC] 2.5 g L^{-1} might have been a result of the effect from the OC on the adsorption strength between the PFASs and the AC discussed above. Some of the interactions would then have been weak enough for the soil extraction to break, why higher concentrations of PFASs were detected in soil containing [AC] 2.5 g L^{-1} than [AC] 0 g L^{-1} .

The strong adsorption observed for PFASs to AC confirms the findings of Carter and Farell (2010), Senevirathna et al. (2010), Yu et al. (2009) and Ochoa-Herrera and Sierra-Alvarez (2008). The results indicate that AC could be an effective remediation agent for PFASs in water as well as in soil and sediment, especially for the longer chained PFASs.

5.6 Calcium ions

Since no $\log K_d$ values could be calculated for PFDODA, PFHxDA and PFOcDA in the calcium experiments both the $\log K_d$ values and the concentrations detected in soil had to be studied in order to create a picture of the partitioning processes in the calcium samples.

For soil 1 the sorption of all PFASs PFHxA and PFNA increased to a level of $[\text{Ca}^{2+}]$ 25 mM. For Ca^{2+} concentrations above this concentration further addition of Ca^{2+} had no or little influence on the sorption (Figure 12 and Figure 13). The largest increase was observed between $[\text{Ca}^{2+}]$ 0 mM and $[\text{Ca}^{2+}]$ 5 mM. The same trend was observed for the PFASs in soil AS except the stagnation in sorption was observed for $[\text{Ca}^{2+}] > 5$ mM (Figure B9, Appendix B). PFHxA and PFNA was found to be uninfluenced by the Ca^{2+} concentration.

The increase in sorption observed with increased addition of Ca^{2+} ions for $[\text{Ca}^{2+}] \leq 5$ mM, could be an effect of the potential neutralizing ability that the Ca^{2+} ions can have on the electrostatic repulsion between the anionic PFASs and the negatively charged organic matter and mineral surfaces. This theory was previously described by You et al. (2010), Higgins and Luthy (2006) and Hyun and Lee (2005). When the Ca^{2+} concentration increases the repulsion decreases benefitting both electrostatic and hydrophobic interactions (Tang et al., 2010; Ochoa Herrera and Sierra Alvarez, 2008; Higgins and Luthy 2006).

The increase in sorption observed for PFASs in soil from $[\text{Ca}^{2+}]$ 0 mM to $[\text{Ca}^{2+}]$ 5 mM was in good agreement with the results reported by Higgins and Luthy (2006). The stagnation in sorption observed for $[\text{Ca}^{2+}] > 5$ mM did however not agree with these results. Higgins and Luthy reported a constant increase in sorption of PFASs to sediment from $[\text{Ca}^{2+}]$ 0 mM to $[\text{Ca}^{2+}]$ 200 mM. The reason for the stagnation in sorption observed in this study was not clear. One reason could be that the sorption of PFASs was only partly controlled by electrostatic interactions. Above a certain level further decrease of electrostatic repulsion seem to have had no influence on the sorption. Above this level other interactions, such as hydrophobic/hydrophilic interactions, might have controlled the sorption. However, more studies need to be conducted in order to examine the chemical processes behind this behavior.

The increase in $\log K_d$ values was higher for all PFASs in soil 1 than in soil AS. The average $\log K_d$ values for the PFASs in soil 1 increased with 0.1 log units (PFOA) to 0.9 log units (PFUnDA and PFOS) from the lowest Ca^{2+} concentration to the highest (i.e. $[\text{Ca}^{2+}]$ 0 mM to $[\text{Ca}^{2+}]$ 200 mM) (Figure 12). The same values for the PFASs in soil AS increased from 0.04 log units (PFOA) to 0.7 log units (PFDS). The $\log K_d$ values of PFHxA, PFBS and PFHxS in soil AS showed no correlation with the Ca^{2+} concentration. The increase in $\log K_d$ values was highest for the longer chained PFASs ($C \geq 8$), indicating that the influence of Ca^{2+} ions was stronger for the longer chained PFASs than for the shorter chained ones ($C < 8$).

The higher influence of Ca^{2+} ions observed for the sorption of PFASs in soil 1 might have been a reflection of the higher CEC and pH measured for soil 1 compared to soil AS (i.e. CEC 9.9, pH 9.0 for soil 1 vs CEC 7.0, pH 6.2 for soil AS). The net charge of the soil particles was thereby likely more negative for soil 1 than for soil AS (Higgins and Luthy, 2006). The suppression of repulsive forces between PFASs and soil caused by the Ca^{2+} ions would then have had a stronger influence on the sorption of PFASs in soil 1 than in soil AS. This suggestion was in agreement with the results reported by You et al. (2010) who showed that the Ca^{2+} ions had a stronger effect on the sorption of PFOS at higher pH than at lower pH. However the correlation between pH increase and increased effect of the Ca^{2+} ions observed in this study was weaker than that reported in the study by You et al.

The different influence of Ca^{2+} ions on the sorption of PFASs in soil 1 and soil AS could however also be a result of the different sorption behavior observed for soil AS compared to the natural soils in the OC experiments. The reason for the differing sorption properties of the soils was however not clear.

Nordskog (2012) found the Ca^{2+} concentration to have a positive influence on the sorption of PFNA, PFDA and PFOS and a negative effect on PFHxA and PFBS. In agreement with these results this study found a positive correlation between Ca^{2+} concentration and sorption of PFOS and PFDA in both investigated soils. However, the influence of Ca^{2+} concentration on the sorption of PFBS was rather positive (soil 1) or uninfluenced (soil AS). Also, the sorption of PFHxA and PFNA was found to be uninfluenced by the Ca^{2+} concentration. These results were in contrast to the results reported by Nordskog.

The positive influence of Ca^{2+} ions observed for the sorption of PFASs for $[\text{Ca}^{2+}] \leq 5 \text{ mM}$ was in good agreement with previously reported results (You et al., 2010, Tang et al., 2010, Higgins and Luthy, 2006). The results were also in good agreement with the hypothesis of this study. The stagnation in effect of increased Ca^{2+} concentration observed for $[\text{Ca}^{2+}] > 5 \text{ mM}$, was however not included in the hypothesis.

5.7 Field contaminated samples

The log K_{oc} values calculated from PFASs detected in the field contaminated samples were similar to the ones calculated from spiked samples (Table 6 and Table 7). This indicates that similar amounts of PFASs will leach out from aged soil as from newly contaminated soils once equilibrium has been reached. The equilibrium time, however, differed substantially between spiked and field contaminated soils (i.e. 48 h for spiked samples vs 240 h for contaminated samples, Figure 6 and Figure 7). This indicated that the aged PFASs bind strongly to soil. As a result of these strong bonds aged PFASs will be washed out slowly from soil, forming a long term contamination source of PFASs in soil. The strong interactions between the aged PFASs and soil could also result in a decreased bioavailability of PFASs to plants and other biota such as earthworms.

Another interesting observation was that the total concentrations of PFASs detected in the samples which had been shaken with Millipore water for 240 hours were generally higher than concentrations detected in the directly extracted samples, where no water had been added to the soil (Table 8). PFOS was by far the PFAS detected in highest concentrations in soil C1,

C2 and C4 (204.3 pmol L⁻¹ to 511.7 pmol L⁻¹ for the shaken samples). The PFOS concentrations detected in the shaken samples were a factor of 1.2 to 1.3 higher than the concentrations detected in the directly extracted samples. The largest difference in concentrations between the shaken and directly extracted samples was, however, found for PFOA. The average concentrations of PFOA detected in the shaken soil samples were a factor 1.8- 2.2 higher than the concentrations detected in the directly extracted samples. For PFHxA the same factor ranged between 1.5 and 1.8, and for PFHxS the factor ranged between 1.4 and 1.7. The results indicate that the soil extraction method (normally used directly without initial shaking with water (Powley et al., 2005)) was not sufficient enough to extract many of the aged PFASs from soil.

The soil extraction method used in this study is one of few methods developed for extracting PFASs from solid environmental matrixes (Powley et al., 2005). The result suggests that the time for which the samples are shaken with methanol (30 minutes times two) might be insufficient to extract all PFASs from contaminated matrixes. It is therefore of interest to further investigate the sufficiency of the extraction method.

6 Conclusions

PFASs are a large group of organic chemicals with different physiochemical properties. This study has focused on two subgroups, PFCAs and PFSA. The structure of the PFASs in these two groups are similar, however, the functional group of the PFCAs and PFSA differ. For the PFCAs the functional group consists of a carboxylic group while the functional group of the PFSA is a sulfonic group. This difference in functional group was found to have a significant effect on the sorption of PFASs to soil. Also, the carbon chain length was found to be an important parameter influencing the sorption.

For all batch experiments, the number of CF₂ moieties was found to positively influence the sorption of PFASs to soil. Each CF₂ moiety was found to contribute to an increase of the log *K*_{oc} value with 0.4 to 0.6 log units for the longer chained PFASs (C ≥ 7) (Figure 8). These results were in good agreement with the hypothesis which stated that the sorption would increase with increased chain length. The chain length had however a lower influence on the partitioning of the shorter chained PFASs (C < 7). Further the sulfonic group of the PFSA was found to have a positive influence on the sorption to soil. Each sulfonate moiety was found to contribute with an extra increase of the log *K*_{oc} value with 0.5 to 0.6 log units for the longer chained PFSA (C ≥ 7).

Organic carbon was found to be a soil parameter of great importance for the sorption of PFASs to soil. The log *K*_d value increased with 0.1 log units per % increase of TOC for all PFASs except PFOS and PFDA who increased with 0.3 and 0.2 log units respectively (Figure 9). This positive correlation between sorption of PFASs and TOC concentration was in good agreement with the hypothesis. Ca²⁺ ions were also found to positively influence the sorption of PFASs to soil, however, the influence was not as strong as for the TOC (Figure 12 and Figure 9). The average log *K*_d values for all PFASs increased to a [Ca²⁺] level of 5 mM above which the values stagnated. The sorption of PFHxA and PFNA was not influenced by the Ca²⁺ concentration. The positive influence of Ca²⁺ ions on the sorption of PFASs were in

good agreement with the hypothesis. However, the stagnation in effect of Ca^{2+} concentration observed for $[\text{Ca}^{2+}] > 5\text{mM}$ was unexpected. More studies need to be conducted in order to understand the chemical processes underlining this behavior.

The interactions between the AC and PFASs were strong, especially for the longer-chained PFASs. Some interactions were even too strong for the soil extraction method to break. The concentrations of PFASs detected in soil increased to a [AC] level of 2.5 g L^{-1} . For $[\text{AC}] > 2.5\text{ g L}^{-1}$ the concentrations stagnated or decreased (Figure 11). The decrease was believed to be a reflection of the insufficiency of the soil extraction method to break the strong bonds between the AC and the PFASs. As the AC concentration increased, more strong interactions could be formed between the AC and the PFASs. The sufficiency of the soil extraction thereby decreased as the AC concentration increased. The strength of the interactions between the PFASs and the AC seemed to correlate with carbon chain length, indicating that the chain length had a positive influence on the sorption of PFASs to AC. The strong influence that the AC showed on the sorption of PFASs was in good agreement with the hypothesis. All PFASs in the AC samples were sorbed to either the AC or the soil. For all AC samples, no PFASs could be detected in the water phase. This shows that, out of all studied parameters, the AC had the strongest influence on the sorption of PFASs.

The equilibrium time for the field contaminated and spiked soils differed substantially (i.e. 48 h for spiked samples vs 240 h for contaminated samples, Figure 6 and Figure 7). This result indicated strong interactions between the aged PFASs and soil, as was also suggested by the hypothesis. Aged PFASs might thereby be washed out slowly from soil, forming a source of long term contamination of PFASs in soil. Also, the strong bonds resulting from aging could potentially decrease the bioavailability of PFASs to plants and other biota.

Further, the experiments with field contaminated samples unexpectedly found that the total PFAS concentrations detected in the contaminated soil samples that had been shaken with Millipore water for 240 hours were a factor 1.2 to 2.2 higher than concentrations detected in directly extracted contaminated soil samples. This result questions the sufficiency of the extraction method on contaminated soils.

The organic carbon-normalized distribution coefficients (K_{oc}) found in this study were within the range of previously reported K_{oc} values. The K_{oc} values showed a positive correlation with the carbon chain length of the PFAS molecules. The sulfonic group was shown to have a positive influence on the K_{oc} value. The $\log K_{oc}$ values calculated from this study decreased in the following order PFDS ($\log K_{oc} 3.8 \pm 0.3$) > PFUnDA ($\log K_{oc} 3.2 \pm 0.2$) > PFOS > ($\log K_{oc} 2.8 \pm 0.1$) > PFDA ($\log K_{oc} 2.7 \pm 0.009$) > PFNA ($\log K_{oc} 2.0 \pm 0.1$) > PFOA ($\log K_{oc} 1.9 \pm 0.2$) > PFHxS ($\log K_{oc} 1.9 \pm 0.1$) > PFHxA ($\log K_{oc} 1.7 \pm 0.3$) > PFBS ($\log K_{oc} 1.5 \pm 0.1$). No $\log K_{oc}$ values could be calculated for PFDoDA, PFHxDA and PFOcDA since the concentrations of these compounds were under the MDL for all water phases. These results, however, indicated that the three compounds sorbs strongly to soil.

The results from this study clear show that soils with high concentrations of TOC will retain PFASs more strongly than soils with lower TOC concentrations. The concentrations of Ca^{2+} ions and BC will also positively affect the sorption potential of the soil. Further, based on the

log K_{oc} values, both the carbon chain length and the functional group of the PFASs will affect the sorption. The longer-chained PFASs sorb more strongly to the soil than shorter-chained PFASs. The shorter-chained PFASs will thereby leach to the groundwater to a greater extent than the longer-chained PFASs. Also, due to the influence of the functional group, the PFASs will be retained more effectively in the soil than their PFCA analogs.

The risk for leaching of PFASs to the ground water, and thereby also potentially the drinking water, will be lower for soils with high concentrations of TOC, Ca^{2+} ions and BC. The risk will also decrease for soils contaminated with longer chained PFASs, especially PFASs. However, for these soils, the risk for long-term contamination will be higher, resulting in an increased risk of bioaccumulation in biota and long-term leaching to ground and surface waters. The bioavailability and leaching of PFASs will, however, potentially decrease with time due to the strong interactions formed between PFASs and soil as a result of aging.

The findings of this study can act as a supplement to previously reported results on the partitioning behavior of PFASs. The results can be used to evaluate the potential transport of PFASs from soil to groundwater in different soils. Even though the results of this study were generally in good agreement with previous results reported for sediment and soil, more research still needs to be performed in order to strengthen the knowledge about PFASs behavior in soil.

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Appendix A

Characterization

The samples were dried at 105 °C and then analyzed for organic matter and grain size distribution. Part of the soil was homogenized with a mortar and sieved through a 2 mm sieve. Approximately 10 mL of each sample was collected for determination of organic matter through incineration at 550 °C for 3 hours. The mass before and after incineration was documented and the fraction of organic matter was calculated as the weight loss after incineration divided with the weight before incineration as described in equation A1.

$$f_{om} = \frac{m_{before} - m_{after}}{m_{before}} * 100\% \quad (A1)$$

Where f_{om} is the fraction organic matter, m_{before} is the mass before incineration, and m_{after} is the mass after incineration. The fraction of organic matter was corrected for clay content with equation A2.

$$f_{omcor} = f_{om} - (0.0075 + 0.1c) * 100\% \quad (A2)$$

Where f_{omcor} is the corrected fraction organic carbon, f_{om} is the calculated fraction of organic carbon and I_c is the fraction of clay. The total organic carbon (TOC) concentration was calculated by multiplying the concentration of organic matter with a factor of 0.58 as described by Schumacher, 2002.

In order to determine the fractions of grain size classes < 2 mm, 50 g of dried sieved soil from each sample was collected for sedimentation. Each sample was diluted with 100 mL of dispersing agent and then shaken in a mechanical shaker for 4 hours. The mixed samples were then placed in sedimentation cylinders and diluted with water to 1 L. The suspensions were agitated vigorously until full suspension was obtained. The density of the suspensions was then measured with a hydrometer after 0.5, 1, 3, 8, 20, 100 and 1000 minutes. Before the sedimentation start the hydrometer was calibrated in clean tap water. The measured values were corrected from the value obtained in the calibration (-4 mm). The sedimentation process is visualized in Figure A1. The pH of each suspension was measured with a pH-meter. The results are listed in Table 3 in the main report.

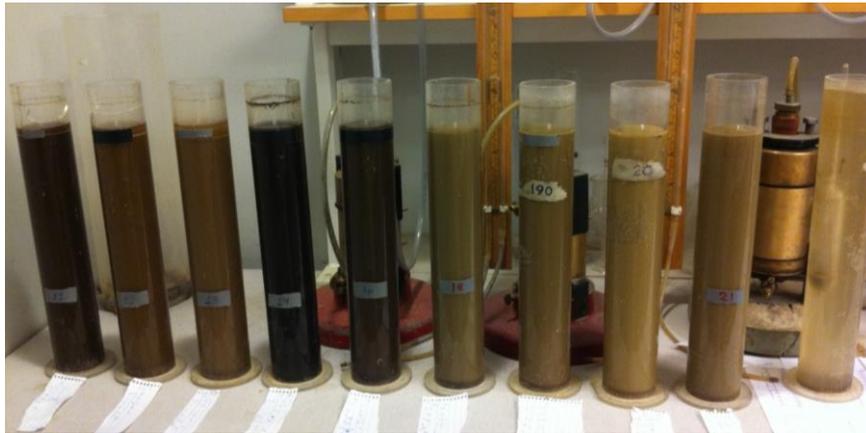


Figure A1. Sedimentation cylinders with 50g of soil, 100 ml of dispersing agent and 1 L of water. The suspension was agitated vigorously and the density of the suspension was measured with a hydrometer (far right) after 0.5, 1, 3, 8, 20, 100 and 1000 minutes. The results was used in order to determine the fractions of grain sizes < 0.063 mm.

The fractions of grain size classes > 0.063 mm were determined with dry separation through sieving. The remaining parts of the dried soil samples were weighed and then washed through a 0.063 mm sieve with tap water. The washing was done in order to prevent the smaller fractions to disturb the separation process. After washing the samples were dried at 105 °C. Each sample was then separated through dry sieving and the weight of different size fractions were documented. Swecos soil characterization program GeoSiktNET was used in order to create sieving curves for all characterized soils. The sieving curves were based on the documented data from the dry sieving and the sedimentation. The sieving curves are presented in Figure A2 through A5.

Sieving curves

The sieving curves for the examined soils are presented with the original sample names. The samples were renamed for the thesis in order to facilitate for the reader. In Table A1 the soil samples are listed with their respective sample alias. The samples collected from F18 airport all starts with the prefix SLU while the soils collected from the firefighting training site airport starts with the prefix B. Soil SLU 6 were among the contaminated soils used for the experiments.

TableA1. Sample name with corresponding alias that was used in the report. Also, the x- and y-coordinates are listed for the SLU samples.

Sample	Sample alias	X-coordinate	Y-coordinate
SLU soil 1	soil 2	6564351	1621081
SLU soil 2	soil 4	6564280	1620916
SLU soil 3	soil 5	6564922	1620820
SLU soil 4	soil 3	6564977	1620781
SLU soil 5	soil 1	6564049	1612036
SLU soil 6	soil C4	6563546	1620796
B2 0-0.1 m	soil C1		
B2 0.1-0.3 m	soil C2		
B3 0.0-0.1 m	soil C3		
Artificiell	soil AS		

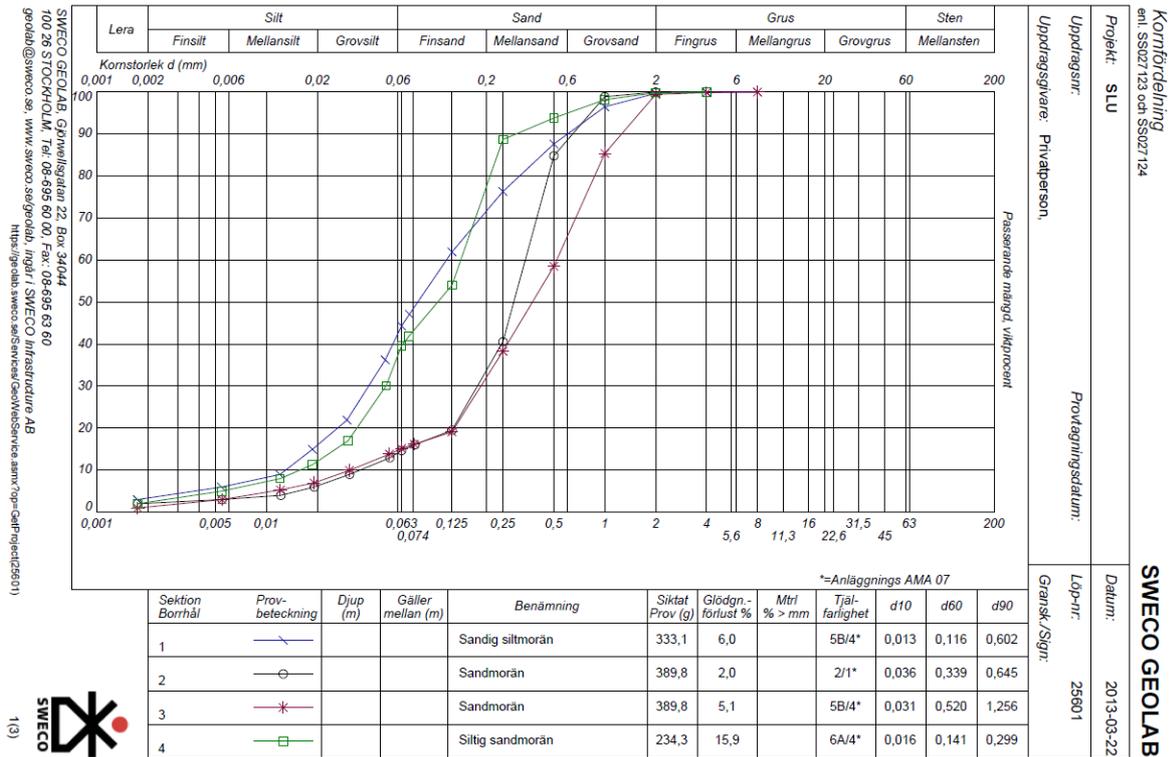


Figure A2. Sieving curves for soil SLU 1 (1), SLU 2 (2), SLU 3 (3), SLU 4 (4). The soils went under following alias in the report: SLU 1: soil 2, SLU 2: soil 4, SLU 3: soil 5, SLU 4: soil 3.

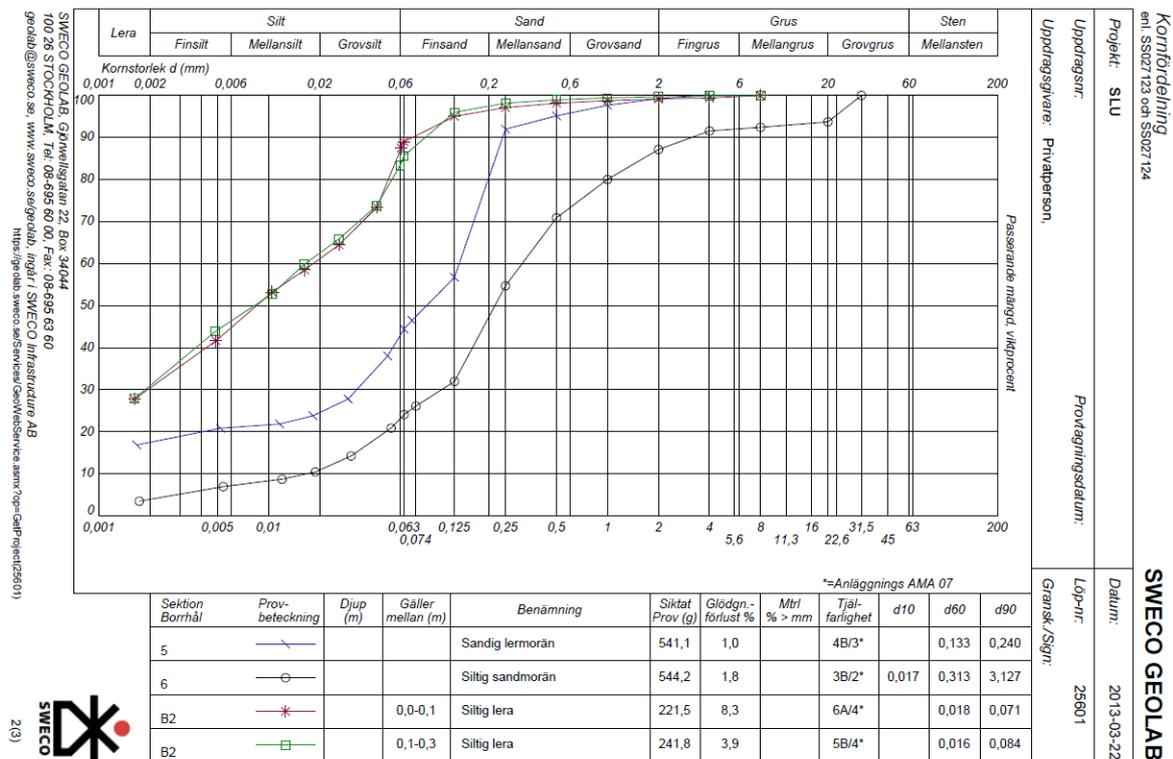


Figure A3. Sieving curves for soil SLU 5 (5), SLU 6 (6), B2 0.0-0.1 and B2 0.1-0.3. The soils went under following alias in the report: SLU 5: soil 1, SLU 6: soil C4, B2 0.0-0.1: soil C1, B2 0.1-0.3: soil C2.



Figure A4. Sieving curve for soil B3 0.0-0.1. The soil went under the alias soil C3 in the report.

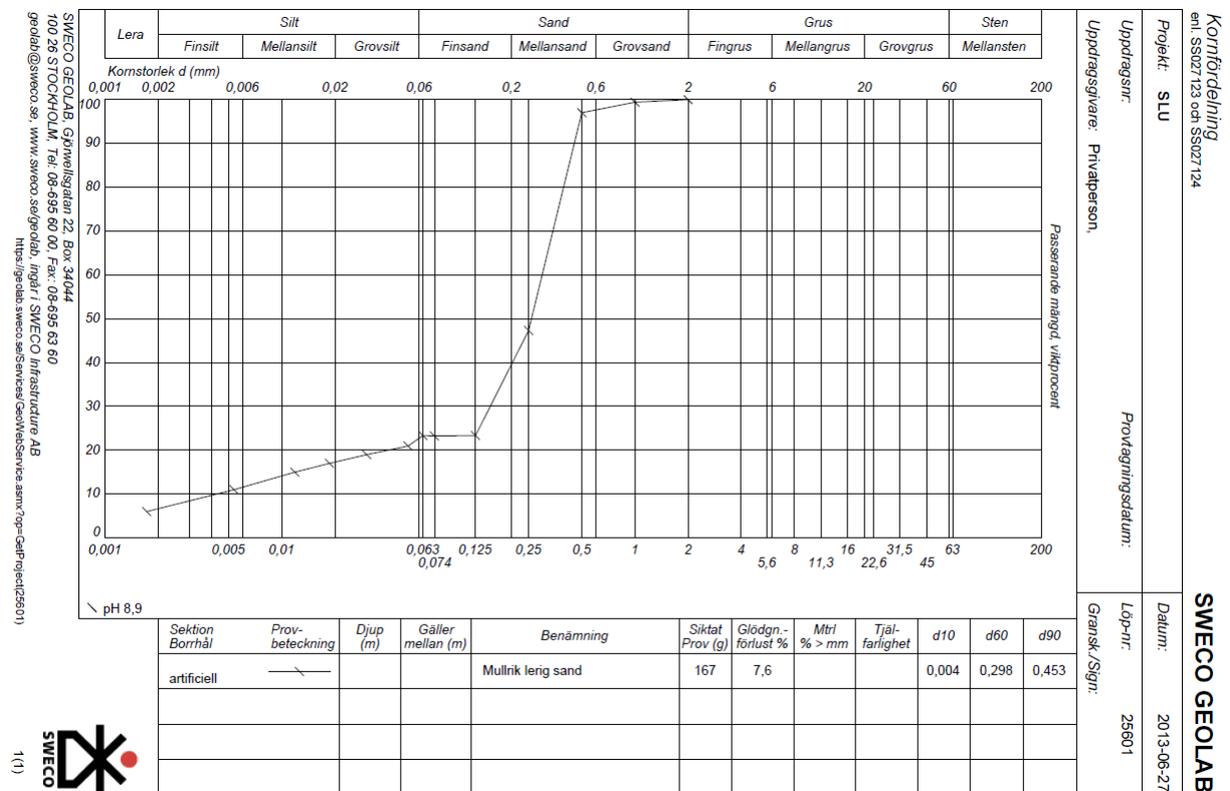


Figure A5. Sieving curve for the artificial soil (artificiell). The soil went under the alias soil AS in the report.

Appendix B

Results

Equilibrium tests

The results for PFHxA from the equilibrium test are presented in Figure B1. The compound reached equilibrium after 24 hours in soil 1 and 48 hours in soil AS.

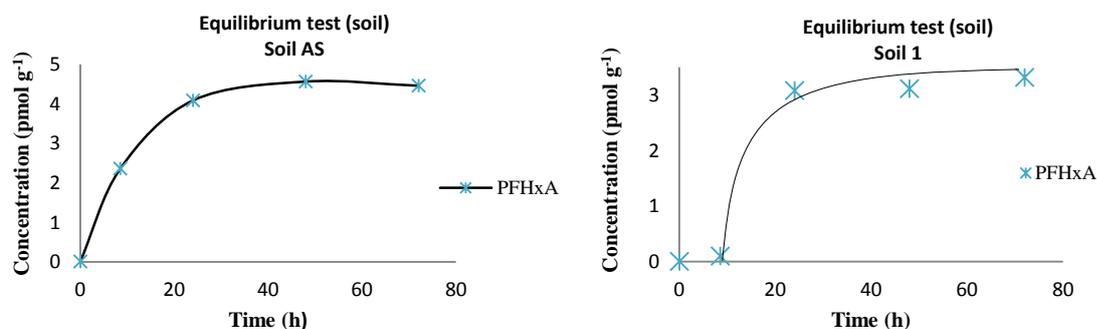


Figure B1. The scatter plots show how the concentration of PFHxA (pmol g⁻¹) changes with time for soil 1, upper plot, and soil AS, lower plot.

Distribution coefficients, K_d and K_{oc}

Table B1 and Table B2 lists the log K_d and log K_{oc} values calculated from PFAS concentrations detected in soil and water from the organic carbon experiments ((i.e. soil 1, soil 2, and soil 3). The [TOC] differed from 0.6 % (soil 1) to 9.2 % (soil 3). The [TOC] for soil 2 was 3.5 %. The average log K_{oc} value ranged from 1.4 ± 0.1 for PFBS to 3.8 ± 0.1 for PFDS. No K_d and K_{oc} values could be calculated for PFDoDA, PFHxDA and PFOcDA since no concentrations of compound was detected in the water phase after equilibrium. This was also the case for PFHxA in soil 1 and soil 2.

Table B1. Calculated log K_d (cm³g⁻¹) values from experiments with soils containing different amounts of organic carbon (TOC). Soil 1 had the lowest TOC (0.6 %) and soil 3 had the highest TOC (9.2 %).

	Log K_d (cm ³ g ⁻¹)							
	Soil 1	<i>n</i>	Soil 2	<i>n</i>	Soil 3	<i>n</i>	Average	<i>n</i>
PFHxA					1.0±0.02		1.3	8
PFOA	-0.02±0.03	3	0.4±0.03	2	1.1±0.005	3	0.5±0.4	8
PFNA								
PFDA	0.3±0.1	3	1.1±0.01	2	1.9±0.03	3	1.1±0.6	8
PFUnDA	1.0±0.1	3	1.4±0.03	2	2.2±0.03	3	1.5±0.5	8
PFDoDA								
PFHxDA								
PFOcDA								
PFBS	-0.7±0.03	3	-0.2±0.04	2	0.4±0.02	3	-0.2±0.4	8
PFHxS	-0.2±0.0.03	3	0.5±0.004	2	1.0±0.005	3	0.5±0.5	8
PFOS	0.3±0.0	3	1.3±0.03	2	2.5±0.03	3	1.4±0.9	8
PFDS	1.9±0.1	3	2.0±0.0	2	2.7±0.1	3	2.2±0.4	8

Table B2. Calculated log K_{oc} values (cm^3g^{-1}) from experiments with soils containing different amounts of organic carbon (TOC). Soil 1 had the lowest TOC (0.6 %) and soil 3 had the highest TOC (9.2 %).

	Log K_{oc} (cm^3g^{-1})							
	Soil 1	<i>n</i>	Soil 2	<i>n</i>	Soil 3	<i>n</i>	Average	<i>n</i>
PFHxA					2.0±0.02	3	2.0	3
PFOA	2.2±0.03	3	1.8±0.03	2	2.1±0.005	3	2.0±0.2	8
PFNA								
PFDA	2.5±0.1	3	2.6±0.01	2	2.9±0.03	3	2.7±0.2	8
PFUnDA	3.2±0.1	3	2.8±0.03	2	3.3±0.03	3	3.1±0.2	8
PFDODA								
PFHxDA								
PFOcDA								
PFBS	1.5±0.03	3	1.3±0.04	2	1.4±0.02	3	1.4±0.1	8
PFHxS	2.1±0.03	3	1.9±0.004	2	2.1±0.005	3	2.0±0.1	8
PFOS	2.5±0.0	3	2.7±0.03	2	3.5±0.03	3	2.9±0.4	8
PFDS	4.2±0.1	3	3.4±0.0	2	3.8±0.1	3	3.8±0.3	8

Calculated log K_d and log K_{oc} values for the field contaminated samples ($n=2$) are listed in Table B3 and Table B4. An empty row means that no concentration of the specific PFAS was detected in the soil. The average log K_{OC} value ranged from 1.4±0.2 for PFHxA to 3.4±0.0 for PFUnDA. The [TOC] decreased as follows 4.8 % (soil C1) > 3.4 % (soil C3) > 2.3 % (soil C2) > 1.0 % (soil C4).

Table B3. Calculated log K_d values ($n=2$) from experiments with field contaminated soils. Soil C4 had the lowest TOC (1.8 %) and soil C1 had the highest TOC (8.3 %).

	log K_d (cm^3g^{-1})									
	Soil C1	<i>n</i>	Soil C2	<i>n</i>	Soil C3	<i>n</i>	Soil C4	<i>n</i>	Average	<i>n</i>
PFHxA	-0.1±0.01	2	-0.1±0.1	2	0.0±0.05	2			-0.1±0.1	6
PFOA	0.1±0.003	2	-0.1±0.1	2	0.2±0.1	2	0.2±0.03	2	0.1±0.2	8
PFNA	0.6±0.05	2	0.4±0.1	2					0.5±0.1	4
PFDA	1.2±0.1	2	1.1±0.02	2					1.2±0.1	6
PFUnDA	2.1±0.004	2					1.4±0.2	2	1.8±0.5	4
PFBS	0.2±0.1	2	0.1±0.2	2	-0.03±0.1	2	-0.1±0.2	2	0.0±0.1	8
PFHxS	0.3±0.02	2	0.2±0.1	2	0.4±0.1	2	-0.002±0.005	2	0.2±0.2	8
PFOS	1.2±0.03	2	1.1±0.1	2	1.5±0.03	2	0.8±0.002	2	1.1±0.3	8

Table B4. Calculated $\log K_{oc}$ values ($n=2$) from experiments with field contaminated soils. Soil C4 had the lowest TOC (1.8 %) and soil C1 had the highest TOC (8.3 %).

	$\log K_{oc} (\text{cm}^3 \text{g}^{-1})$									
	Soil C1	n	Soil C2	n	Soil C3	n	Soil C4	n	Average	n
PFHxA	1.2±0.01	2	1.5±0.1	2	1.5±0.05	2			1.4±0.2	6
PFOA	1.4±0.05	2	1.6±0.1	2	1.6±0.1	2	2.2±0.03	2	1.7±0.3	8
PFNA	1.9±0.0	2	2.1±0.1	2					2.0±0.1	4
PFDA	2.5±0.1	2	2.8±0.02	2				2	2.6±0.2	6
PFUnDA	3.4±0.004	2					3.4±0.2	2	3.4±0.02	4
PFBS	1.5±0.1	2	1.8±0.2	2	1.4±0.1	2	1.8±0.2	2	1.6±0.2	8
PFHxS	1.6±0.02	2	1.8±0.1	2	1.9±0.1	2	2.0±0.005	2	1.8±0.2	8
PFOS	2.5±0.03	2	2.7±0.1	2	3.0±0.03	2	2.7±0.002	2	2.7±0.2	8

Influence of carbon chain length and functional group

The influence of carbon chain length and functional group on the $\log K_{oc}$ value of the PFASs in soil AS is illustrated in Figure B2. The figure plots the $\log K_{oc}$ values for PFCAs and PFSAs as a function of CF_2 chain length. The carbon chain length seem to have had a positive effect on the $\log K_{oc}$ value for the longer chained PFCAs ($C > 9$) and the longer chained PFSAs ($C > 8$).

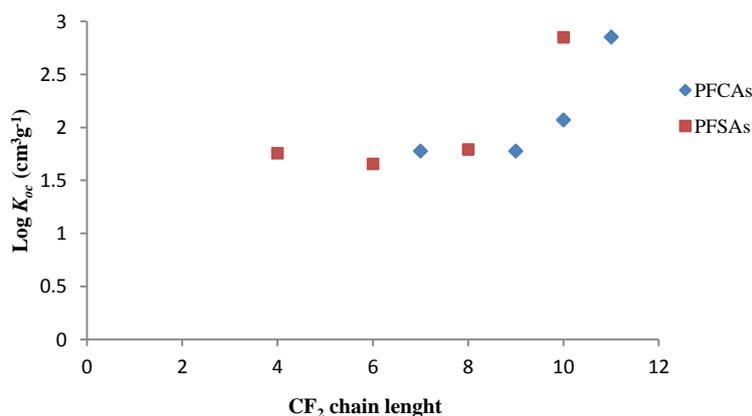


Figure B2. Average $\log K_{oc}$ ($\text{cm}^3 \text{g}^{-1}$) values for PFCAs and PFSAs plotted as a function of CF_2 chain length. The average $\log K_{oc}$ values were calculated from concentrations of PFASs detected in soil and water for soils 1, 2 and 3 in the organic carbon experiments and soils C1, C2, C3 and C4 in the experiments with field contaminated soils.

Organic Carbon

Figure B3 shows a scatter plot with concentrations of PFASs detected for different concentrations of TOC. The TOC concentrations ranged from 0.6 % (soil 1) to 9.2 % (soil 3). The TOC concentration of soil 2 and soil AS were 3.5 and 4.2 % respectively. Lines were drawn between the markers in order to illustrate the deviant behavior of soil AS (TOC 4.2 %).

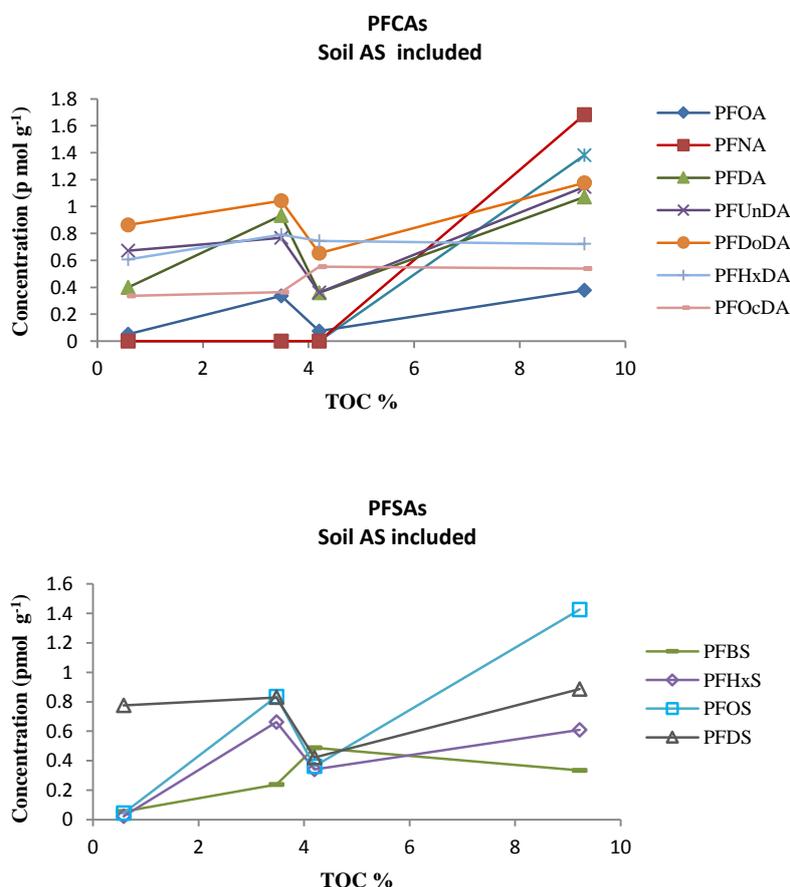


Figure B3. Scatter plot over concentration (pmol g^{-1}) of PFCAs (upper diagram) and PFSA (lower diagram) detected in soil at different TOC concentrations (%) (i.e. 0.6, 3.5, 4.2 and 9.2 %). In this plot the results for soil AS (TOC = 4.2 %) is included.

Figure B4 shows the concentration detected in water for soil 1, 2, and 3 (TOC = 0.6 %, 3.5 % and 9.2 % respectively). The PFAS concentration constantly decreased with increased [TOC] for all PFASs except for PFDoDA, PFHxDA and PFOcDA. For these compounds the concentrations were constantly below the MDL for all TOC concentrations. The [TOC] soils 1, 2 and 3 (TOC = 0.6 %, 3.5 % and 9.2 % respectively).

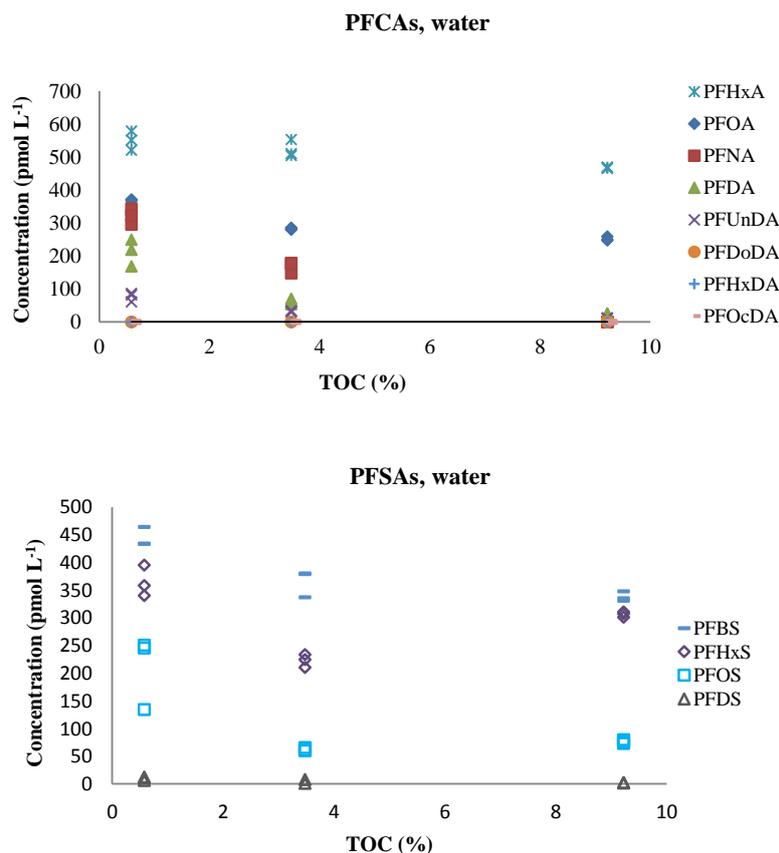


Figure B4. The upper scatter plot shows the concentration (pmol L⁻¹) of PFCAs detected in water phase for different TOC concentrations (%) (i.e. TOC = 0.6, 3.5 and 9.2 %). The lower scatter plot shows the same result but for PFSAs.

Active carbon

The concentrations detected in soil AS (Figure B5) increased to a level of [AC] 2.5 g L⁻¹ where it saturated. However for [AC] 25 g L⁻¹ the concentrations for all PFCAs except PFNA, PFUnDA and PFDoDA decreased. The concentration of PFOcDA was highest for [AC] 0 g L⁻¹, the concentration then decreased with increasing AC concentration. The concentration of PFHxA was higher than the other PFCAs, thereby this compound is plotted in Figure A11. The highest concentrations of PFOS and PFDS were observed for [AC] 2.5 g L⁻¹, the concentrations then decreased for [AC] > 2.5 g L⁻¹. For PFBS and PFHxS the highest concentrations were observed for [AC] 12.5 g L⁻¹. For [AC] > 12.5 g L⁻¹ the concentrations of PFBS and PFHxS decreased.

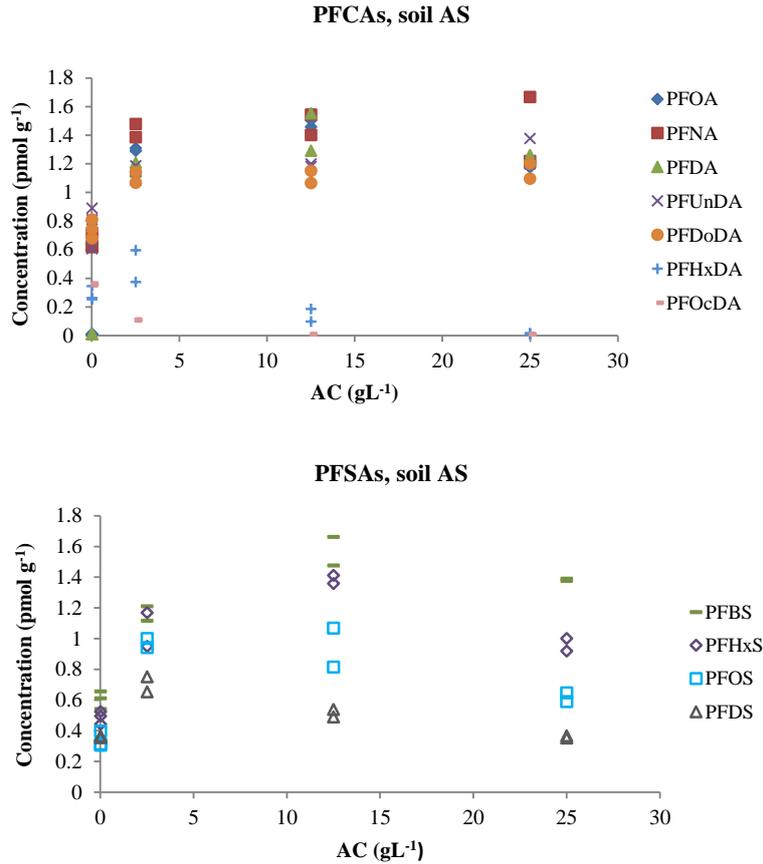


Figure B5. Concentration of PFCAs (pmol g⁻¹) detected in soil AS at different concentrations of AC (g L⁻¹) (i.e. 0, 2.5, 12.5 and 25 g L⁻¹).

The concentrations of PFHxA was higher than of the other PFASs in both soil 1 and soil AS. The concentrations of PFHxA is thereby presented in Figure B6.

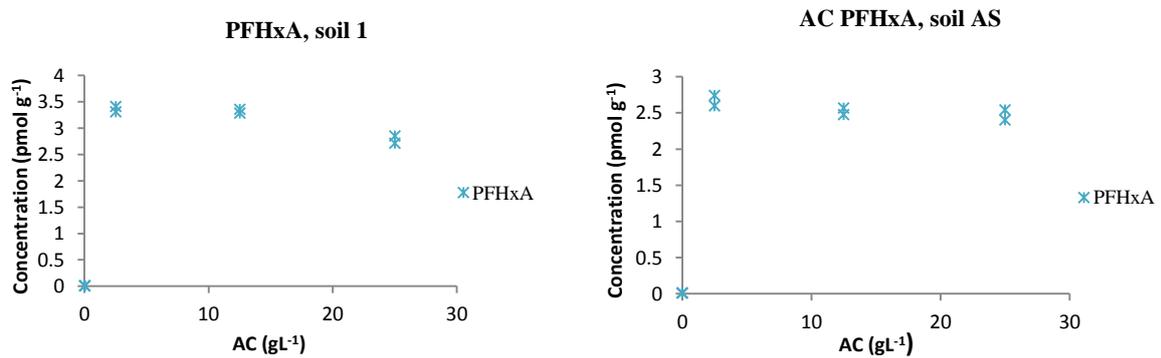


Figure B6. Concentration of PFHxA (pmol g⁻¹) detected in soil AS at different concentrations of AC (g L⁻¹) (i.e. 0, 2.5, 12.5 and 25 g L⁻¹).

As illustrated in Figure B7 and Figure B8 the mass balances of the different PFASs in the AC experiments decreased with increased concentrations of AC. This showed that the loss of compounds increased with increased AC concentrations. However, the results for PFUnDA and PFDoDA in soil AS differs. For these compounds the mass balance increased with increased AC concentration. Also for soil 1 PFDoDA shows a differing behavior with an increase of mass balance from AC concentrations 2.5 g L⁻¹ to 12.5 g L⁻¹. After this concentration the mass balance decreases to a value lower than the mass balance detected at the lowest AC concentration (2.5 g L⁻¹).

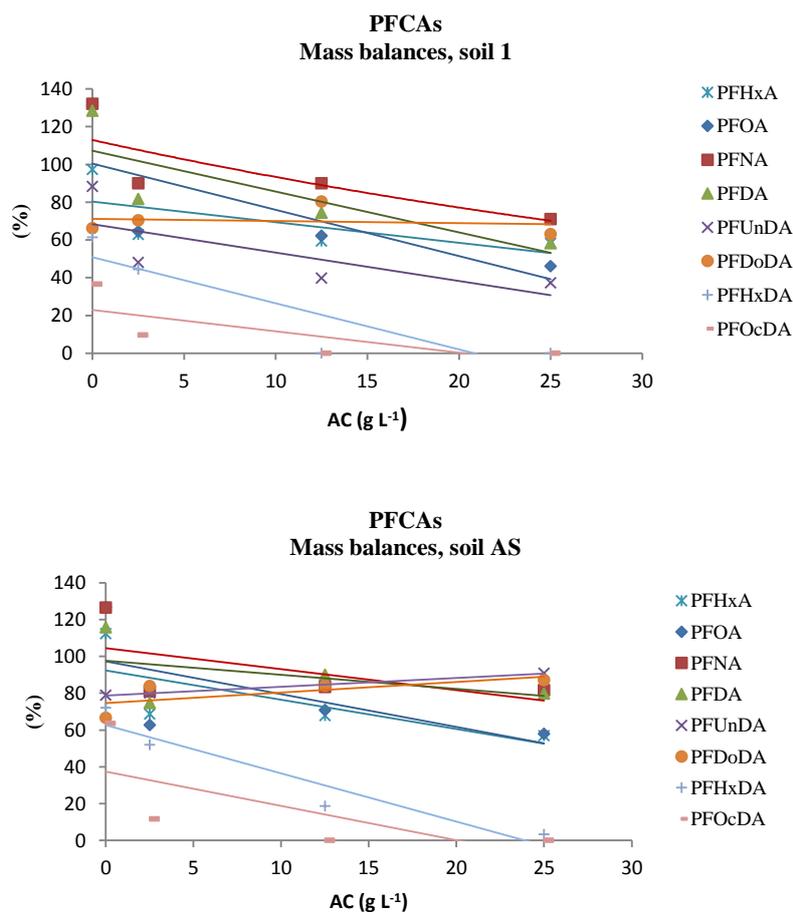


Figure B7. Scatter plot over mass balances calculated for PFCAs at different concentrations of AC (g L⁻¹) (i.e. 0, 2.5, 12.5 and 25 g L⁻¹) for soil 1, upper plot, and soil AS, lower plot.

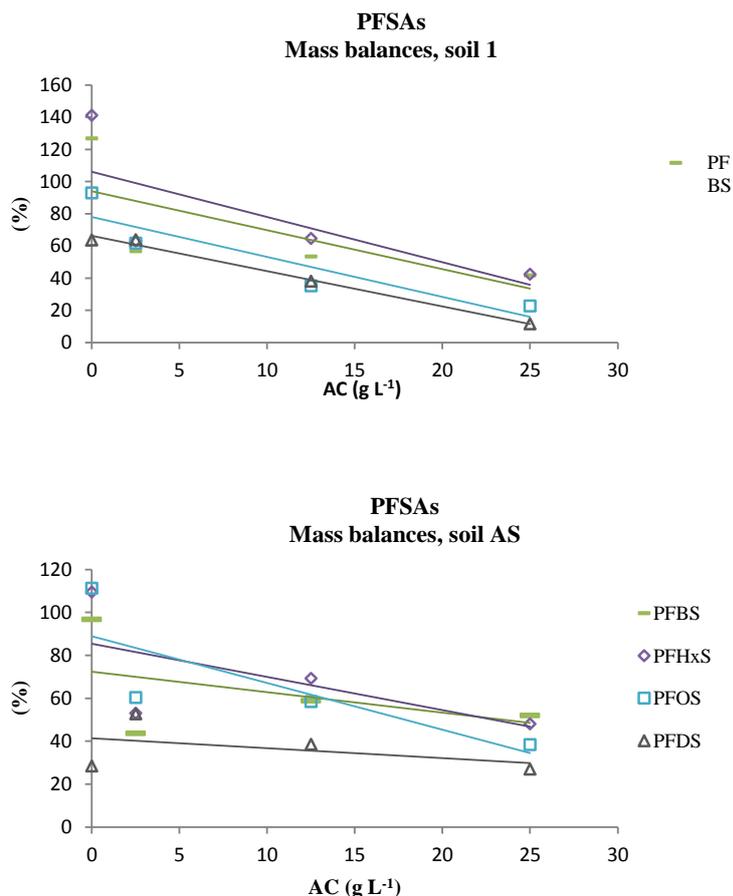


Figure B8. Scatter plot over mass balance calculated for PFASs at different concentrations of AC (g L^{-1}) for soil 1, upper plot, and soil AS, lower plot. The [AC] ranges from 0 g L^{-1} to 25 g L^{-1} .

The mass balances for all PFASs in both soils generally decreased substantially from [AC] 0 g L^{-1} to [AC] 2.5 g L^{-1} . For [AC] $> 2.5 \text{ g L}^{-1}$ the mass balances stabilized or kept decreasing at a lower rate. The exception was PFDoDA in soil 1 and PFDoDA and PFUnDA in soil AS which rather increased for [AC] $> 2.5 \text{ g L}^{-1}$. The highest R^2 values in soil 1 were shown for PFHxDA(0.78), PFOS (0.82) and PFDS (0.99). The R^2 values for the other PFASs ranged from 0.02 (PFDoDA) to 0.71 (PFNA). For soil AS the highest R^2 values were found for PFUnDA(0.99) and PFHxDA (0.91). The values for the other PFASs ranged from 0.20 (PFDS) to 0.63 (PFOS).

Calcium ions

No linear correlation was found between increasing $[\text{Ca}^{2+}]$ and concentration of PFCAs in soil AS (Figure B9). The concentration of all PFASs except PFOA and PFDA increased until a Ca^{2+} concentration of 50 mM, above which the concentrations stagnated. The concentrations of PFDoDA, PFHxDA and PFOcDA decreased for $[\text{Ca}^{2+}]$, 200 mM. The concentrations of PFDoDA and PFDA detected for $[\text{Ca}^{2+}]$ 5 mM was higher than the concentration detected for all other Ca^{2+} concentrations. The concentrations of PFOA and PFDA slightly decreased with

increased Ca^{2+} concentrations. The concentrations detected for PFNA was under the MDL for all Ca^{2+} concentrations.

The concentrations of PFOS and PFDS increased from the lowest calcium concentration to the highest. The concentrations of PFHxS did not change with increased $[\text{Ca}^{2+}]$ while the concentration of PFBS remained unchanged until $[\text{Ca}^{2+}]$ 50 mM. For $[\text{Ca}^{2+}]$ 200 mM the concentration of PFBS decreased.

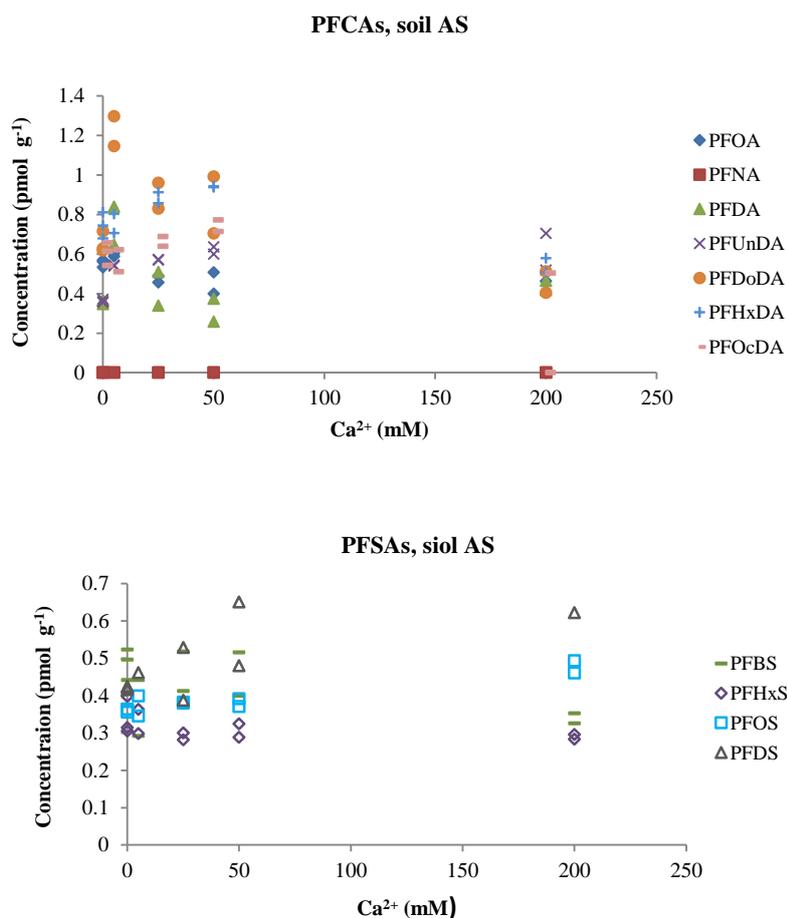


Figure B9. Scatter plot over concentrations of PFCAs (pmol g⁻¹) detected in soil AS at different concentrations of Ca^{2+} ions (mM) (i.e. 0, 5, 25, 50 and 200 mM).

The concentrations detected for PFHxDA was higher than for the other PFASs in soil AS. The concentrations of PFHxDA is thereby presented in Figure B10.

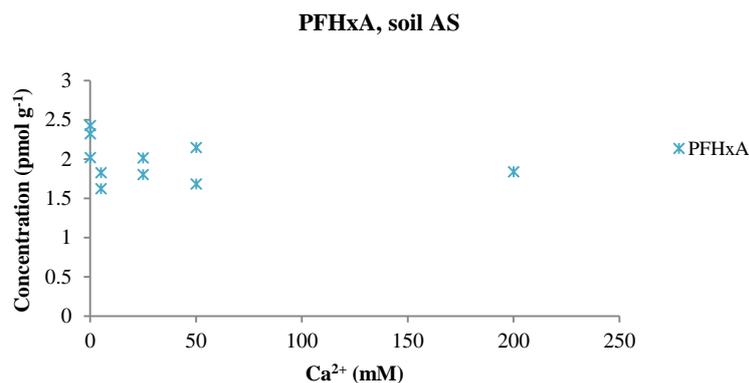


Figure B10. Scatter plot over concentrations of PFASs (pmol g⁻¹) detected in soil AS at different concentrations of Ca²⁺ ions (mM).

Figure B11 shows the PFCA concentration detected in water for soil 1 and soil AS in the Ca²⁺ experiments. The PFAS concentrations of all PFASs in soil 1 decreased to a [Ca²⁺] level of 5 mM where it stagnated. The same trend was observed for PFOS and PFDS (Figure B12). The concentrations detected for PFBS and PFHxS in water did not change for any [Ca²⁺]. The PFASs in soil AS showed the same behavior except for PFOA which did not show any changes in concentrations for the different [Ca²⁺].

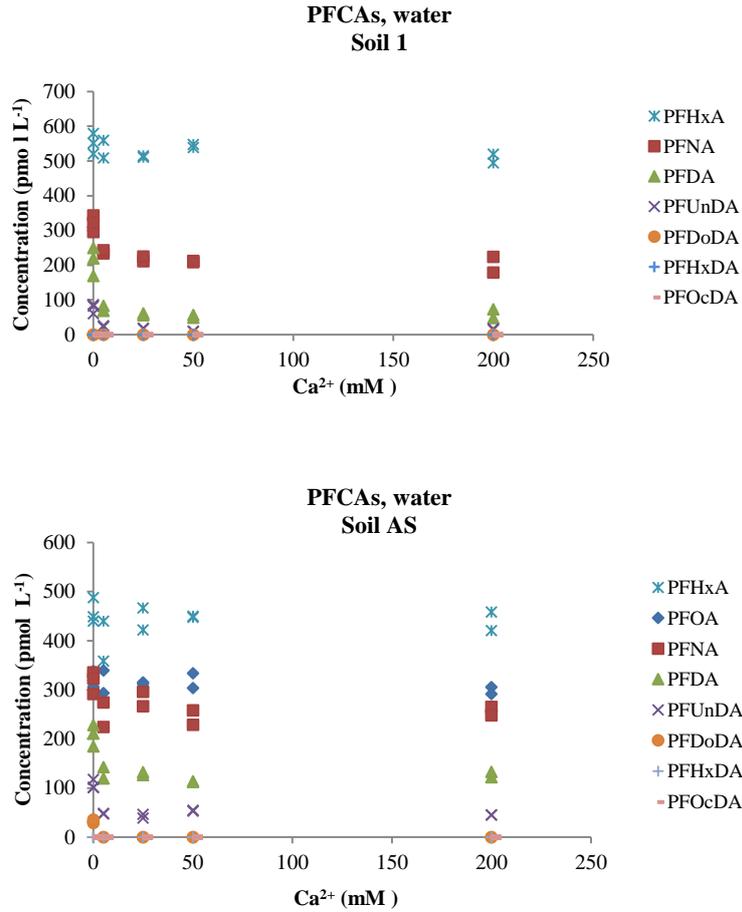


Figure B11. Concentration of PFCAs (pmol L⁻¹) detected in the water phase for soil 1, upper diagram, and soil AS, lower diagram, at different concentrations of Ca²⁺ ions (mM) (i.e. 0, 5, 25, 50 and 200 mM).

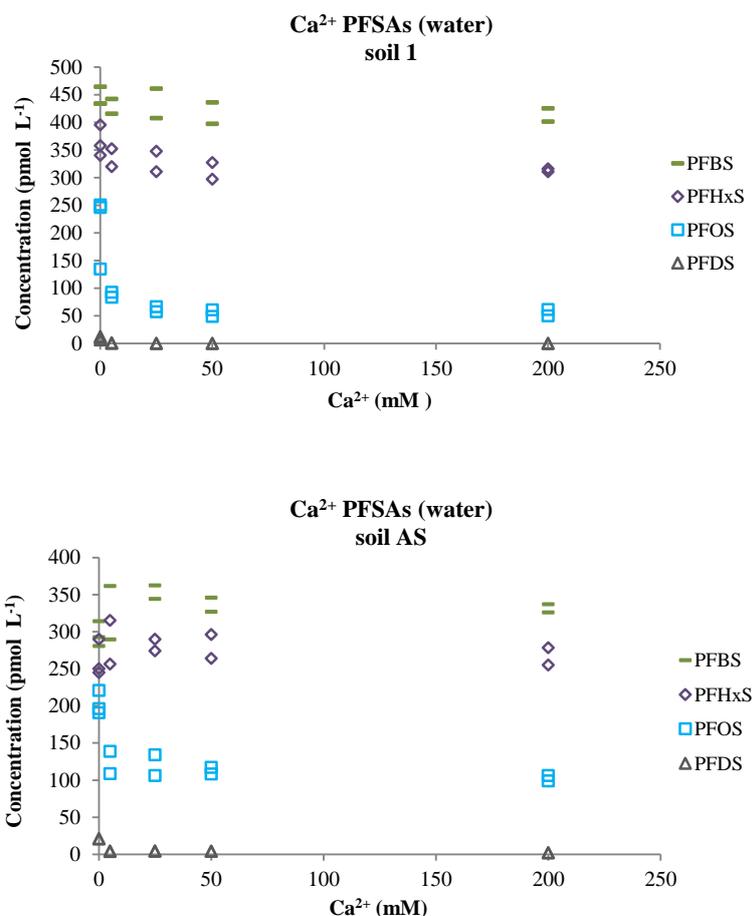


Figure B12. Concentration of PFASs (pmol L^{-1}) detected in water for soil 1, upper diagram, and soil AS, lower diagram, at different concentrations of Ca^{2+} ions (mM).

Mass balances

The mass balances calculated for all samples are presented in Table B5.

Table B5. Mass balance (%) for all duplicates and triplicates in the equilibrium test (Eq test), Ca^{2+} experiments (Ca^{2+}), organic carbon experiments (OC) and active carbon experiments (AC). The average mass balance and standard deviation (Stdv) were calculated for each separate experiment. Also the average and standard deviation for all samples were calculated.

	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxDA	PFOcDA	PFBS	PFHxS	PFOS	PFDS
Eq test	%	%	%	%	%	%	%	%	%	%	%	%
Soil AS												
10 h (I)	112	117	109	115	93	0	62	49	112	114	99	47
10 h (II)	105	119	123	122	97	83	58	38	113	120	89	0
24 h (I)	0	98	92	102	90	73	98	90	76	91	82	51
24 h (II)	0	103	101	132	82	71	98	77	75	89	90	66
48 h (I)	0	66	62	100	68	80	99	100	50	55	61	61
48 h (II)	0	93	75	89	86	86	109	83	74	92	88	70
72 h (I)	0	143	202	190	134	136	101	96	129	144	131	59
72 h (II)	0	146	153	201	153	128	122	109	125	141	109	74
Soil 1												
10 h (I)	86	132	120	121	87	89	55	29	135	134	86	65

10 h (II)	92	138	145	136	104	91	58	22	139	152	111	76
24 h (I)	0	80	68	80	97	102	104	58	63	70	65	83
24 h (II)	0	91	79	91	88	94	78	45	78	85	76	83
48 h (I)	0	0	0	0	0	0	0	0	0	0	0	0
48 h (II)	0	61	93	103	89	103	86	44	37	50	59	66
72 h (I)	0	124	146	147	126	132	115	56	99	118	104	96
72 h (II)	0	126	144	146	123	105	102	70	100	122	105	85
<i>Average</i>	25	102	107	117	95	86	84	60	88	99	85	61
<i>Stdv</i>	44	38	47	46	34	39	31	31	39	41	30	27
Ca²⁺												
Soil AS												
5 mM (I)	0	108	79	88	59	87	78	65	84	98	63	0
5mM (II)	96	134	108	116	62	98	68	54	106	125	85	37
25mM (I)	93	114	98	84	62	73	88	72	108	109	66	31
25 mM (II)	106	116	114	78	59	63	83	67	103	107	80	42
50 mM (I)	98	121	101	66	68	53	91	81	105	117	74	38
50 mM (II)	103	110	83	69	70	75	91	75	98	101	66	51
200 mM (I)	101	116	102	82	58	31	49	0	98	109	73	0
200 mM (II)	0	107	93	82	71	39	56	53	94	99	71	48
Soil 1												
5 mM (I)	96	123	94	92	94	87	82	53	127	140	68	0
5mM (II)	89	128	99	103	103	0	84	54	122	127	80	84
25mM (I)	91	118	87	82	105	71	78	55	121	127	62	69
25 mM (II)	91	129	94	95	105	89	78	49	139	143	61	67
50 mM (I)	96	126	88	78	107	84	80	57	120	124	66	97
50 mM (II)	95	135	85	65	108	81	75	60	130	134	82	95
200 mM (I)	86	119	73	70	78	115	72	57	125	121	63	71
200 mM (II)	90	121	91	87	81	107	72	59	119	122	75	71
<i>Average</i>	83	120	93	84	81	72	77	57	112	119	71	50
<i>Stdv</i>	33	9	11	14	20	30	12	18	15	14	8	32
OC												
Soil AS (I)	106	126	115	105	83	70	66	57	90	107	108	43
Soil AS (II)	113	123	135	118	76	64	72	65	97	103	106	43
Soil AS (III)	118	132	129	124	77	67	79	69	103	118	120	0
Soil 1 (I)	89	118	118	104	84	70	65	37	121	130	70	63
Soil 1 (II)	99	138	143	138	80	63	60	37	126	141	116	65
Soil 1 (III)	104	138	135	143	101	66	59	37	134	153	0	64
Soil 2 (I)	0	0	0	0	0	0	0	0	0	0	0	0
Soil 2 (II)	157	129	75	83	69	82	85	51	112	108	93	66
Soil 2 (III)	144	129	74	99	74	78	76	42	112	122	95	0
Soil 3 (I)	193	152	103	103	112	110	73	64	116	166	189	84
Soil 3 (II)	197	148	95	103	111	105	80	66	114	167	190	77
Soil 3 (III)	191	148	95	102	115	109	67	54	111	167	192	80
<i>Average</i>	126	123	101	102	82	74	65	48	103	124	107	49
<i>Stdv</i>	56	40	39	36	30	29	22	19	35	46	65	32
AC												
Soil AS												
2.5 (I)	68	63	84	76	84	81	41	11	45	48	59	56
2.5 (II)	70	62	78	73	77	87	63	12	42	58	62	49
12.5 (I)	69	70	87	98	85	87	23	0	55	71	51	41
12.5 (II)	67	72	79	82	83	81	14	0	62	68	66	37
25 (I)	58	59	94	80	97	91	7	0	52	50	40	28
25 (II)	55	57	69	80	85	83	0	0	52	46	37	27
Soil 1												
2.5 (I)	61	64	88	78	96	69	39	9	63	63	52	67
2.5 (II)	64	65	93	86	0	72	50	10	51	64	71	61
12.5 (I)	60	62	89	74	80	94	0	0	57	65	35	39
12.5 (II)	58	63	91	75	0	67	0	0	50	65	36	38
25 (I)	57	46	71	61	0	59	0	0	43	43	23	12
25 (II)	60	46	72	55	75	67	0	0	40	41	23	11
<i>Average</i>	62	61	83	76	63	78	20	4	51	57	46	39
<i>Stdv</i>	5	8	9	11	39	11	23	5	7	10	16	18
Overall average	111	122	107	108	92	84	79	59	108	120	94	65
Overall stdv	34	29	31	28	30	20	23	30	28	32	36	35

