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Binding of per- and polyfluoroalkyl substances (PFASs) to organic soil horizons of peat and mor

– effect of solution chemistry and soil organic matter composition

Jennifer Makselon

Master thesis in Environmental Science
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Jennifer Makselon

Supervisor: Hugo De Campos Pereira, Department of Soil and Environment, SLU
Assistant supervisor: Jon-Petter Gustafsson Department of Soil and Environment, SLU
Assistant supervisor: Ellen Kandeler, University of Hohenheim
Examiner: Dan Berggren Kleja, Department of Soil and Environment, SLU

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Faculty of Natural Resources and Agricultural Sciences
Department of Soil and Environment

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Abstract

The understanding of sorption processes of per- and polyfluoroalkyl substances (PFASs) in soils is important for the determination of their fate and transport in the environment. The sorption behavior of PFASs of varying chain length and hydrophilic headgroup was studied in three organic soils, two peat soils and one mor layer, with differing chemical composition of the soil organic matter (SOM). PFAS sorption to the SOM of the peat samples was observed to be overall higher as compared to the mor sample, despite a higher amount of SOM in the latter. These results suggest that not only the quantity of SOM but also its quality pose an important parameter for PFAS binding. The effect of solution pH and added cation concentrations of Al^{3+}, Ca^{2+} and Na^{+} on sorption was investigated by performing batch sorption experiments and using ultra-high performance liquid chromatograph coupled to tandem mass spectroscopy (UHPLC-MS/MS). The evaluation of the organic carbon-normalized partitioning coefficient (log K_{OC}), showed that additions of Al^{3+} and Ca^{2+} yielded a higher sorption as compared to the addition of Na^{+} in all soils. Moreover, sorption was negatively correlated to the pH value. Thus, the results imply an inverse relationship to the net negative surface charge of the soils. Physico-chemical properties of PFASs, such as the hydrophilic head group and hydrophobic carbon tail, affected the sorption to SOM. Perfluorosulfonates (PFSAs) sorbed to a higher extent as compared to perfluorocarboxylates (PFCAs), while fluoroalkyl sulfonamides (FASAs) sorbed the strongest. The extent of PFAS sorption further increased with increasing perfluorocarbon chain length. In addition, specific binding mechanisms could not be observed in this present study and sorption isotherms were predominantly linear for aqueous concentrations ranging from ~1 to 130 ng mL^{-1}. Desorption of PFAS was further characterized to be concentration-dependent and negatively related to the compound hydrophobicity. Moreover, certain PFASs such as Et-FOSA and PFOA showed a hysteretic desorption behavior which further needs to be investigated.

Keywords: Sorption, Desorption, PFOA, PFOS, Cation, Soil organic matter, Partitioning coefficient, Isotherms, Electrostatic interactions

Popular science summary

Per- and polyfluoroalkyl substances (PFASs), the “forever chemicals”, are a group of over 4000 human-made chemicals that are unique due to their water and grease repelling properties. These properties were used commercially since 1960s and led to a widespread production of these synthetic chemicals for instance for the use in firefighting foams, food packaging, clothing, cookware, electronics and plastics. But why is research about PFASs important?

PFASs are everywhere. They cannot only be found at point sources like firefighting stations or airports, but also in our blood or at remote places with no direct exposure to PFAS like the arctic. The unique surfactant properties of PFASs make them attractive for the industry but at the same time they complicate the prediction of their behavior in the environment. The chemical structure of PFASs is characterized by one of the strongest bonds known in nature, the carbon-fluorine bonds, what makes PFASs highly persistent and prevents their degradation in the environment and in our bodies. Therefore, PFASs have the potential to accumulate as they remain intact in the environment for a very long time what leads to increasing contamination levels especially in soil and groundwater but also in wildlife and humans. Despite production limitations of certain PFASs, new PFASs as well as replacement compounds are being produced continuously. Consequently, old and new contaminations pose a risk to human health.

Soils influence the transportation and fate of these contaminants as they are able to bind PFASs. The likeliness of PFASs attaching to soil particles rather than staying in the water phase is not only dependent on the type of PFASs but also on the composition of soils. Therefore, it is important to identify what fraction of soil is relevant for the binding of what type of PFASs. This knowledge contributes to the improvement of the risk assessment of these contaminants in the environment e.g. predicting the risk of the leakage into groundwater what could affect drinking water sources or developing appropriate strategies to treat contaminated soils.

The aim of this study was to expand the knowledge on how and to what extent PFASs are bound in organic soils by varying different parameters of solution chemistry. Soil particles have an overall negative charge and much like a magnet, they can attract positively charged particles like the metals added in the experiment. This leads to a reduced negative charge of the soil particles what allows better sorption of PFASs, which are then less repelled as they bear a negative charge themselves. Additionally, the acidity influenced the negative charge of soil particles, enhancing the PFAS sorption at more acidic conditions. It was also observed that long PFASs bind better than shorter ones, what in turn implies a higher mobility of shorter contaminants in the environment. Moreover, the chemical group at the end of PFAS molecules also influences the extent of sorption in soils. Finally, the results showed that not only the amount of organic matter in soil but also its quality is relevant for PFAS binding and that already rather small changes within the soil composition can have an impact.

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Abbreviations

CP/MAS ^{13}C NMR	Solid-state cross-polarization/magic-angle-spinning ^{13}C nuclear magnetic-resonance spectroscopy
C_x	Fluorocarbon chain of length x
DOC	Dissolved organic matter
Et-FOSA	N-ethyl perfluorooctane sulfonamide
FA	Fulvic acid
FOSA	Perfluorooctane sulfonamide
FTSAs	Fluorotelomer sulfonates
g	relative centrifugal force
GLMM	Generalized linear mixed model
HA	Humic acid
HOC	Hydrophobic organic pollutants
IS	Internal Standard
K_d	Soil-liquid distribution coefficient
K_f	Freundlich sorption capacity parameter
K_{OC}	Organic carbon normalized- water partitioning coefficient
LoQ	Limit of Quantification
MOe	Paskalampa Mor Oe
n	Freundlich non-linearity parameter
n.d.	not determined
PFAS	Perfluorinated alkyl substances
PFASs	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoate
PFBS	Perfluorobutane sulfonate
PFCAs	Perfluorinated carboxylic acids
PFDA	Perfluorodecanoate
PFDoDA	Perfluorododecanoate
PFHpA	Perfluorohepanoate
PFHxA	Perfluorohexanoate
PFHxS	Perfluorohexane sulfonate

PFNA	Perfluorononanoate
PFOA	Perfluorooctanoate
PFOS	Perfluorooctane sulfonate
PFPeA	Perfluoropentanoate
PFSAs	Perfluorinated sulfonic acids
PFTeDA	Perfluorotetradecanoate
PFTeDA	Perfluorotetradecanoate
PFUnDA	Perfluoroundecanoate
POe	Paskalampa Peat Oe
POi	Paskalampa Peat Oi
POPs	Persistent organic pollutants
PP	Polypropylene
ppm	Part per million
RCF	Relative centrifugal force
RMSE	Root Mean Square Error
rpm	Revolutions per minute
RSS	Weighted residual sum
SOM	Soil organic matter
TOC	Total organic carbon
UHPLC-MS/MS	Ultra-high performance liquid chromatograph coupled to tandem mass spectroscopy

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are persistent organic pollutants (POPs) characterized by a fully or partly fluorinated hydrophobic (oleophobic) alkyl chain of varying length and a hydrophilic functional head group. These contaminants have been manufactured and widely used as processing additives in industrial and commercial applications over the last 60 years for instance in firefighting foams, surface protectants, food packaging and insecticides (Kissa, 2001; Wei et al., 2017). Their unique physico-chemical properties are leading to high bioaccumulation and persistence in the natural environment and ecosystems. Natural processes involving soil, water and air are further contributing to an extensive contamination of environmental media (UNEP, 2008a).

Public and scientific awareness concerning the presence of these compounds in the environment increased with the detection of PFOS in blood plasma of nonoccupationally exposed humans as well as in animal tissues collected from around the globe, including the arctic (Schultz et al., 2003). Toxic properties of PFASs include for instance endocrine-disrupting activity, neurotoxicity, carcinogenesis and reproductive toxicity (Chang et al., 2016; Li et al., 2019; UNEP, 2008a).

Soils represent the critical link between hydrological and atmospheric processes which both influence the distribution of PFASs. Thus understanding the sorption behaviour of PFAS in surface soils is an essential element for the comprehension of their accumulation and release in the environment (Strynar et al., 2012). Several studies identified soil/sediment organic matter as the dominant factor controlling sorption of hydrophobic organic pollutants including PFASs (Abelmann et al., 2005; Barzen-Hanson et al., 2017; Ochoa-Herrera and Sierra-Alvarez, 2008; Wang et al., 2012; You et al., 2010). The heterogeneity of organic matter resulting from different origins, maturation and chemical composition impacts sorption behavior (Ahangar, 2010) and therefore needs to be investigated. Binding of PFASs to sediments (Ahrens et al., 2010; Higgins and Luthy, 2006; Pan et al., 2009), soils (Guelfo and Higgins, 2013; Milinovic et al., 2015; You et al., 2010) and specific minerals (Johnson et al., 2007; Wang et al., 2015; Xiao et al., 2011) has been studied in order to investigate sorption mechanisms. Du et al. (2014) reviewed the PFAS sorption over a range of different sorbents and identified electrostatic and hydrophobic interactions as the prominent sorption mechanisms. However, only few studies (Campos Pereira et al., 2018; Milinovic et al., 2015; Zhao et al., 2014; Zhi and Liu, 2018) examined PFAS sorption to organic soils. Consequently, there is a lack of information concerning the sorption of PFASs with different physico-chemical properties to soils with a significant amount of organic matter and the reversibility of these sorption processes.

1.1. Research Questions

The main objective of this study was the comparison of PFAS sorption onto two peat soils and one mor layer by examining the correlation between different soil characteristics and physico-chemical properties of PFASs. For this reason, soil organic matter quality was characterized by solid-state ^{13}C NMR spectroscopy to identify the effect of the structural variation on sorption capacity and mechanisms. The selection of PFASs of varying chain length and head groups, namely perfluoroalkyl carboxylates (PFCAs), perfluoroalkyl sulfonates (PFSAS), fluorotelomer sulfonates (FTSAs) and fluoroalkyl sulfonamides (FASAs), allowed the quantitative evaluation of these structural component's contribution to the sorption potential. The sorption behavior of PFASs was further investigated by assessing the effect of solution pH, solution cation composition (Al^{3+}, Ca^{2+} and Na^+) and metal binding. The logarithmised organic carbon normalized distribution coefficient log K_{OC} was used as a key parameter to asses contaminant mobility due to the high amount of total organic carbon present in the soils (> 44.9 %).

In order to better understand the sorption-desorption behavior of PFASs, equilibrium sorption isotherms over a range of concentrations were analyzed to examine the relationship between sorption irreversibility and distribution coefficients.

Such obtained data are essential for the modelling of biological availability, transport and fate of already existing and emerging PFASs in the environment.

The following main hypotheses were elaborated:

- There is a negative relationship between the logarithmical partitioning coefficient $log\ K_{OC}$ and the pH value in organic soils.
- The effect of Al^{3+} addition on PFAS sorption is larger than the effect of Ca^{2+} and Na^+ additions in all three organic soil samples.
- The influence of humic and fulvic acids on the binding of PFASs to organic matter is described by a negative relationship, as the sorption affinity among the soils is expected to increase in the order of soil Paskalampa Mor Oe (MOe) > Paskalampa Peat Oe (POe) > Paskalampa Peat Oi (POi).
- The differences in metal binding elucidate the differences in the overall PFAS sorption as the effect of cation additions on sorption is expected to decrease in the order of MOe > POe > POi.

- The PFAS sorption increases with increasing perfluorinated carbon chain length in all soil samples, where it is expected that sulfonated PFASs of a certain chain length bind stronger than the respective carboxylated PFASs of the same chain length.
- Sorption isotherms are predominantly linear.

2. Background

2.1. Per- and polyfluorinated substances (PFASs)

PFASs are aliphatic substances and comprise thousands of different compounds, spanning a wide range of exposure and hazardous characteristics (Banzhaf et al., 2017). The contaminants belong to a class of organofluorine compounds characterised by a functional head group and an alkyl chain of varying chain length, where one or more hydrogen atoms are replaced by a fluorine atom (Du et al., 2014). Carbon-fluorine bonds which are among the strongest bonds in organic chemistry are contributing to a high chemical stability and resistance towards physical and biological degradation (Lau et al., 2007; Li et al., 2018; Zhang et al., 2013). The unique hydrophobic and hydrophilic properties are reflected in a reduced surface tension and their surfactant characteristics, making them favourable for a wide range of technical and consumer applications (Ding and Peijnenburg, 2013).

PFASs are of global concern due to their ubiquitous presence and detection even in remote areas of the northern hemisphere with no direct sources of PFAS emissions (Lau et al., 2004). Long-range dissemination can occur both over aquatic and atmospheric routes depending on the solubility and volatilization of a specific compound (Krafft and Riess, 2015). Most commonly studied PFASs are perfluorinated sulfonates (PFSAs) and perfluorinated carboxylates (PFCAs) (Ding and Peijnenburg, 2013). Especially, a prevalence of PFOS, PFOA and PFHxS in humans and almost all environment samples lead to actions concerning the restriction in usage and production of these compounds (Krafft and Riess, 2015; Lau et al., 2004). Several studies reported potential adverse effects on humans and wildlife due to their bioaccumulative behaviour (Giesy and Kannan, 2001; Kelly et al., 2009). However, the presence of PFASs in biota is not uniform as the degree of exposure varies, for instance effecting populations living close to contamination sources stronger than background populations (Krafft and Riess, 2015). PFASs behave comparable to free faty acids within organisms, as they accumulate most commonly in blood, liver and eggs (Kannan et al., 2004). Dose-response curves and the quantification of adverse health effects is difficult due to the ubiquitous presence of PFASs, long-body half-lives and lack of unexposed control populations (Krafft and Riess, 2015). However, potential links between PFAS exposure and diseases were found for instance for PFOA and high cholesterol, pregnancy induced hypertension and kidney cancers (Krafft and Riess, 2015). Moreover, bioconcentration and bioaccumulation were observed to increase with increasing perfluorinated chain length of PFASs and influenced by the functional head group due to better binding of PFSAs as compared to PFCAs to proteins (Ng and Hungerbühler, 2013). Main exposure pathways for humans arise from food consumption, house dust and contaminated drinking water (Banzhaf et al., 2017; Krafft and Riess, 2015). Understanding the transport and fate of PFASs in the environment is essential for the risk assessment of their exposure. Consequently, PFASs pose a multidisciplinary challenge involving different research fields, industry and public action on a global scale.

2.2. Regulations and Guidelines

The implementation of risk reduction actions due to the potential negative impacts of PFASs on the environment and humans initiated restrictions of the production and use of certain long chain PFASs and their precursors on international, regional and national level (OECD, 2019).

In 2009, perfluorooctanesulfonic acid (PFOS) and its precursors were added to Annex B of the Stockholm Convention on Persistent Organic Pollutants, while perfluorooctanoate (PFOA) is planned to be phased out by 2020 and perfluorohexane sulfonate (PFHxS) is currently being reviewed by the POPs Committee (UNEP, 2008b)

The Swedish Chemical Agency decided that companies must provide information on intentionally added PFASs in their products starting from January 2019. However, they are not obliged to state the specific concentrations (KEMI, 2018).

Despite various approaches, regulatory actions are still limited which is assigned to the unique qualities of PFASs and a lack of alternatives. Hence, the resulting global restrictions in production and usage of PFOS and soon PFOA are leading to the development of new PFAS classes, such a short chain PFASs which are expected to have a higher mobility (Ahrens, 2011). According to EurEau (2018), PFASs should be controlled at the source and prevented from reaching the environment, thus promoting the *polluters pays principle* and preventing further contamination.

According to the Swedish Geotechnical Institute, the extent of existing data is insufficient to calculate generic guidelines values for most PFASs. Solely for PFOS preliminary guideline values were derived for sensitive land use such as residential areas with 0.003 mg PFOS/kg dryweight (dw) soil and less sensitive land use e.g. industrial areas with 0.020 mg PFOS/kg dw

(Pettersson et al., 2015). Reported highest concentrations of PFOS and PFOA in soils collected from locations absent of direct point sources and human activity, were found in literature at 10 and 30 µg kg^{-1} in Japan, Mexico, USA and China (Li et al., 2010; Rankin et al., 2016; Strynar et al., 2012). Significantly higher levels of PFAS contamination can be found in soils at hotspots such as PFAS manufacturing industries, chromium-plating industries or airfields (Banzhaf et al., 2017). Concentrations of PFOS and PFOA in soils at fire-fighting training sites close to Stockholm were identified to be ranging from 2.18 to 8520 µg kg^{-1} dry weight and <0.12 – 287 µg kg^{-1} dry weight respectively (Filipovic et al., 2015). Leakage of PFASs from airports and fire-fighting training areas around Sweden lead to the contamination of ground and drinking water as well as consumption of PFAS-contaminated water for a period of at least 20 years (Gyllenhammar et al., 2015). As a reaction, the Swedish National Food Agency issued an action limit of 90 ng L^{-1} for PFASs in drinking water based on a sum of 11 PFAS (Livsmedelsverket, 2016).

Guideline values for PFOA and PFOS in drinking water have been proposed or established also in other countries, such as 0.1 µg L^{-1} by the German Environment Agency, 0.07 µg L^{-1} by the US EPA, ≤ 0.03 µg L^{-1} for PFOS and ≤ 0.05 µg L^{-1} for PFOA by the Institute of Health in Italy. However, in certain EU Member States maximum values of 11.5 µg L^{-1} for PFOA and 0.41 µg L^{-1} for PFOS were found in drinking water (WHO, 2017).

2.3. Basic chemical structure of PFASs

Perfluorinated substances are composed of a fully fluorinated alkyl tail and nonfluorinated functional head group. The synthetic chemicals contain one or more carbon atoms, where all hydrogen are replaced with fluorine atoms yielding the perfluoroalkyl moiety C_nF_{2n+1}- (Figure 1) (Buck et al., 2011). Polyfluoroalkyl substances on the other side, are partly fluorinated and not all H atoms are replaced by F atoms. Fluorotelomer substances for instance are characterized by the prefix n:x with n > 2 indicating the number of fully fluorinated C atoms and x > 1 marking the number of partly fluorinated carbons (e.g. 6:2 FTSA) (ITRC, 2017). Polyfluorinated substances can be potentially biotically or abiotically transformed to perfluorinated substances (Buck et al., 2011). In general, hydrophobic as well as oleophobic properties (Zhang et al., 2013) are ascribed to the fluorinated carbon tail which contrasts with traditional hydrocarbons and poses a challenge to determine their amphiphobicity. Functional groups on the other side, such as for example carboxylic or sulfonic moieties, are hydrophilic and enhance the water solubility (Du et al., 2014). It is widely observed in literature that sorption capacity of PFASs increases with the number of CF_2 moieties in the molecule, which is assigned to an enhanced hydrophobicity and lower water solubility (Du et al., 2014).

Based on the definition provided by OECD (2011), PFASs are classified as short-chain and long-chain compounds. Hereby, perfluoroalkyl carboxylates with 7 or more perfluorinated carbons and perfluoroalkyl sulfonates with 6 or more perfluorinated carbons are defined as long-chain compounds. The difference in definition between PFCAs and PFSAs results from the greater tendency of PFSAs to bioconcentrate or bioaccumulate as compared to PFCAs of the same chain length. Other PFASs are generally referred to as long-chain when having a perfluoroalkyl chain of 7 or more (Buck et al., 2011).

The production of PFASs in the telomerization process yields predominantly linear isomers, where carbons are bound to one or two other C atoms. The occurrence of PFASs as branched isomers is ascribed to the electrochemical fluorination production process, resulting in C atoms being bound to more than two C atoms (Buck et al., 2011). Both structures were taken into account in the present study.

Beside the above described structures, emerging cyclic compounds such as perfluoro-4-ethylcyclohexanesulfonate (PFECHS) were detected in seawater samples from the Baltic Sea (Joerss et al., 2019). According to Joerss et al. (2019), cyclic PFASs were observed to have a lower sorption affinity for solid environmental matrices as compared to linear and branched PFAS.

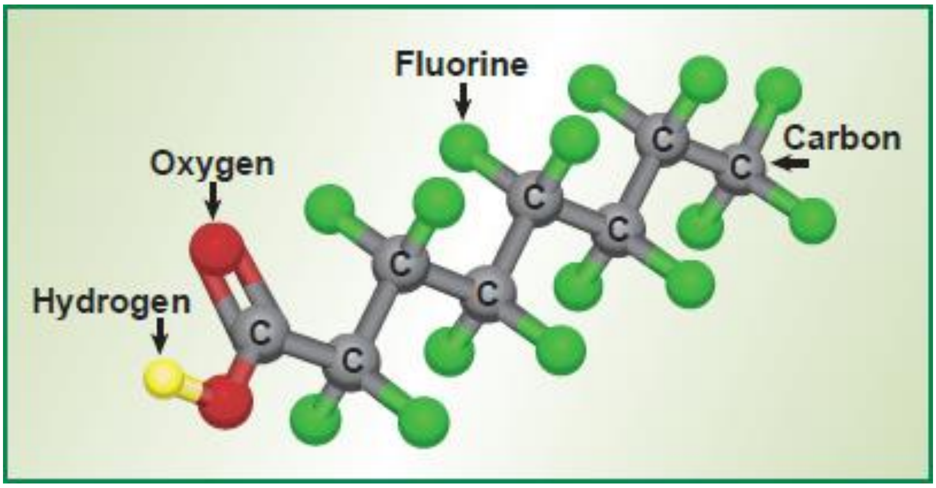

Figure 1 Basic molecular structure of PFOA showing a hydrophobic tail consisting of 7 perfluorinated carbon atoms and the hydrophilic carboxylic head group (XDD Environmental, 2017).

2.4. Acid dissociation constant

The presence of PFASs in the neutral (protonated) or anionic form depends on the pH value as well as the acid dissociation constant (pK_a). PFASs mainly exists in their anionic form within the studied pH range (pH 3–6). The acid dissociation constant allows the quantitative measurement of strength of an acid in solution, thus contributing to the understanding of fate and transport of PFASs in the environment (ITRC, 2017). PFSAs are considered as strong acids while PFCAs are assumed to be weak acids (Du et al., 2014). According to Ding et al. (2013), there are discrepancies regarding the pK_a of PFCAs due to experimental difficulties in their determination. Nonetheless, pK_a values of C_1–C_{11} PFCAs are expected to weaker than 3.5 while increasing with the number of CF_2 moieties (Moroi et al., 2001). Experimental and modelled values for PFOA varied for instance between –0.5 to 3.8 (Barton et al., 2007; Burns et al., 2008; Kissa, 2001) which further reflects the disagreement in literature. PFSAs have usually much lower pK_a values than analogous carboxylic acids of the same chain length. As a result, most PFASs exist in the dissociated anionic form under environmentally relevant pH values which is also the form that is referred to in this study. Despite the importance of distinguishing the acid and anionic form of PFASs due to differing physical and chemical properties, names are often used interchangeably in literature.

2.5. Sorption mechanisms

PFAS sorption to natural organic matter is, at dilute PFAS concentrations, assumed to be a phase transfer process between the aqueous solution and soil organic material (Higgins and Luthy, 2007). Hereby, anionic surfactants may be hypothesized to be absorbed completely into the organic matter or partly, with the functional head group being at or near the organic matter-water interface (Higgins and Luthy, 2007).

One of the main sorption mechanisms identified in literature are electrostatic interactions between anionic PFASs and charged adsorbents (Du et al., 2014; Johnson et al., 2007; Xiao et al., 2011). The negative charge of PFASs in water originates principally from their functional head group (Johnson et al., 2007). Additionally, the positively charged core of PFAS molecules is surrounded by a negatively charged shell which results from the highly electronegative fluorine atoms (Du et al., 2014). However, electrostatic interactions exhibited by the fluorinated tail are rather weak and overwhelmed by hydrophobic interactions (Xiao et al., 2011). The complexation of multivalent cations is known to decrease the net negative charge present on natural organic matter, and thus increase the sorption of anionic compounds such as PFASs (Jafvert, 1990; Zhang et al., 2013).

Hydrophobic interactions describe the affinity of nonpolar hydrophobic compounds to repel water molecules and aggregate in aqueous solutions (Chandler, 2005; Du et al., 2014). PFASs anions can sorb to organic hydrophobic surfaces or negatively charged surfaces, overcoming electrostatic repulsion, as the compounds prefer to bind onto surfaces rather than staying in solution (Du et al., 2014). It is also widely observed that more hydrophobic PFASs are sorbed at higher amounts as compared to less hydrophobic compounds (Campos Pereira et al., 2018; Higgins and Luthy, 2006; Wei et al., 2017; Zhao et al., 2014). It is assumed that PFAS tails are arranged closely and parallel to the adsorbent surface to minimize the contact to water molecules (Du et al., 2014). Due to the oleophobic properties of the C–F chain, PFASs have contrasting characteristics as compared to conventional hydrocarbons which further poses a challenge when discerning PFAS sorption mechanisms.

Other sorption mechanisms involve ligand and ion exchange (Gao and Chorover, 2012; Wang et al., 2012; Wei et al., 2017). Hydrophilic heads of PFASs may act as paired groups for functionalities on adsorbents such as metal oxides and ion exchange resins. Several researchers also hypothized that polar interactions such as the formation of hydrogen bonds between the oxygen-containing functional headgroups of PFASs and the carboxylic or phenolic moieties of adsorbents, are a relevant sorption mechanisms (Du et al., 2014). Such sorption mechanisms might play a role in soils with a high amount of metal oxides or clay. Deng et al. (2012) for instance reported an insignificant effect of hydrogen bond on PFOS sorption.

2.6. Soil organic matter as sorbent

PFASs sorption is influenced by the surface chemistry of adsorbents. Previous studies have identified the importance of aromatic and aliphatic structures in SOM in respect to sorption of hydrophobic organic contaminants (HOC) (Abelmann et al., 2005; Chen et al., 2017). Furthermore, several studies have suggested the polarity of SOM as the determining factor for the magnitude of K_{OC} in respect to sorption of non-ionic HOCs and identified an inverse relationship between these two parameters (Abelmann et al., 2005; Kile et al., 1999). Studies about the removal efficiency of PFAS with activated carbon, also underline the role of the non-polarity of the sorbent (Du et al., 2014). Consequently, an increasing sorbent polarity is expected to lead to a higher affinity of PFASs to water molecules, thus reducing hydrophobic interactions with SOM (Zhi and Liu, 2015). However, there are many discrepancies in literature, for instance Zhao et al. (2014) reported an increased sorption despite increasing polarity which was assigned to physico-chemical properties of PFASs such as their possible presence as protonated species at lower pH ranges (pH 3–5).

Humic substances are extracellular decomposition products and can be classified into humic acid (HA) and fulvic acid (FA) as well as humin fraction of SOM (Huang et al., 2003). Their determination is tied to the alkaline extraction procedure and depends on their solubility under different alkaline conditions, thus humic acid, fulvic acid and humin fraction are solely operationally defined (Kleber and Lehmann, 2019).

In general, their composition and functionalities are influenced by different environmental factors, the origin and age of the organic material (Zhao et al., 2014). Humic substances are characterized by an amorphous and polymeric structure (Hayes and Swift, 1978). Inter- and intramolecular interactions of humic substances can affect their physical properties and are dependent on the pH, salt concentration and ions in solution (Benedetti et al., 1996), consequently affecting the binding of organic compounds to the humic substances.

HA is soluble in base but not in acids, while FA is soluble in both (Zhao et al., 2014). FA contains usually a higher amount of carboxylic and phenolic acids as compared to HA. Moreover, acid-base titrations indicate continuous protonation/deprotonation of HA and FA over a solution pH range of pH 3 to above 10, implying the binding of carboxylic and phenolic functional groups to C atoms (Huang et al., 2003).

The so called humin fraction of SOM is operationally defined as insoluble in aqueous alkali solution (Hayes et al., 2017) and represents more than 50% of the total organic carbon found in SOM (López et al., 2012). It is the least understood humic substance due to its non-extractability (Huang et al., 2003), yet it can be assumed that it contains fewer ionizable functional groups than HA and FA due to its insolubility. It consists predominantly of aliphatic hydrocarbons functionalities and partially of carbohydrates, peptides and peptidoglycans (Hayes et al., 2017). Moreover, the humin fraction is of all humic substances most resistant to degradation and contains relatively unchanged plant-derived materials. Consequently, the relative abundance of humin in the respective soil can be considered to roughly correspond to the carbohydrate content of the soil.

Kleber and Lehmann (2019) discussed the implied difficulties and uncertainties that arise from the inability of the alkaline extraction to separate humic from non-humic substances. There is a lacking differentiation of products from secondary synthesis from other ionizable compounds as the alkaline extraction solubilizes organic compounds with attached ionizable functional groups such as phenolic or carboxylic groups, leading to unpredictable reactions that would not occur under natural pH conditions.

Chen et al. (2017) identified condensed carbon domains in humin fractions as enriched in aliphatic carbons for relatively young SOM of a peat soil thus becoming a key factor for the sorption of polycyclic aromatic hydrocarbons (PAH). This suggests that the humin fraction is more important for sorption of hydrophobic organic compounds as compared to humic and fulvic acids. Similar results were also reported by Zhang et al. (2015), with a dominant effect of humin components on PFOS sorption. Humic and fulvic acids were observed to contribute less to PFOS sorption, due to their hydrophilic and polar characteristics, leading to a stronger electrostatic repulsion of PFOS anions. Additionally, Balnois et al. (1999) reported the formation of aggregates by peat humic acids, thus enhancing the hydrophobicity and leading to a higher sorption of hydrophobic chemicals at acidic conditions (Balnois et al., 1999; Terashima et al., 2004).

2.7. Effect of solution pH

In general, PFAS sorption has been observed to be negatively correlated with pH (Campos Pereira et al., 2018; Higgins and Luthy, 2006; Zhang et al., 2013).

Dissociation of functional groups in organic matter as well as protonation and deprotonation of surface functional groups on mineral surfaces is pH dependent and affects the surface charge of adsorbents (Deng et al., 2012). The variable surface charge becomes more negative or less positive with increasing pH thus leading to repulsion or weaker attraction of anionic PFASs through electrostatic interactions (Du et al., 2014). Zhao et al. (2014) also reported a decreasing impact of electrostatic interactions and hydrogen bonding on sorption to humic substances with increasing pH, leading to hydrophobic interactions being the dominant force at pH between 5 to 9. According to Zhang et al. (2013) and Chen et al. (2009), the effect of pH on sorption is due to pH-dependent changes of the sorbent rather than protonation/deprotonation of the PFAS molecules, as the pKa values of PFASs were assumed to be similar or lower as compared to the examined pH range.

2.8. Effect of cation additions on sorption

Previous studies have examined the effect of polyvalent cation additions on sorption of PFASs (Campos Pereira et al., 2018; Higgins and Luthy, 2006; You et al., 2010). Increasing PFAS sorption with increasing polyvalent cation concentrations were assigned to the neutralization of the negative surface charge of adsorbents, as observed by Higgins and Luthy (2006) for Ca^{2+} addition. However, increasing Na^+ or K^+ concentrations did not show any significant effect on PFAS sorption (Higgins and Luthy, 2006; Wang et al., 2015). According to Zhang et al. (2013), divalent cations enhanced PFAS sorption to a greater extent than monovalent cations either by forming a positively charged complex with PFASs or by binding directly onto sludge, thus reducing the overall electrostatic repulsion by reducing the negative surface charge. Additionally, Chen et al. (2009) observed a PFAS solution concentration dependent effect on the sorption enhancement by Ca^{2+}, resulting in a stronger cation effect at lower PFOS concentrations. It was further hypothesized that divalent cations have the potential to form bridges with carboxylic and/or sulfonic groups enhancing the sorption of PFASs (Wang and Shih, 2011), hereby it was observed that the sorption on alumina decreased with increasing ionic strength due to the compression of the electrical double layer. You et al. (2010) also reported a salting-out effect after addition of salts to solution, leading to a decreased solubility of PFASs and enhanced sorption.

The presence of trivalent cations such as Al^{3+} is expected to have a greater impact on sorption as compared to divalent and monovalent cations due to its higher potential to bind to soil organic matter, as the AL^{3+} ion has a smaller ionic radius in combination with a higher valency. Such a sorption behavior was observed by Campos Pereira et al. (2018) for PFASs of intermediate chain length (C_5 – C_8 PFCAs, PFHxS). Similarly, Wang et al. (2015) observed stronger PFAS sorption under Al^{3+} and Fe^{3+} treatment as compared to Ca^{2+} and Na^+.

3. Materials and methods

3.1. Soil characteristics

Two *Sphagnum* peat soil samples (Oi and Oe horizons, sampling depth 10 – 25 cm) were taken from a fibric *Histosol* and one mor humus layer (Oe horizon, 5 – 20 cm) was collected from the organic horizon of a *Podsol* in 2016. The sampling site Paskalampa is located in central Sweden (60°1´45.7”N 15°24`39.9”E) and may be considered representative for northern latitude organic surface horizons. Soil *Paskalampa peat Oi, Paskalampa peat Oe* and *Paskalampa mor Oe* are hereafter abbreviated POi, POe and MOe, respectively. The predominant vegetation at the sampling sites was *Sphagnum fuscum* (soil POi, POe) and *Pinus sylvestris* (soil MOe). The three soils were subject of several previous studies in respect to metal binding (Gustafsson et al., 2014, Gustafsson et al., 2007; Gustafsson and Tiberg, 2015; Gustafsson and van Schaik, 2003). The soils were selected for the current study due to expected differences in PFAS binding properties based on contrasting soil characteristics, especially in terms of soil organic matter quality. Soil chemical properties are presented in Table 1. After collection, the samples were sieved (POi and POe at <8 mm; Moe at <2 mm) prior to homogenization and stored at +5 °C in their field-moist state until further use. A portion of each sample was air-dried for the purpose of soil chemical extractions, determination of total organic carbon (TOC) and ^{13}C NMR analysis.

The soil moisture content was determined gravimetrically by ovendrying at 105°C for 24 h.

3.2. Soil chemical properties

TOC was analyzed at the commercial lab of ALS Scandinavia according to SS-EN 13137 (accredited) using the direct procedure by acidifying the samples to remove carbonates prior to combustion and CO_2 measurement by IR spectrometry. Soil pH was measured in pure Milli-Q water as well as in a solution with a 10 mM $NaNO_3$ electrolyte background, using a 40 mL g^{-1} dw solution-to-soil ratio and a GK2401C combined pH electrode (Radiometer Analytical).

Concentrations of active humic (HA) and fulvic acids (FA) were determined using a method similar to the IHSS method (Swift, 1996). 0.1 M NaOH was added under an atmosphere of N_2 to the soil samples, resulting in an 80 mL g dw^{-1} solution-to-soil ratio. After intermittent shaking and settling of the alkaline suspension overnight, the extracted supernatants were adjusted to pH 1 with 6 M HCl. After 16 h the precipitated humic acid and the dissolved fulvic acid were separated by means of centrifugation. Active HA and FA were subsequently determined from measurement of dissolved organic carbon (DOC) using the accredited methods CSN EN 1484 and CSN EN 16192, SM 5310 (ALS Scandinavia).

Solid-state cross-polarization/magic-angle-spinning ^{13}C nuclear-magnetic-resonance spectroscopy (CP/MAS ^{13}C NMR) was performed on all soil samples at the Technical University of Munich, Germany, to obtain information about the chemical structure of the organic matter. The relative intensity of the resulting peaks was utilized for comparative purposes and for the calculation of integrals corresponding to the relative abundance of the different chemical environments of the carbon atom (Abelmann et al., 2005; Baldock et al., n.d.; Kögel-Knabner, 1997; Kögel-Knabner et al., 1988). The results were further used for the determination of the A/O-alkyl ratio as well as the polarity, aromaticity and hydrophobicity indices (Eq. 1-4) (Abelmann et al., 2005; Baldock et al., 1997; Piterina et al., 2009).

$$Polarity = \frac{Carbonyl\ (160-220ppm)+O-alkyl\ (45-110ppm)+O-aryl\ (142-160ppm)}{C/H-aryl\ (90-142ppm)+alkyl\ C\ (0-45ppm)} \tag{1}$$

$$Aromaticity = \frac{Aromatic\ C\ (110-160ppm)}{Aromatic\ C+Alkyl\ C+O-akyl\ C\ (0-160ppm)} * 100 \tag{2}$$

$$A/O-A = \frac{Alkyl\ C\ region\ (0-45ppm)}{O-alkyl\ C\ region\ (45-110ppm)} \tag{3}$$

$$Hydrophobicity = \frac{Aromatic\ (110-160ppm)+alkyls(0-45ppm)}{Carbonyl/Acyl(160-220ppm)+O-alkyl(45-110ppm)} \tag{4}$$

Measurements of ultraviolet (UV) absorbance (Avantes, AvaSpec-3648, AvaLight DH-S-BAL) were conducted on HA and FA extractions of the soil samples to obtain additional information on the nature of DOC and extractable humic substances, especially regarding the abundance of aromatic structures (Appendix III). UV absorbance at a wavelength of 254 nm (cm^{-1}) was normalized for DOC concentration, yielding the specific ultraviolet absorbance (SUVA) (Piterina et al., 2009).

Geochemically active concentrations of Ca^{2+}, Mg^{+}, K^{+}, Mn^{2+}, Al^{3+}, Fe^{3+} and Cu^{2+} were determined by extractions with 0.1 mol L^{-1} nitric acid (HNO_3) on 1.0 g dw in 30 mL solution. Exchangeable cations were extracted with 0.1 M $BaCl_2$ using 2.5 g dw in 100 mL solution.

Oxalate-extractable (0.2 M oxalate) Al and Fe were determined according to a method described elsewhere (Table 1) (Gustafsson, 2002).

Table 1 Soil chemical characteristics.

Soil	POi (Paskalampa peat Oi)	POe (Paskalampa peat Oe)	MOe (Paskalampa mor Oe)	Unit
pH (H_2O)	4.7	4.1	4.0	
pH (10 mM NaNO3)	3.7	3.5	3.5	
Water content of field-moist soil	93.44	91.16	55.96	%
Total organic carbon	44.90	46.60	53.60	% dw
Humic acid[a]	1.47	2.85	4.85	% C of dw soil
Fulvic acid[b]	1.94	2.83	4.03	% C of dw soil
BaCl2-extractable cations				
Al^{3+}	2.46	8.70	4.51	mmol kg^{-1} dw
Ca^{2+}	21.17	38.82	40.60	mmol kg^{-1} dw
K^{+}	11.10	9.23	14.96	mmol kg^{-1} dw
Mg^{+}	20.56	18.09	18.24	mmol kg^{-1} dw
Na^{+}	5.56	7.20	6.45	mmol kg^{-1} dw
0.1 M HNO_3 extractable cations				
Ca^{2+}	23.19	40.24	42.68	mmol kg^{-1} dw
Fe^{3+}	5.10	12.95	1.99	mmol kg^{-1} dw
K^{+}	16.05	13.87	22.70	mmol kg^{-1} dw
Mg^{2+}	21.30	17.54	18.12	mmol kg^{-1} dw
Al^{3+}	3.55	15.18	12.25	mmol kg^{-1} dw
Cu^{2+}	15.68	18.98	30.55	mmol kg^{-1} dw
Mn^{2+}	909.16	398.76	1663.47	mmol kg^{-1} dw
0.2 M oxalate extractable cations				
Al^{3+}	4.03	17.25	15.38	mmol kg^{-1} dw
Fe^{3+}	6.77	27.99	5.01	mmol kg^{-1} dw

[a] Soluble in 0.1 M NaOH; precipitated at pH 1 using HCl.
[b] Soluble in 0.1M NaOH and at pH 1

3.3. PFAS standards

The analytical standards of the fifteen PFASs examined in this study were purchased from Sigma-Aldrich (Saint Louis, MO, US), including C_4, C_6 – C_{11} and C_{13} perfluoroalkyl carboxylates (PFCAs), C_4, C_6 and C_8 perfluoroalkyl sulfonates (PFSAs), perfluorooctane sulfonamide (FOSA), *N*-ethyl perfluorooctane sulfonamide (Et-FOSA) and C_6 and C_8 fluorotelomer sulfonates (6:2 and 8:2 FTSA). PFCAs C_4 – C_6 and C_8 – C_9 were not analyzed in the pH-dependent sorption experiment but included in the sorption isotherm experiment.

Isotopically labeled internal standards (ISs) were used for quality control, including $^{13}C_4$ PFOA, $^{13}C_5$ PFNA, $^{13}C_2$ PFDA, $^{13}C_2$ PFUnDA, $^{13}C_2$ PFDoDA, $^{13}C_2$PFTeDA, $^{18}O_2$ PFHxS, $^{13}C_4$ PFOS,

$^{13}C_8$ FOSA, d_3-N-EtFOSA, $^{13}C_2$ 6:2 FTSA and $^{13}C_2$ 8:2 FTSA (>98% purity, Wellington Laboratories, Guelph, ON).

The PFAS standard stock solution contained a mix of all compounds under study with a concentration ranging approximately from 1.92 ng mL^{-1} (PFTeDA) to 28.50 ng mL^{-1} (PFOS). The standard stock solution as well as an IS stock mix ($c = 0.05$ µg mL^{-1}) were prepared in LC grade methanol (LiChrosolv®, Merck, Germany) and stored at −18 °C in amber glass vials with polyethylene (PE) caps.

Table 2 Physico-chemical properties of selected PFASs.

Compound	Acronym	Chemical formula	Molecular weight [g mol^{-1}]	*log K_{oc}* [mL g^{-1}]	IS
PFCAs					
Perfluoropentanoate	PFPeA	$C_4F_9COO^-$	263.05	1.37 [d]	$^{13}C_2$ PFHxA
Perfluorohepanoate	PFHpA	$C_6F_{13}COO^-$	363.07	1.63 [d], 2.1 [a]	$^{13}C_4$ PFOA
Perfluorooctanoate	PFOA	$C_7F_{15}COO^-$	413.08	1.89–3.5[b,c,d,e,f]	$^{13}C_4$ PFOA
Perfluorononanoate	PFNA	$C_8F_{17}COO^-$	463.09	2.36–4.0 [a,c,d,e]	$^{13}C_5$ PFNA
Perfluorodecanoate	PFDA	$C_9F_{19}COO^-$	513.10	2.96–4.6 [a,c,d,e]	$^{13}C_2$ PFDA
Perfluoroundecanoate	PFUnDA	$C_{10}F_{21}COO^-$	563.11	3.3–5.1 [a,c,d,e]	$^{13}C_2$ PFUnDA
Perfluorododecanoate	PFDoDA	$C_{11}F_{23}COO^-$	613.12	5.6 ± 0.2 [a]	$^{13}C_2$ PFDoDA
Perfluorotetradecanoate	PFTeDA	$C_{13}F_{27}COO^-$	713.14		$^{13}C_2$ PFTeDA
PFSAs					
Perfluorobutane sulfonate	PFBS	$C_4F_9SO_3^-$	299.11	1.22, 1.79 [d]	$^{13}C_2$ PFHxA
Perfluorohexane sulfonate	PFHxS	$C_6F_{13}SO_3^-$	399.11	2.05–3.7 [a,c,d]	$^{18}O_2$ PFHxS
Perfluorooctane sulfonate	PFOS	$C_8F_{17}SO_3^-$	499.12	2.6–3.8 [a,b,c,d,e,f]	$^{13}C_4$ PFOS
FASAs					
Perfluorooctane sulfonamide	FOSA	$C_8F_{17}SO_2NH_2$	499.14	4.2–4.5 [c,e]	$^{13}C_8$ FOSA
N-ethyl perfluorooctane sulfonamide	Et-FOSA	$C_8F_{17}SO_2N(C_2H_5)H$	527.20		d_3-N-EtFOSA
FTSAs					
6:2 fluorotelomer sulfonate	6:2 FTSA	$C_8H_4F_{13}SO_3^-$	427.16		$^{13}C_2$ 6:2 FTSA
8:2 fluorotelomer sulfonate	8:2 FTSA	$C_{10}H_4F_{17}SO_3^-$	527.17		$^{13}C_2$ 8:2 FTSA

[a] Labadie and Chevreuil, 2011.
[b] Ahrens et al., 2011.
[c] Ahrens et al., 2010.
[d] Guelfo and Higgins, 2013. .
[e] Higgins and Luthy, 2006
[f] Milinovic et al., 2015

3.4. Chemicals

All aqueous solutions for the experiments were prepared using LC-PAK® filtered Milli-Q water (LC-PAK® Polisher, Merck Millipore). Methanol (99.9% hyper grade for LC-MS, LiChrosolv®, Merck, Germany) in this study was used for preparation of PFAS stock solutions, sample preparation and chemical analysis. Hydrochloric acid fuming 37 % (EMSURE® ACS, ISO, Reag. Ph Eur), nitric acid 65 % (EMSURE® Reag. Ph Eur, ISO), sodium hydroxide titrosol (for 1000 ml, c(NaOH) = 0.1 mol/l (0.1 N) Titrisol®), sodium nitrate (> 99.5 % purity, EMSURE® ACS, ISO, Reag. Ph Eur), calcium nitrate (> 98.5 % purity, EMSURE® ACS) and aluminium nitrate (> 98.5 % purity, EMSURE®) were purchased from Merck, Germany.

3.5. Batch sorption and desorption experiments

3.5.1. pH-dependent binding under treatments with Al^{3+} and Ca^{2+}

PFAS sorption to the three soils was measured at four different pH levels under varying Al^{3+}, Ca^{2+} and Na^+ additions using the batch equilibration technique. The sorption experiment was conducted with the soils in their field-moist state, using 50 mL polypropylene (PP) centrifuge tubes (Corning™ Falcon®) in sets of duplicates resulting in a total of 24 samples per soil. The samples were prepared by suspending 1.0 g dw soil per 40 mL solution according to the recipe in Table 3. Varying amounts of dissolved nitrate (NO^{3-}) salts were added to the soil suspensions to reach cation concentrations of ~10.0 mM Na^+, 5.0 mM Ca^{2+} or 2.0 mM Al^{3+}. Additional sodium nitrate ($NaNO_3$) was added to the Ca^{2+} and Al^{3+} treatments to ensure a similar NO_3^- background concentration (~10 mM) in all samples. Varying volumes of sodium hydroxide (NaOH) or nitric acid (HNO_3) were added to reach the target pH values of 3, 4, 5 and 6. Lastly, 50 µL of the stock solution of the fifteen PFASs dissolved in methanol was spiked to each suspension. This yielded a MeOH fraction of 0.13% v/v in the equilibrated suspensions, i.e. well below the level where co-solvent effects may become significant (Schwarzenbach et al., 2017).

Additionally, *n* = 3 negative blanks were prepared for each soil by adding 1.0 g dw soil to 40 mL of LC-PAK Milli-Q water. These blanks provided information about background concentrations of PFASs in the soils. Apart from the soil suspensions, *n* = 3 positive blanks without any soil material were produced by spiking 50 µL PFAS stock solution to 40 mL MeOH. This allowed the quantification of the actual spiked concentration of each PFAS in the experiment.

Soil suspensions were end-over-end shaken at 20 °C for 7 days (168 h) to reach sorption equilibrium (Ahrens et al., 2011; Higgins and Luthy, 2006). Immediately afterwards suspensions were centrifuged for 20 min at a relative centrifugal force of 2100 *g*. The subsequent pH measurement was conducted in subsamples using a two-point calibration at pH 4.0 and 7.0.

Table 3. Batch sorption recipe for the different cation treatments and pH values using 1.0 g dw soil per 40 mL total solution volume. Stated pH values are target values. Letters a, b, and c assign the respective recipe used for a specific soil.

[mL]	30 mM $NaNO_3$	20 mM HNO_3	20 mM NaOH	30 mM $Ca(NO_3)_2$	20 mM $Al(NO_3)_3$	H_2O
Al, pH 3 [a,b,c]	5.3	0	0	0	4	30.7
Al, pH 4 [c]	5.3	0	10	0	4	20.7
Al, pH 4 [a,b]	5.3	0	14	0	4	16.7
Al, pH 5 [b,c]	5.3	0	20	0	4	10.7
Al, pH 5 [a]	5.3	0	26	0	4	4.7
Al, pH 6 [a,b,c]	5	0	31	0	4	0
Ca, pH 3 [a,b,c]	0	4	0	6.7	0	29.3
Ca, pH 4 [c]	0	0	10	6.7	0	23.3
Ca, pH 4 [a,b]	0	0	15	6.7	0	18.3
Ca, pH 5 [a,b,c]	0	0	24.2	6.7	0	9.1
Ca, pH 6 [a,b,c]	0	0	33.3	6.7	0	0
Na, pH 3 [a,b,c]	10.7	4	0	0	0	25.3
Na, pH 4 [a,b,c]	13.3	0	6	0	0	20.7
Na, pH 5 [b]	13.3	0	12	0	0	14.7
Na, pH 5 [a,c]	13.3	0	19.4	0	0	7.3
Na, pH 6 [a,b,c]	13.3	0	26.7	0	0	0

[a] POi
[b] POe
[c] MOe

3.5.2. Sorption and desorption isotherms

Isotherm sorption and desorption experiments were conducted for the soils POi and MOe. Eight samples were prepared in duplicates for each soil by suspending 0.75 g dw in 30 mL solution using a background electrolyte concentration of 10 mM $NaNO_3$.

The resulting soil suspensions were spiked with the various volumes of the same PFAS stock mix as used in the pH-dependent experiment by covering a range for the initial addition of approximately 1.5 log units for each PFAS. The highest initial addition for each isotherm ranged from 13 ng mL^{-1} (PFTeDA) to 190 ng mL^{-1} (PFHxS). The resulting 32 soil suspensions were equilibrated by end-over-end shaking for 7 days and centrifuged for 20 min at 2100 *g* before subsequent PFAS analysis (section 3.5.3). The pH of the respective isotherm was 3.5 for soil MOe and pH 3.7 for soil POi (Appendix X).

Following equilibration, selected samples were used for a subsequent desorption experiment according to the successive dilution method (Pan et al., 2009). 20 mL of the centrifuged supernatant (including 500 µL for PFAS analysis) were extracted from the MOe samples and refilled with PFAS-free 20 mL of 10 mM $NaNO_3$ to conserve the soil suspension volume as well as the underlying ionic strength of NO_3^-. The soil suspensions were re-equilibrated for 7 days as described in the previous sorption experiments. The dilution and re-equilibration step were repeated in total four times to yield desorption isotherms. The same procedure was carried out for the POi samples by extracting 15 mL of the supernatant and replacing it with PFAS-free 15 mL of 10 mM $NaNO_3$ solution. The pH increased marginally for both soils during the desorption experiment, which can be attributed to a certain gradual decrease in DOC acidic groups as aliquots of the initial solution were removed and replaced by the same non-DOC-containing volumes (10 mM $NaNO_3$ Milli-Q water).

n = 3 positive blanks were produced by spiking 20 µL of PFAS stock solution to 30 mL MeOH, corresponding to the isotherm point of the highest initial suspension concentration.

3.5.3. UHPLC-MS/MS analysis

For the quantification of the target PFASs, aliquots of 500 µL of the aqueous supernatants from the batch experiments were transferred to PP tubes (Eppendorf, Germany) together with 400 µL of MeOH and 100 µL of IS stock. The positive blanks were prepared by extracting 500 µL of their solution and transferring it together with 400 µL of Milli-Q water and 100 µL of IS to PP tubes.

Prior to analysis, the samples were vortexed and filtered through a 0.45 µm Minisart® RC hydrophilic syringe filter (Sartorius™, Germany) into 2.0 mL chromatographic analysis vials. Analysis was conducted using ultra-high performance liquid chromatograph coupled to tandem mass spectroscopy (UHPLC-MS/MS) (TSQ Quantiva, Thermo Fisher). The analytical column Acquity UHPLC BEH-C18 (1.7 µm, 50 mm, Waters Corporation, UK) connected to a triple quadrupole detector and an injection volume of 10 µL were used to analyze the processed samples. The mobile phases consisted of 5 mM ammonium acetate that was gradually changed to acetonitrile with an eluent gradient set to 12 min.

The data was evaluated by using the TraceFinder™ 3.3 software (Thermo Fisher). The identification of the compounds was based on characteristic retention times and quantification transitions from precursor to product ions. PFHxS, PFOS, FOSA and Et-FOSA generated two peaks that were integrated as a sum. Peaks with somewhat longer retention time corresponded to the more abundant, linear PFAS isomer whereas the earlier peaks were attributed to the branched isomers (Langlois and Oehme, 2006). All peak integrations were checked manually.

3.5.4. Quality assurance and control

Fluorinated materials were avoided to minimize contamination during the experiment. A nine-point calibration curve (1:1 MeOH:H_2O) ranging from 0.01 to 100 ng mL^{-1} was used for PFAS quantification based on the isotope dilution method. The limit of quantification (LoQ) for the individual compounds is presented in Appendix XII and was defined as the lowest calibration point for which the response factor was within ±30% of the average response factor of the calibration curve (Higgins et al., 2005). LoQs ranged from 0.02 ng mL^{-1} (FOSA) to 0.14 ng mL^{-1} (8:2 FTSA), and from 0.01 ng mL^{-1} (FOSA) to 0.19 ng mL^{-1} (8:2 FTSA), in the pH-dependent sorption experiment and in the isotherm experiment, respectively. Exceptions to the above were the most short-chain PFCAs (C_4, C_6), for which LoQs ranged from 0.38 ng mL^{-1} (PFPeA) to 0.57 ng mL^{-1} (PFHpA). Measured concentrations below the respective LoQ were excluded from further data analysis. The coefficient of determination (R^2) was >0.99 for all calibration curves. All PFAS concentrations in negative control blanks were below the respective LoQ. Consequently, the soils themselves did not contribute to any detectable extent to aqueous concentrations of target PFASs in any of the experiments.

Internal standards selected for this study corresponded to the respective native PFAS, i.e. true IS matching was employed, with the exception of PFBS and PFPeA (IS: $^{13}C_2$ PFHxA), and PFHpA (IS: $^{13}C_4$ PFOA).

The method recovery of individual PFASs (Appendix XIX) was on average 93±16 % and was determined based on the loss of IS during sample preparation in comparison to the calibration curve. Absolute recovery was on average 80±30 %. PFDA, PFNA, PFUnDA, PFTeDA and PFDoDA yielded low absolute recoveries ranging between 23 % and 45 %. Relative errors between native PFAS concentrations in duplicate samples were on average lower for soil POe (6 %) as compared to soil MOe (9 %) and soil POi (15 %). The highest relative errors between duplicates were observed for the most long-chain PFASs in all soils, with the largest relative errors being those for soil POi, i.e. for PFUnDA (≤65%), PFDoDA (≤72%), PFTeDA (≤46%), FOSA (≤69 %) and 8:2 FTSA (≤42%).

3.5.5. Quantification of sorption and desorption parameters

The concentration of the PFASs sorbed to soil, C_s (ng g^{-1}), was calculated according to the following equation:

$$C_s = \frac{\left(C_{in} - C_{eq}\right) * V}{m_{soil}} \tag{5}$$

where C_{in} (ng mL^{-1}) refers to the initial PFAS concentration spiked to the soil suspension, C_{eq} (ng mL^{-1}) is the PFAS concentration measured directly in the aqueous phase by UHPLC-MS/MS, V (mL) is the solution volume and m_{soil} corresponds to the dry weight (g) of the soil sample.

The solid-liquid distribution coefficient, K_d (mL g^{-1}), was calculated as the ratio of sorbed to aqueous concentration of the respective PFAS:

$$K_d = \frac{C_s}{C_{eq}} \tag{6}$$

Moreover, the organic carbon-water partitioning coefficient, K_{OC} (mL g^{-1}), was calculated as the normalization of K_d to the organic carbon content C *(%)* of the soil.

$$K_{OC} = \frac{K_d}{f_{OC}} \tag{7}$$

The percentual sorption of the respective PFAS, S (%), was calculated using the following equation:

$$S(\%) = \frac{C_{in} - C_{eq}}{C_{in}} * 100 \tag{8}$$

The sorption reversibility was based on the ratio between the concentration of PFAS desorbed to the concentration present in the soil prior to the respective desorption round. The resulting desorption yield, D (%), was calculated with the equation:

$$D(\%) = \frac{C_{in,des} - C_{des}}{C_{in,des}} * 100 \tag{9}$$

where $C_{in,des}$ (ng g^{-1}) is the initial concentration of PFAS sorbed to the soil residue prior to the desorption step and C_{des} (ng g^{-1}) is the concentration of PFAS sorbed to the soil after changing the equilibrium. C_{des} was determined based on the concentrations of PFAS in the solid and aqueous phase prior to the desorption step, $C_{in,des}$ (ng g^{-1}) and $C_{in,eq}$ (ng mL^{-1}), respectively, which was further adjusted for the amount of remaining PFAS in the aqueous phase after the solution extraction, V_{ex} (mL). $C_{eq,des}$ (ng mL^{-1}) refers to the PFAS concentration in the aqueous phase after the desorption step, V (mL) is the solution volume and m_{soil} the dry weight of the soil mass used in the desorption experiment. At the first desorption step, $C_{in,des}$ and $C_{in,eq}$ refer to the respective concentrations at the end of the sorption experiment:

$$C_{des} = C_{in,des} + \frac{\left(C_{in,eq} * \left(1 - \frac{V_{ex}}{V}\right) - C_{eq,des}\right) * V}{m_{soil}} \tag{10}$$

3.5.6. Fitting of sorption isotherms

The sorption and desorption isotherm data were evaluated by fitting the data to the linear and Freundlich isotherm model. Both models are widely used for hydrophobic compounds and have been applied for the description of PFAS sorption to soils and sediments in several studies (Ahrens et al., 2011; Higgins and Luthy, 2006; Milinovic et al., 2015). The Freundlich model is defined as:

$$C_s = K_F * (C_{eq})^n \tag{11}$$

where K_F (ng^{1-n} mL^{n} g^{-1}) is the Freundlich sorption coefficient representing the sorption capacity and n is the unitless Freundlich non-linearity parameter. Eq. (11) can be linearized by taking the logarithm of both sides of the equation:

$$log\ C_s = log\ K_F + n\ log\ C_{eq} \tag{12}$$

Fitting Eq. (12) to the respective sorption isotherm data allowed determining the parameters K_F and n that can be used for the comparison of PFAS sorption onto different soils. The application of the Solver function of Microsoft Excel^{TM} spreadsheet lead to a further adjustment of the parameters K_F and n to minimize the root mean square error (*RMSE*). However, the comparison of extrapolated K_F values from nonlinear isotherms can lead to biased results. Therefore concentration-specific K_d values were interpolated by calculating:

$$K_d = K_F * (C_{eq})^{n-1} \tag{13}$$

For $n = 1$, K_d is considered concentration independent and the isotherm is linear. $n < 1$ results in K_d values decreasing with C_s, whereas for $n > 1$, K_d values are increasing with C_s.

The isotherm data were also fitted to the linear model which is described by a constant slope of C_{eq} vs. C_s. In this case, K_d corresponds to the slope of the isotherm. The evaluation of the model-fit was conducted using the goodness of fit, by comparing the *RMSE*, of both models:

$$RMSE = \left(\frac{RSS}{m-p}\right)^{\frac{1}{2}} \tag{14}$$

where p is the number of adjustable fitting parameters and *RSS* is the weighted residual sum of squares for m experimental data points:

$$RSS = \sum_{i=1}^{m} \frac{\left(C_{s,exp,i} - C_{s,cal,i}\right)^2}{\left(C_{s,cal,i}\right)^2} \tag{15}$$

where $C_{s,exp,i}$ and $C_{s,cal,i}$ are the experimental and calculated concentrations of sorbed PFAS to soil. Appendix III sums up the model-fitted sorption and desorption parameters.

3.6. Dissolved organic carbon

Dissolved organic carbon (DOC) was measured for all samples in the pH-dependent sorption experiment. For this purpose, the experiment was repeated according to the previous recipe (Table 3) in the absence of added PFASs in order to avoid the influence of MeOH on DOC measurements. The extracted supernatants of the equilibrated soil solutions were diluted with Milli-Q water and filtered through 0.8/0.2 µm syringe filters (Acrodisc® syringe filters with Supor® membrane). The diluted samples were further acidified with 2 M HCl to remove any carbonates prior to analysis (TOC-V CPH analyzer, Shimadzu).

3.7. Metal analysis

Elemental analysis (Al^{3+}, Ca^{2+}, Na^{+}) of the aqueous phase was conducted for the pH-dependent sorption experiment using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-

OES). A volume of 1.20 mL of the equilibrated and centrifuged PFAS-spiked supernatants was diluted in 2 % nitric acid (HNO_3) using a 1:10 ratio. The solution was filtered through 0.8/0.2 µm syringe filters (Acrodisc® syringe filters with Supor® membrane) and stored at + 8 °C until analysis.

3.8. Statistical analysis

Statistical analysis was conducted using a generalized linear mixed model (GLMM) in RStudio to test for statistically significant differences ($p \leq 0.05$) between average log K_{OC} values across the cation treatments in the pH-dependent sorption experiment (Table A 13-Table A 14). Differences between the geometrical means of the cation treatment groups were calculated under consideration of different pH values as well as data log transformation. The GLMM was extended by adding a variable describing the cation treatment to evaluate differences in PFAS sorption between the soils under study. Sorption behavior of individual compounds in the isotherm experiment was evaluated under consideration of different PFAS spiking concentrations.

Application of the Shapiro-Wilk test showed a normal distribution of the log-transformed sorption data. Linear regression analysis was performed to examine the relationship between log K_{OC} and pH using the Pearson correlation coefficient r^2 and its associated *p*-value.

4. Results and Discussion

4.1. Characterization of soil organic matter

All three soils were characterized by high TOC contents with 45% (soil POi), 47% (Peat soil POe) and 54% (soil MOe) (Table 1) and can be therefore classified as organic soils. The organic matter composition analysed with CP/MAS ^{13}C NMR spectra is presented in Figure 2 and summarized Table 4. All soils showed a predominance of O-alkyl C and Di-O-alkyl C, with peaks at 72 ppm, resulting from C-O carbon atoms in carbohydrates or ethers as well as the peak at 105 ppm. Soil MOe was additionally characterized by considerable amounts of alkyl C with a relatively high signal intensity at 30 ppm originating from methylenic C in long-chain aliphatic compounds. Short-chain alkyl C does not contribute significantly to the peak intensity due to low proportion at 23 ppm. This indicates a larger biodegradation of the material as compared to soil POe and POi, which is reflected in the Alkyl/O-alkyl ratio describing the extent of decomposition (Table 4) (Abelmann et al., 2005; Kögel-Knabner, 1997).

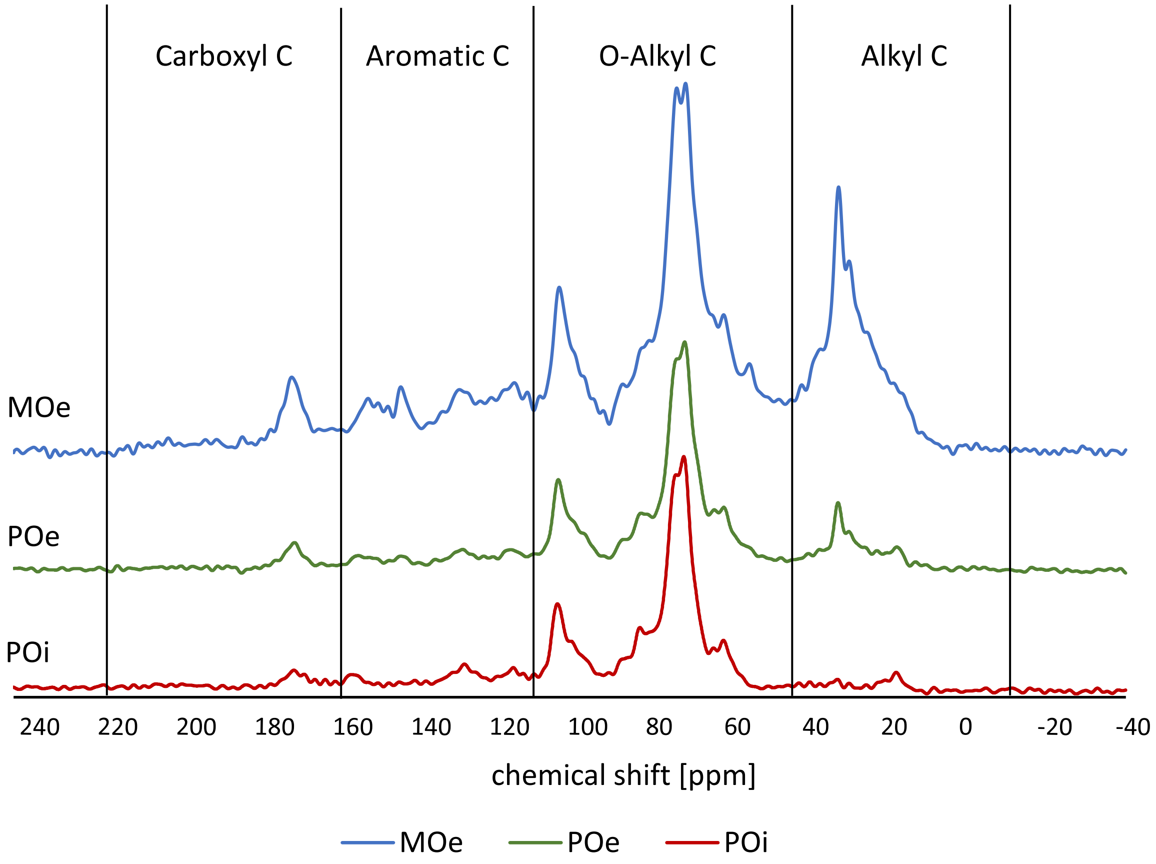

Figure 2 CPMAS ^{13}C-NMR spectra of Paskalampa Peat Oi (POi), Paskalampa Peat Oe (POe) and Paskalampa Mor Oe (MOe).

Soil MOe further differed from the two peat soils in terms of higher extracted amounts of humic and fulvic acids (Table 1), as well as in terms of somewhat higher abundancies of aromatic, carboxylic and phenolic moieties. The higher proportion of phenolic C in soil MOe as compared to the peat soils can be explained by the woody material origin and consequently indicating an enrichment of the soil with lignin-like structures (Kögel-Knabner, 1997). The soil hydrophobicity index decreased in the order of soil POi (0.72) > soil POe (0.70) > soil MOe (0.37) (eq. Table 4). In other words, the hydrophobicity of the two peat soils was calculated to be approximately double that of the mor layer sample MOe.

Table 4 Integration values for main organic C-type domains in ^{13}C- NMR spectra of Paskalampa soil samples and assignment to chemical shift regions (ppm). Integration values of total C are expressed as relative values (%). Additionally, the polarity, aromaticity, hydrophobicity and alkyl-to-O-alkyl ratio of organic matter of the mor and peat soils under study were calculated based on data from the chemical shift regions and according to the equations 1 to 4.

		Chemical shift region [ppm]	Paskalampa Peat Oi [%]	Paskalampa Peat Oe [%]	Paskalampa Mor Oe [%]
Alkyl C	Alkyl C	-10 – 45	2.9	14.9	25.3
O-Alkyl C	Methoxyl C	45 – 60	3.9	6.7	7.9
	Carbohydrate	60 – 90	58.1	46.7	33.2
	Di-O Alkyl C	90 – 110	16.3	13.7	11.0
Aromatic C	Aryl C	110 –142	9.4	8.2	10.9
	Phenolic C	142 – 160	3.1	3.6	4.9
Carboxyl C	Carboxyl C	160 – 220	6.3	6.2	6.9
Polarity *R*			2.48	1.72	1.12
Aromaticity [%]			13.35	12.61	16.96
A/O-A ratio			0.04	0.22	0.49
Hydrophobicity Index			0.72	0.70	0.37

4.2. pH-dependent sorption experiment

4.2.1. Sorption across all soils in the pH-dependent sorption experiment

The sorption affinity of PFASs onto the three soils was evaluated based on average log K_{OC} values (Table A 9, 10, 11) and is presented in Figure 5 as well as more in detail in Figure 3 to 4. Log K_{OC} describes the extent to which organic soil contaminants are sorbed in relation to the organic carbon content of the sorbent. Consequently, it is a useful predictor in terms of mobility of hydrophobic compounds. The extent of sorption for PFUnDA, PFDoDA and PFTeDA followed, on average, the order of POi > POe > MOe. PFOA, PFBS, FOSA, Et-FOSA, 6:2 FTSA and 8:2 FTSA yielded similar average log K_{OC} in soils POi and POe, e.g. sorption decreased in the order of POi ≈ POe > MOe. Sorption of PFHxS and PFOS was observed to follow the order of POe > MOe > POi. Statistically significant differences ($p \leq 0.05$) between the soils were identified using a generalized linear mixed model under consideration of different pH levels and cation treatments (Table A 14). Sorption affinities to soil POi and POe were not significantly different from each other for PFBS, FOSA, 6:2 FTSA and 8:2 FTSA. Sorption to soil MOe did not differ significantly from POi for PFOA and neither did it differ from POe for PFDoDA and PFOS, respectively. Moreover, no significant sorption differences between the soils could be identified for PFUnDA.

Previous studies (Higgins and Luthy, 2006; Milinovic et al., 2015; Zareitalabad et al., 2013) identified SOM as the dominant controlling factor in respect to PFAS sorption mechanisms in soils and sediments. In the present study, the highest overall sorption could be observed in soils POi (OC = 44.90 %) and POe (OC = 46.60%) for most compounds, despite the soils´ lower OC content as compared to soil MOe (OC = 53.60%). The present results contrast with those of the above stated papers, which reported increased sorbed concentrations of PFASs with increasing SOM content of the soils. Consequently, it is evident that not only the quantity of soil organic matter is important for PFAS binding, but also its composition (Wang et al., 2015).

The carbohydrate content of the soils, with higher proportions of O-alkyl C in POi (58%) as compared to POe (47 %) and MOe (33 %) (Table 4), reflects the relative abundance of the humin fraction in SOM (Chen et al., 2017). This suggests the dominant role of humin substances for sorption of PFASs in soil, what is further supported by the on average higher sorption of PFASs in POi as compared to POe and MOe despite lower amounts of HA and FA (Table 1). However, the role of humic and fulvic acids cannot be neglected as previous studies found a possible impact of both humin and HA/FA fractions on PFAS sorption (Campos Pereira et al., 2018; Zhang et al., 2015).

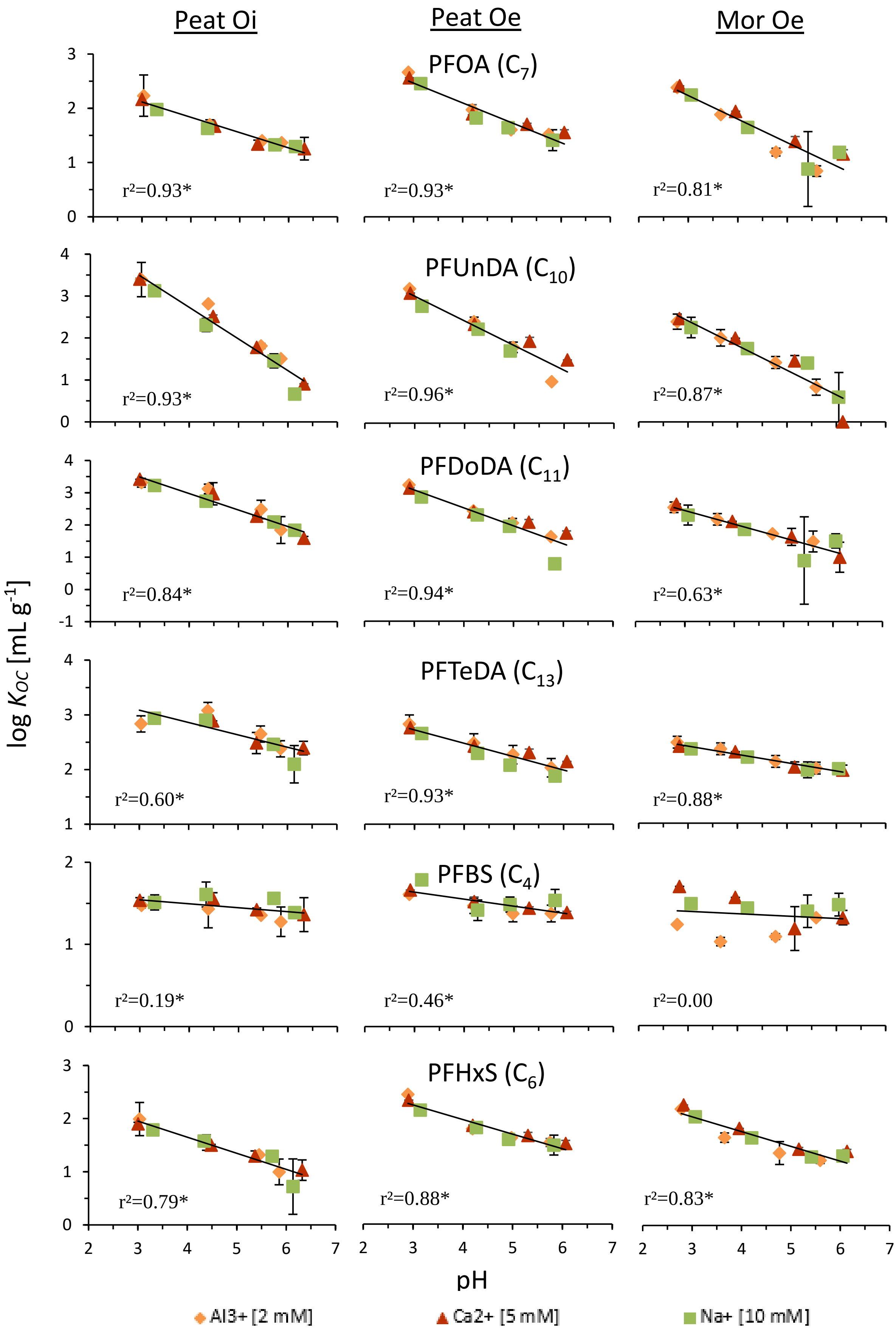

*Figure 3 Effect of pH on log K_{OC} in the Al^{3+} (2 mM), Ca^{2+} (5 mM) and Na^{+} (10 mM) cation treatment for PFCAs (C_7, C_{10}, C_{11}, C_{13}) and PFSAs (C_4, C_6) for three soils under study in the pH sorption experiment. Each data point represents the average of duplicates with respective standard deviation. *$p \leq 0.05$*

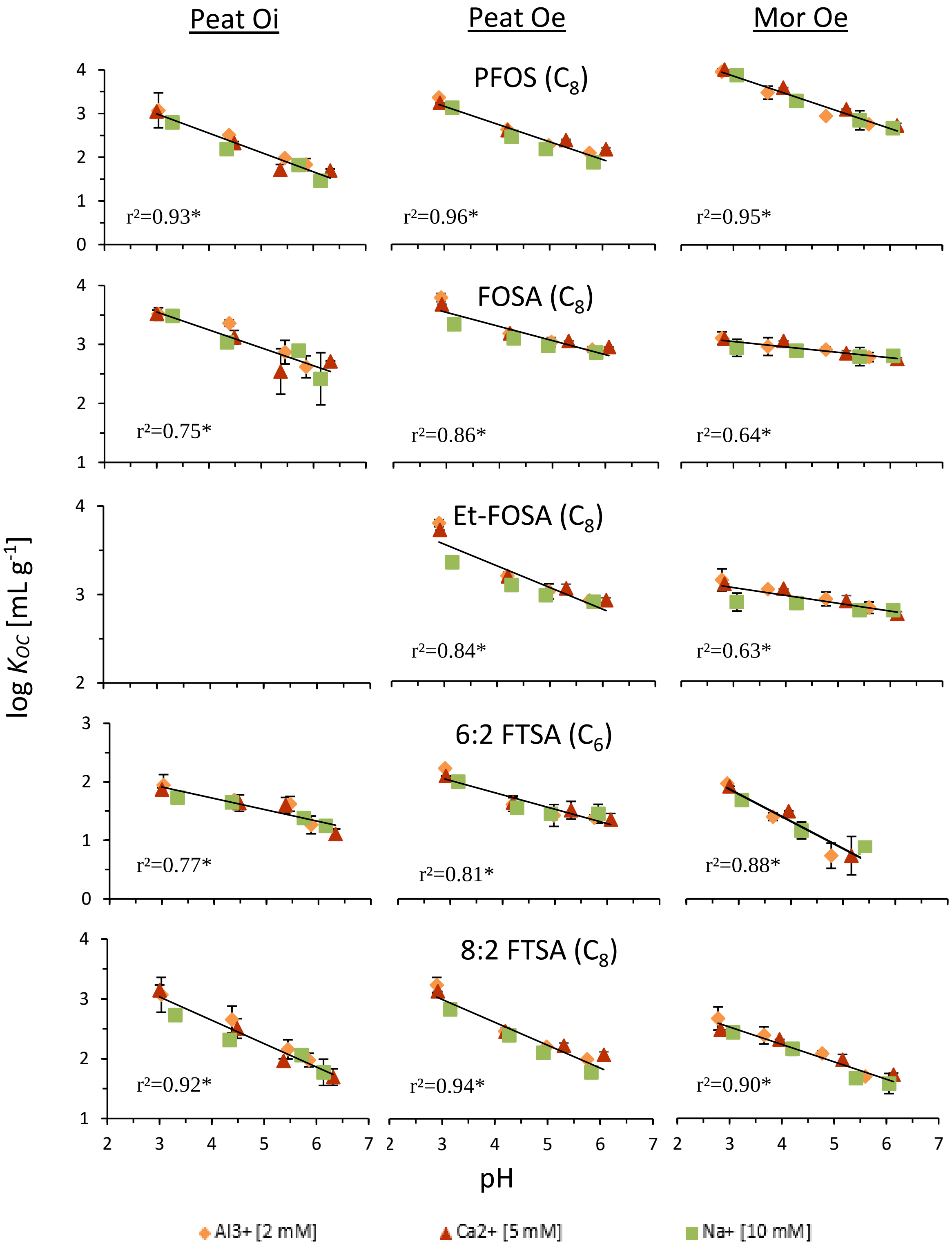

Figure 4 Effect of pH on log K_{OC} *in the* Al^{3+} *(2 mM),* Ca^{2+} *(5 mM) and* Na^{+} *(10 mM) cation treatment for PFOS, FOSA, Et-FOSA and FTSAs (*C_6*,* C_8*) for three soils under study in the pH sorption experiment. Each data point represents the average of duplicates with respective standard deviation.* $*p \leq 0.5$

The ^{13}C NMR spectral intensities of the soils showed a higher proportion of polar structures as compared to nonpolar aliphatic and aromatic carbon, which suggest a sorption influenced by polar interactions. Abelmann et al. (2005) and Kile et al. (1999) identified an inverse relationship between the polarity of SOM and sorption of non-ionic organic contaminants. The present data, however, indicated an increase of log K_{OC} despite increasing polarity of SOM for PFAS under study, with exception of PFOA, PFHxS and PFOS, where no clear trends could be observed. This result suggests polar interactions being overwhelmed by hydrophobic interactions. A similar observation was made by Zhao et al. (2014) for PFSA sorption to humic substances. Such discrepancies reported in literature might result from differences in the origin and chemical composition of organic matter. Previous studies also reported a positive relationship between the aromaticity of SOM and sorption of HOCs (Chen et al., 2007). However, the resulting aromaticity index, varying between 13 (POe) to 17% (MOe), indicates that these aromatic compounds play a subordinate role in explaining sorption differences between the three soils under study.

Consequently, stronger sorption to soil POi can be explained by the higher hydrophobicity as well as the lower abundance of negatively charged carboxylic and phenolic moieties as compared to soil MOe.

Another measure of PFASs sorption to soil is expressed as the fraction sorbed to soil particles which describes the same pattern as log K_{OC}. FOSA and Et-FOSA were bound strongest and reached a sorbed fraction of more than 89 % in all soils. PFCAs showed a trend towards higher sorption with increasing chain length with PFOA sorbing between 34 to 41 % and PFTeDA sorbing between 64 to 81 %. Sorption in the homologous groups of PFSAs and FTSAs increased likewise with the highest sorbed fraction of 70 % for PFOS (MOe) and 67 % for 8:2 FTSA (POi, POe) (Table A 12).

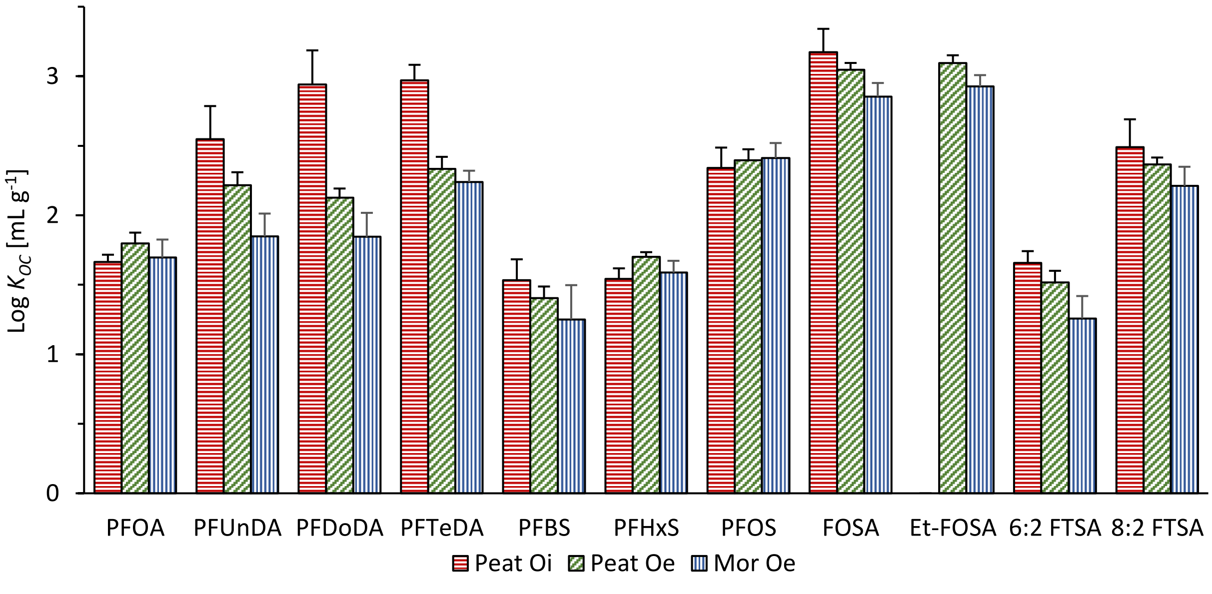

Figure 5 Average log K_{OC} distribution coefficient (mL g^{-1}) of PFASs for the three soils in the pH–dependent sorption experiment across all cation treatments. Average values refer to log K_{OC} at the target pH 4 which is similar to the natural soil pH (H_2O).

4.2.2. Effect of solution pH on sorption

Solution-specific parameters such as the pH value influence the sorption of PFASs due to their impact on soil surface net charge (Campos Pereira et al., 2018; Oliver et al., 2019; Zhang et al., 2013). The relationship between the dependent parameter log K_{OC} and the independent variable pH was evaluated based on the Pearson correlation coefficient r^2 over a range of roughly pH 3 to pH 6 (Figure 3 and Figure 4). The observed negative relationship was significant ($p \leq 0.05$) for all compounds in all soils except for PFBS in MOe (Appendix IX). In general, PFBS showed a weak correlation between log K_{OC} and pH in all three soils with $r^2 < 0.46$ and a slope of almost zero indicating essentially no effect of pH on sorption. A rather weak influence of pH on sorption was also observed for PFTeDA, FOSA and Et-FOSA in soil MOe ($r^2 = 0.63$; slopes of 0 to –0.15 log K_{OC} units per unit pH).

The enhanced sorption with decreasing pH is an indication for electrostatic interactions influencing the sorption behavior of anionic PFASs, as well as uncharged PFASs such as FOSA. Within the pH range under study, PFAS molecules are expected to be negatively charged (i.e. dissociated), in other words their charge is not expected to be affected by pH (Deng et al., 2012). Hereby, it is hypothesized that the negative surface charge of SOM decreases with decreasing pH which consequently governs the sorption of PFASs to soil (Campos Pereira et al., 2018; Zhang et al., 2013).

The log K_{OC} values decreased per unit pH by, on average, 0.34 ± 0.18 log units in POi, 0.34 ± 0.16 log units in POe and 0.26 ± 0.16 log units in MOe (Figure A 6). The obtained values are similar to results from previous studies with 0.32 log units (Campos Pereira et al., 2018) and 0.37 log units (Higgins and Luthy, 2006). The effect of pH decreased with additional CF_2 moieties for the most long-chain PFCAs (C_{10}, C_{11}, C_{13}) in soils POi and POe. Sorption to soil MOe showed a slightly weaker dependency of pH for PFDoDA ($r^2 = 0.63$) as compared to PFUnDA ($r^2 = 0.87$) and PFTeDA ($r^2 = 0.88$), what is consistent with previous results for a similar mor layer sample from the same location (Campos Pereira et al., 2018). Furthermore, pH had a stronger impact on sorption of PFSAs with increasing chain length in all soils with r^2 values of 0 – 0.46 for PFBS, 0.79 – 0.88 for PFHxS and 0.93 – 0.96 for PFOS. The influence of the perfluorocarbon chain length on the log K_{OC}-pH relationship is further described by the regressed slopes which are becoming steeper with additional CF_2 moieties for PFSAs and less steep within the class of PFCAs (Figure A 7). Sorption of fluorotelomer sulfonates was well predicted by pH with an increasing Pearson r^2 value with increasing perfluorocarbon chain length. Sorption of PFOA, FOSA and Et-FOSA was also well correlated with pH in all soils ($r^2 = 0.76 – 0.93$) with exception of FOSA ($r^2 = 0.64$) and Et-FOSA ($r^2 = 0.63$) in MOe.

4.2.3. Effect of cation additions on sorption

Addition of cations were identified to influence the sorption behavior of PFASs to organic soils (Figure 6, Table A 13). The enhanced sorption based on the added cations may be explained by the adsorption of cations to SOM, which reduces the negative surface charge of the material and consequently reduces the electrostatic repulsion of PFASs (Campos Pereira et al., 2018; Higgins and Luthy, 2006; Zhang et al., 2013). Sorption governed by specific chemical interactions such as cation bridging via complexation as suggested by Wang et al. (2015) and You et al. (2010) was not supported by present observations. In such a case, a stronger sorption of carboxylates as compared to sulfonates of the same chain length would have been observed, due to the higher complex-forming affinity of carboxylates as well as sulfonates being known to be poor ligands (Higgins and Luthy, 2007; Lawrance, 1986).

Trivalent cation additions (Al^{3+}) enhanced sorption of most PFASs to a greater degree than those of divalent (Ca^{2+}) and monovalent (Na^{+}) cations, which is consistent with previous research (Campos Pereira et al., 2018; Higgins and Luthy, 2006; Oliver et al., 2019; Zhang et al., 2013). The sorbed cations partly neutralize the negative surface charge of natural organic matter, which promotes PFAS binding. The overall stronger effect of Al^{3+} additions on PFAS sorption is explained by its higher charge density as compared to Ca^{2+} and Na^{+} which leads to a higher complex-forming affinity with organic functionalities (Campos Pereira et al., 2018). In general, it can be assumed that an even larger addition of Al^{3+} as compared to the employed 2 mM would have resulted in a more pronounced sorption difference. However, a drawback of a larger Al^{3+} addition would have been the risk of formation of aluminum hydroxide precipitates which would make hinder further increase of Al concentration in solution. Furthermore, the observed pattern of log K_{OC} increasing in the order of Al^{3+} (2 mM) > Ca $^{2+}$ (5 mM) > Na^{+} (10 mM) was not entirely consistent, which underlines the complexity of PFAS–organic matter interactions. PFOA and PFUnDA in soil MOe as well as PFUnDA in POe showed the highest average log K_{OC} values upon Ca^{2+} instead of Al^{3+} additions. Increased sorption upon treatment with Na^{+} as compared to that of Ca^{2+} could be also observed for PFUnDA (POe), PFDoDA (POi, POe), PFTeDA (POi) and 6:2 FTSAs (MOe). PFBS was the only compound following a sorption pattern of $Na^{+} > Ca^{2+} > Al^{3+}$ in all soils. In combination with the weak relationship between PFBS sorption and the pH value, this finding corroborates that other mechanisms rather than electrostatic or hydrophobic interactions likely are more important for sorption of PFBS to soil organic matter.

Despite the different sorption magnitude resulting from varying cation additions, only a few statistically significant differences ($p \leq 0.05$) were identified (Table A 13). In general, the sorption within the Al^{3+} treatment was significantly different ($p \leq 0.05$) from that of Na^+ treatment. Moreover, differences were more pronounced in soil POe as compared to soils POi and MOe, suggesting a stronger effect of cations additions for soil POe as compared to the other soils.

The comparison of the soils under study revealed a similar pattern within individual cation treatments. Average sorption in MOe was the lowest for all target PFASs in all cation treatments, except for PFHxS and PFOS where POi had the lowest log K_{OC} values. PFUnDA (except for the Na^+ treatment), PFDoDA, PFTeDA, PFBS and FTSAs were bound the strongest in POi, while PFOA, PFUnDA (in Na^+), PFHxS, PFOS and FOSA showed the highest log K_{OC} values in POe.

Humic substances are commonly complexed with metal ions in the environment which is attributed to their high content of functional groups such as carboxylic, phenolic or aliphatic groups (Eshwar et al., 2017; Gustafsson and van Schaik, 2003). Consequently, it could have been expected that the higher amount of HA and FA present in the mor layer would contribute to a stronger binding of Al^{3+} and Ca^{2+} as compared to the soils POi and POe. However, all added cations were sorbed to a higher degree in soil POi as compared to POe and MOe, thus showing an overall similar sorption pattern as compared to the PFAS sorption. Therefore, differences in PFAS sorption between the peat soils and mor layer might be partly explained by the differences in metal binding. If solution cation concentration rather than sorbed cations would predominantly affect PFAS binding, than a higher PFAS sorption would have been expected under the Na^+ treatment as it is present at a higher concentration in solution as compared to Al^{3+} and Ca^{2+} cations. An exception poses the sorption of PFHxS and PFOS in the Ca^{2+} and Na^+ treatment, where MOe showed a higher sorption than POi (Appendix X). Moreover, observed differences between both peat soils were rather explained by other factors as PFOA, PFHxS, PFOS and FOSA were sorbed more strongly under all cation treatments in POe as compared to POi.

The simultaneous variation of solution parameters such as pH and cation concentrations requires a differentiation of the effects on PFAS sorption in order to be able to make a priori estimations of distribution coefficients. The surface net charge of soil is influenced by changes of ionic strength and the pH, thus the modelling of the surface charge would make the differentiation between these parameters unnecessary (Löfgren et al., 2010).

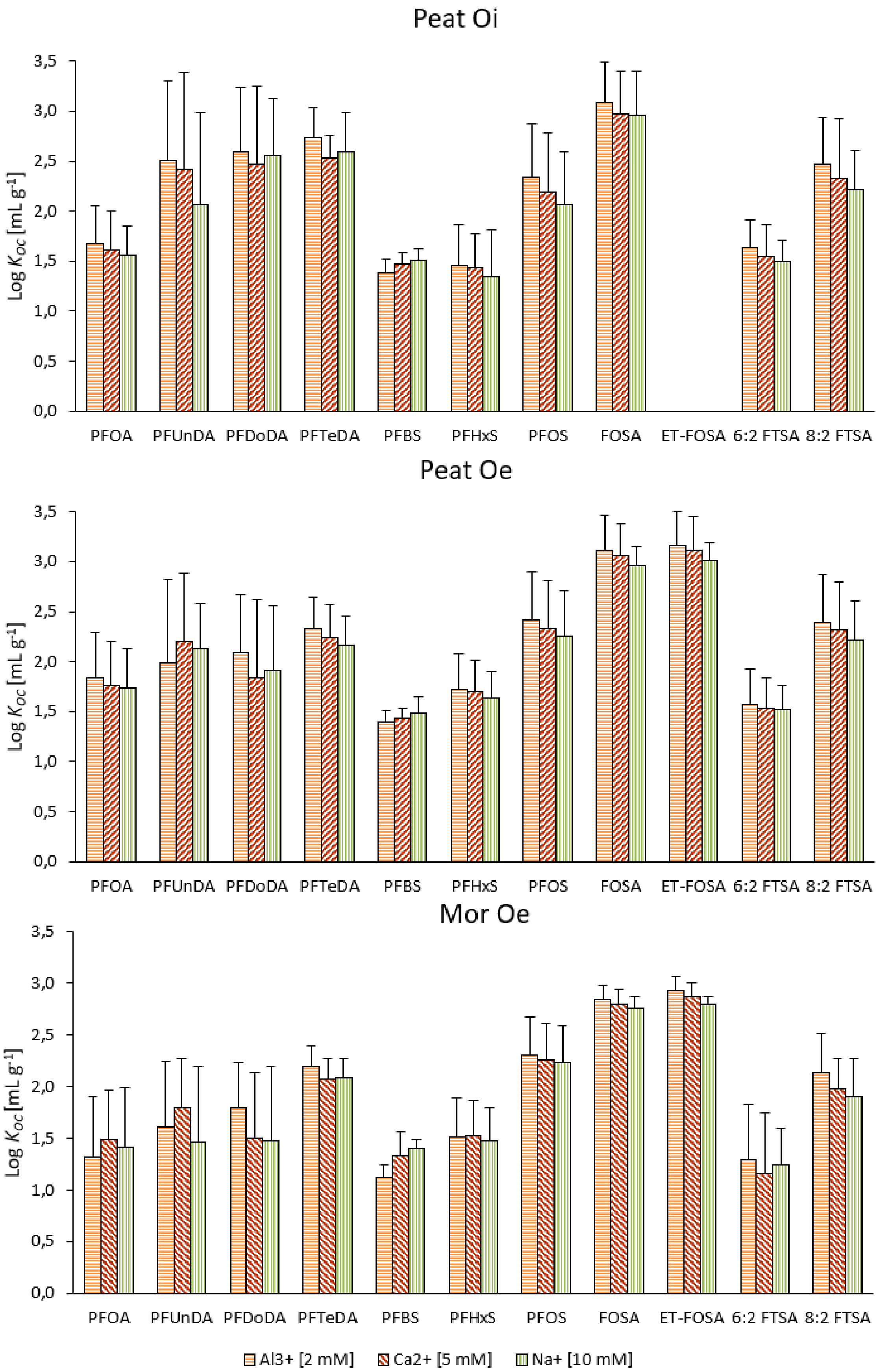

Figure 6 Comparison of the Al^{3+}, Ca^{2+} and Na^{+} treatments based on average log K_{OC} values (mL g^{-1}) for all target compounds within respective soils and across all measured pH values.

4.3. Description of sorption isotherms

The soils POi and MOe were selected for the isotherm experiment due to the highest sorption differences identified between these soils in the previous pH-dependent experiment. Figure 7 - Figure 9 show the sorption and desorption isotherms for PFCAs (C_4, C_6-C_{11}, C_{13}), PFSAs (C_6, C_8), FOSA (C_8), Et-FOSA (C_8) and FTSAs (C_6, C_8). Under the experimental conditions, sorption and desorption data for certain compounds were below the limit of quantification and are therefore not shown.

4.3.1. PFASs sorption on soils

Isotherm parameters for the linear and Freundlich model are summarized in Table 5. All compounds are well described by the linear model and the Freundlich model in soil POi ($R^2 \geq 0.97$). The isotherm of PFTeDA ($R^2 = 0.85$ and $R^2 = 0.91$, respectively) showed a weaker fit to both models due to the strong scattering of the data points.

In contrast to POi, the better sorption prediction by the Freundlich model was more evident in MOe with $R^2 \geq 0.98$, while the coefficient of determination varied between 0.71 (PFPeA) and 0.99 (FOSA) in the linear model. The linear model revealed a better isotherm fit with increasing chain length for all homologous PFAS groups. Also, Et-FOSA was better predicted ($R^2 = 0.99$) than the weaker sorbing FOSA ($R^2 = 0.96$). An exception from the observations can be seen for PFCAs C_{10}, C_{11} and C_{13} where R^2 drops to 0.80 before increasing again to 0.98. The better sorption prediction by the Freundlich model can be explained by a better fit of the isotherm data at lower concentrations as compared to the linear model as well as the optimization of isotherm parameters in the Freundlich model. Average log K_{OC} values obtained from both models differ less than 0.14 log units from each other in POi and less than 0.16 log units in MOe. Only PFDoDA and PFTeDA showed a 0.25 and 0.37 log units higher log K_{OC} value in the linear model as compared to the Freundlich model in POi.

The Freundlich sorption parameter *n*, describing the nonlinearity, is between 0.63 and 0.98 for most compounds in POi and between 0.70 to 1.30 for all compounds in MOe (Table 5). Values of $n \neq 1$ indicate nonlinear sorption (Higgins and Luthy, 2006). Sorption processes are then attributed to e.g. site heterogeneity and sorbate-sorbate interactions including electrostatic repulsion (Higgins and Luthy, 2006). Surface saturation as a cause for nonlinearity is however not expected due to added PFAS concentrations being far below the concentration anticipated for monolayer coverage (Li et al., 2019). The compounds PFDoDA (Freundlich parameter

n = 1.71), PFTeDA (n = 1.81) and FOSA (n = 1.34) in POi had values of $n > 1$what indicates sorbate-sorbate interactions (Barzen-Hanson et al., 2017) and might explain the increasing log K_{OC} value with increasing spiking concentration. Despite n > 1 for PFHpA (n = 1.07), PFNA (n = 1.30), PFDA (n = 1.13), PFTeDA (n = 1.03), PFHxS (n = 1.19), Et-FOSA (n = 1.11) and 8:2 FTSA (n = 1.07) in MOe a consistent increase in log K_{OC} could not be observed. The overall slightly lower n values in POi could indicate a stronger heterogeneity of sorption sites (Guo et al., 2010), suggesting n as an index for site energy distribution (Weber et al., 1992). A linear isotherm (n = 1) could be identified for FOSA in MOe. According to Schwarzenbach et al. (2017), linear isotherms are expected for sorption processes driven by equilibrium partitioning between two phases. Competitive effects resulting from the multisolute batch sorption experiment being responsible for nonlinear isotherms is considered unlikely in this study and would potentially occur only at much higher spiked concentrations. However, tests comparing the sorption of selected compounds under the presence of other PFASs and alone would provide certainty.

According to Pan et al. (2009), sorption of PFASs is not concentration independent and distribution coefficients increase with decreasing aqueous concentration for concave isotherms ($n < 1$). Despite noticing a variation in log K_{OC} values, such trends describing an increasing log K_{OC} value with decreasing aqueous concentration could be only identified for PFOA, PFDA, PFUnDA, PFOS, 6:2 FTSA and 8:2 FTSA in POi. Other compounds showed slightly higher log K_{OC} at the lowest aqueous concentrations, but values were overall rather stable. For PFDoDA, PFTeDA and FOSA however, it has been observed that the distribution coefficient increased with increasing aqueous concentration which corresponds to $n > 1$. In MOe, log K_{OC} values decreased with increasing aqueous concentration for all compounds, however for compounds with $n > 1$ an initial increase in log K_{OC} could be observed followed by further decrease at higher solution concentrations. Et-FOSA was the only compound for which sorption increased with aqueous concentration, while PFTeDA, FOSA and 8:2 FTSA which showed n values close to 1, showed an indifferent pattern (Table A 21, Table A 22).

The PFAS concentration spiked in the pH-dependent experiment corresponds to a concentration between the sorption isotherm points S3 and S4 (Appendix IX) which allows a comparison across the two experiments. The average log K_{OC} value obtained from the Na^+ treatment at pH 3 and pH 4 in the pH-dependent experiment fitted well into the sorption isotherms in MOe differing less than 0.16 log units from the expected isotherm sorption point, with exception of PFUnDA which showed a 0.28 log units stronger sorption than predicted. However, log K_{OC} values from the pH-dependent experiment did not fit well for PFUnDA, PFDoDA, PFTeDA and PFHxS in POi, being 0.24 to 0.35 log units lower than expected as in the sorption isotherms. The stronger difference might be partly explained by higher variation between duplicates in the POi soil, especially for long chain compounds.

Table 5 Isotherm sorption parameters obtained by fitting data to the linear and to the Freundlich model.

Compound	Linear Model			Freundlich Model				
	Log K_d [mL g^{-1} dw]	Log K_{OC} [mL g^{-1} dw]	R²	Log K_F [ng$^{(1-n)}$ mL^{n} g^{-1} dw]	n	R²	Log K_d [mL g^{-1} dw]	Log K_{OC} [mL g^{-1} dw]
				Paskalampa Peat Oi				
PFPeA*								
PFHpA	1.71	2.05	0.98	1.85	0.89	1.00	1.75	2.10
PFOA	1.51	1.86	0.99	1.71	0.88	1.00	1.59	1.94
PFNA	1.45	1.80	0.97	1.63	0.88	1.00	1.56	1.91
PFDA	1.95	2.29	0.98	2.10	0.86	1.00	2.07	2.42
PFUnDA	2.46	2.81	0.99	2.50	0.97	1.00	2.50	2.85
PFDoDA	2.94	3.29	0.98	2.92	1.71	0.95	2.69	3.04
PFTeDA	3.23	3.58	0.85	3.78	1.81	0.91	3.04	3.39
PFHxS	1.36	1.70	0.98	1.34	1.01	1.00	1.35	1.70
PFOS	2.16	2.51	0.99	2.37	0.85	1.00	2.26	2.61
FOSA	3.11	3.45	0.99	2.96	1.34	0.99	2.98	3.32
ET-FOSA	3.93	4.28	1.00	3.93	0.95	1.00	3.97	4.31
6:2 FTSA	1.30	1.65	0.99	1.49	0.88	1.00	1.39	1.74
8:2 FTSA	2.18	2.52	1.00	2.17	1.02	1.00	2.18	2.52
				Paskalampa Mor Oe				
PFPeA	1.16	1.43	0.71	1.41	0.73	0.99	1.20	1.47
PFHpA	1.42	1.69	0.73	1.28	1.07	1.00	1.34	1.61
PFOA	1.30	1.57	0.95	1.55	0.84	1.00	1.43	1.70
PFNA	1.11	1.39	0.96	0.77	1.30	0.99	0.98	1.25
PFDA	1.28	1.55	0.97	1.16	1.13	1.00	1.23	1.50
PFUnDA	1.01	1.28	0.80	1.07	0.91	1.00	1.03	1.30
PFDoDA	1.06	1.33	0.87	1.27	0.77	0.99	1.21	1.48
PFTeDA	1.80	2.07	0.98	1.80	1.03	1.00	1.75	2.02
PFHxS	1.22	1.49	0.92	0.91	1.19	0.99	1.12	1.39
PFOS	1.89	2.16	0.94	2.11	0.88	1.00	2.03	2.30
FOSA	2.31	2.58	0.96	2.27	1.00	1.00	2.27	2.54
ET-FOSA	2.62	2.89	0.99	2.55	1.11	1.00	2.61	2.88
6:2 FTSA	0.78	1.05	0.75	1.10	0.70	0.99	0.92	1.20
8:2 FTSA	1.72	1.99	0.98	1.66	1.07	1.00	1.72	1.99

*omitted from results

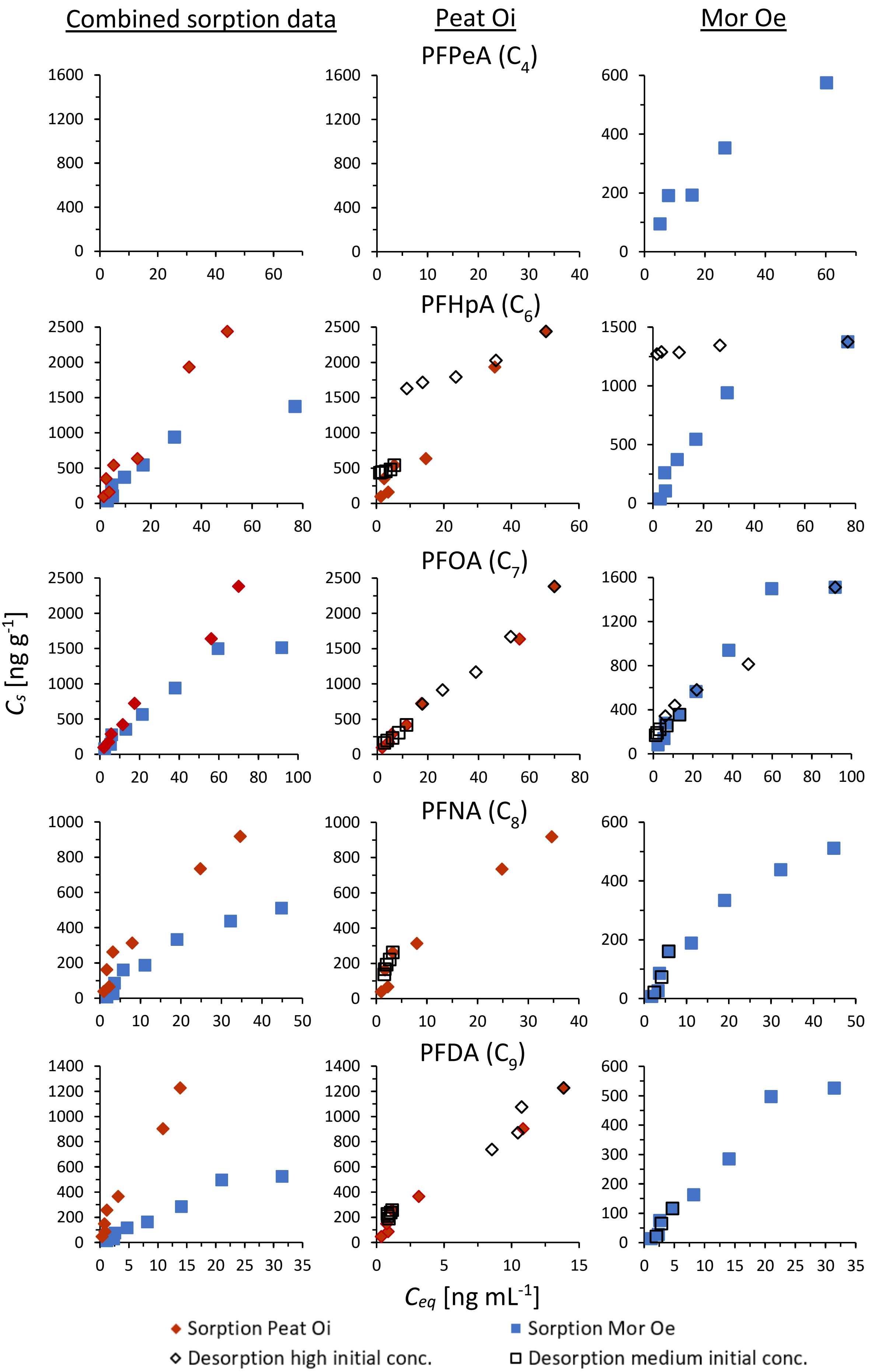

Figure 7 Sorption and desorption isotherms of PFPeA, PFHpA, PFOA, PFNA and PFDA for the soils Peat Oi and Mor Oe. Solid markers represent sorption data, open markers represent desorption data. Each data point represents the average of duplicates.

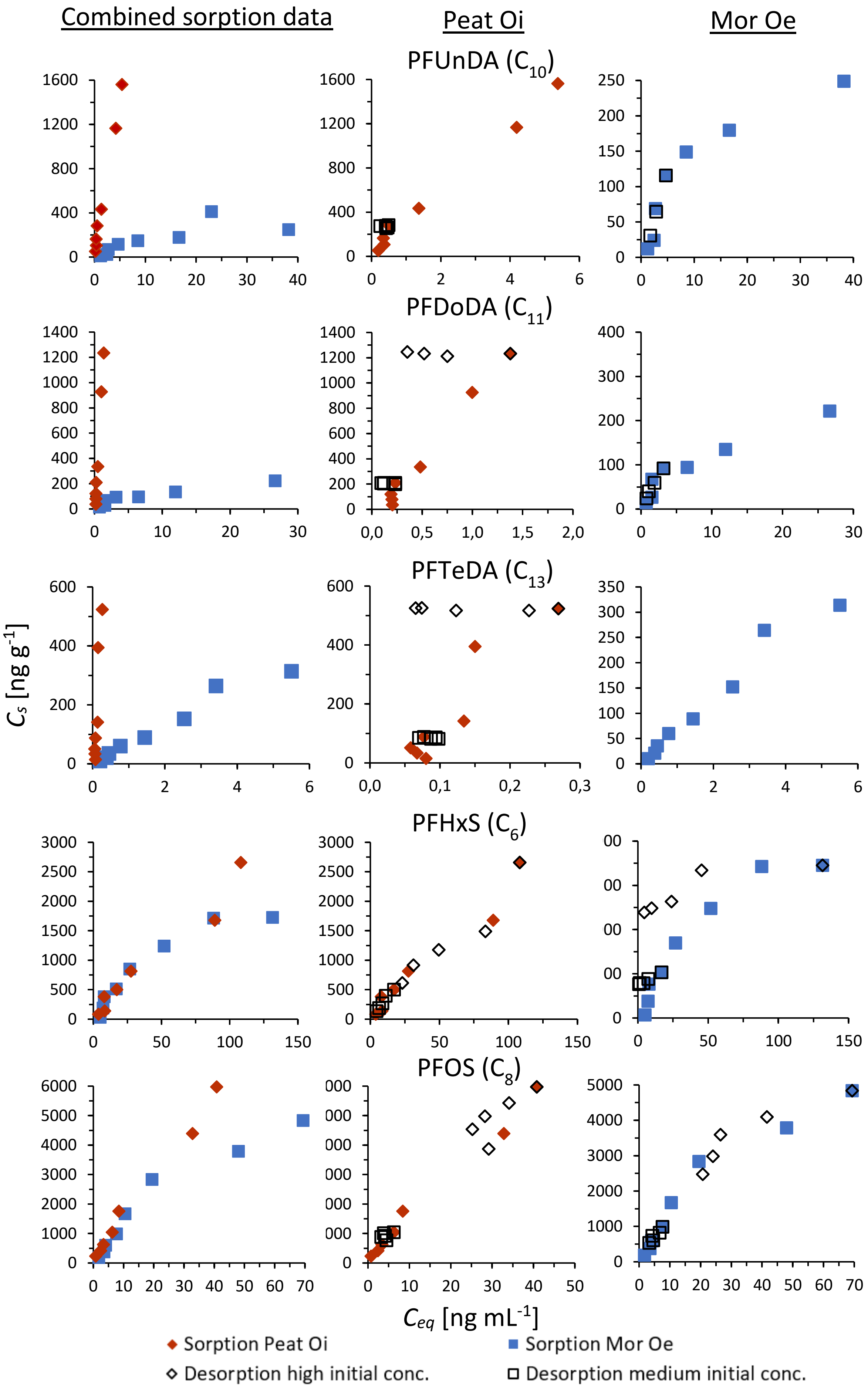

Figure 8 Sorption and desorption isotherms of PFUnDA, PFDoDA, PFTeDA, PFHxS and PFOS for the soils Peat Oi and Mor Oe. Solid markers represent sorption data, open markers represent desorption data. Each data point represents the average of duplicates.

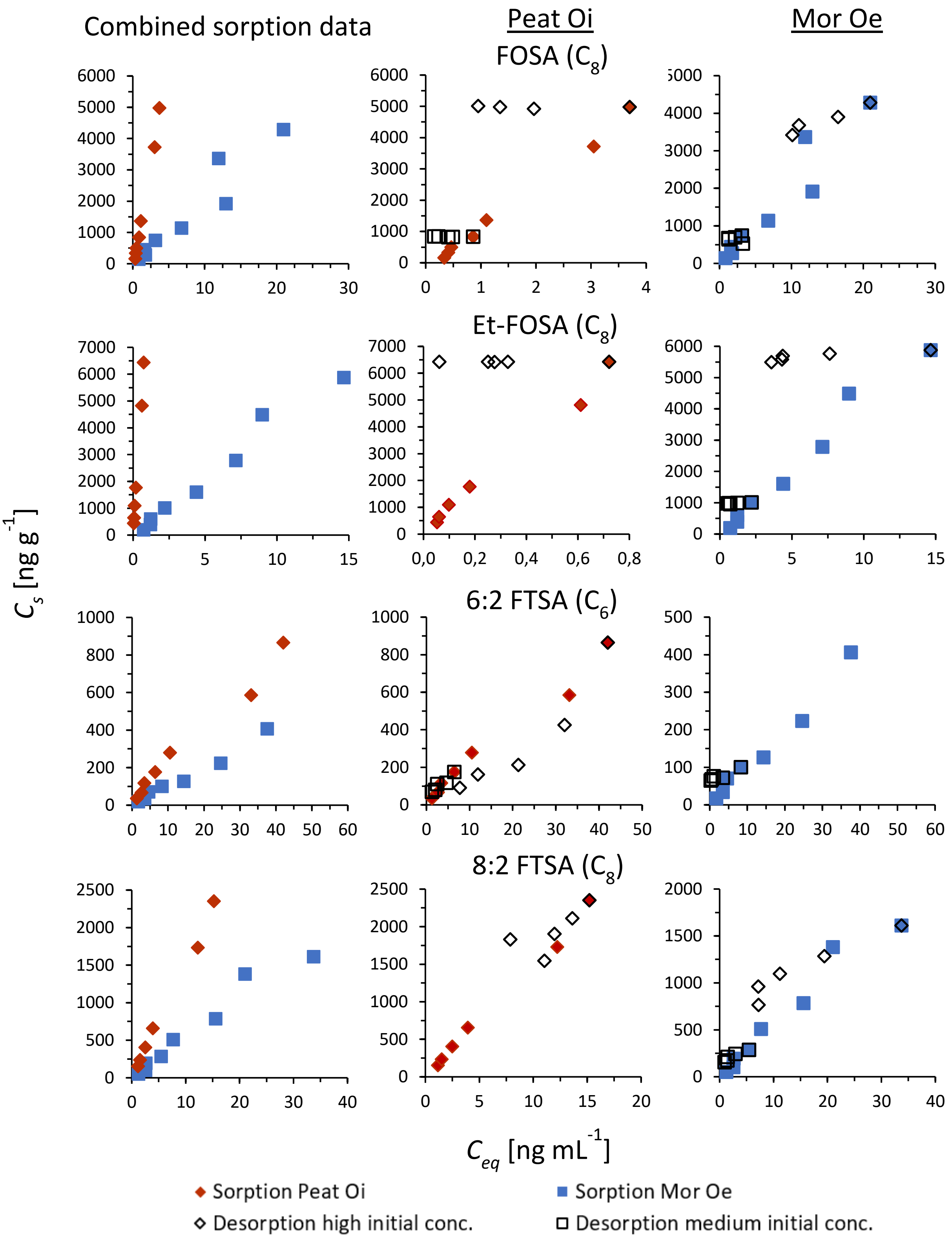

Figure 9 Sorption and desorption isotherms of FOSA, Et-FOSA, 6:2 FTSA and 8:2 FTSA for the soils POi and MOe. Solid markers represent sorption data, open markers represent desorption data. Each data point represents the average of duplicates.

Previously identified sorption patterns in the pH-dependent experiment for PFHxS and PFOS, showing marginal differences between POi and MOe, are underlined in the isotherm experiment. The left hand side of the graphs in Figure 7 - Figure 9 shows that sorption differences for these compounds are more evident at the highest spiked concentrations. Nonetheless, according to the log K_{OC} values, soil POi sorbed slightly stronger than soil MOe at spiking concentrations similar to the pH-dependent experiment (Figure 6). This result promotes the effect of cation additions, as in the pH-dependent experiment sorption was stronger for these compounds in soil MOe (Figure 6). In general, soil POi showed a larger sorption capacity as compared to soil MOe for all target compounds, which furthermore became more pronounced at higher spiking concentrations, as well as for the longer-chained PFASs as compared to the shorter-chained PFASs (Figure A 11). Sorption differences increased from C_6 to C_8 for PFSAs and from C_7 to C_{11} for PFCAs. However, Δlog K_{OC} decreased for PFTeDA (C_{13}) and a higher Δlog K_{OC} was observed for PFHpA (C_6) as compared to PFOA (C_7). Moreover, there was no increased difference observed within the class of FTSAs what could be assigned to the similar slopes (~0.39 log units per CF_2 moiety) describing the relationship between log K_{OC} and chain length (Figure A 10). The same observation was made for PFSAs were the slopes differed less (0.44 log units per CF_2 moiety in soil POi, and 0.37 log units per CF_2 moiety in soil MOe) as compared to the class of PFCAs (POi: 0.27 log units per CF_2 moiety, MOe: 0.07 log units per CF_2 moiety). Consequently, the capacity of the two soils to bind PFCAs increased only slightly with the number of CF_2 moieties in the PFCA molecule.

The Freundlich parameter K_f, describing the sorptive capacity, also supports the influence of hydrophobic interactions in the sorption process, as it was increasing with increasing soil hydrophobicity. However, it can be seen in Table 5 that the increase in K_f is more consistent and reaches higher values in POi as compared to MOe. This underlines the stronger sorption in POi as well as higher relevance of hydrophobic interactions what can also be derived from slopes in Figure A 10.

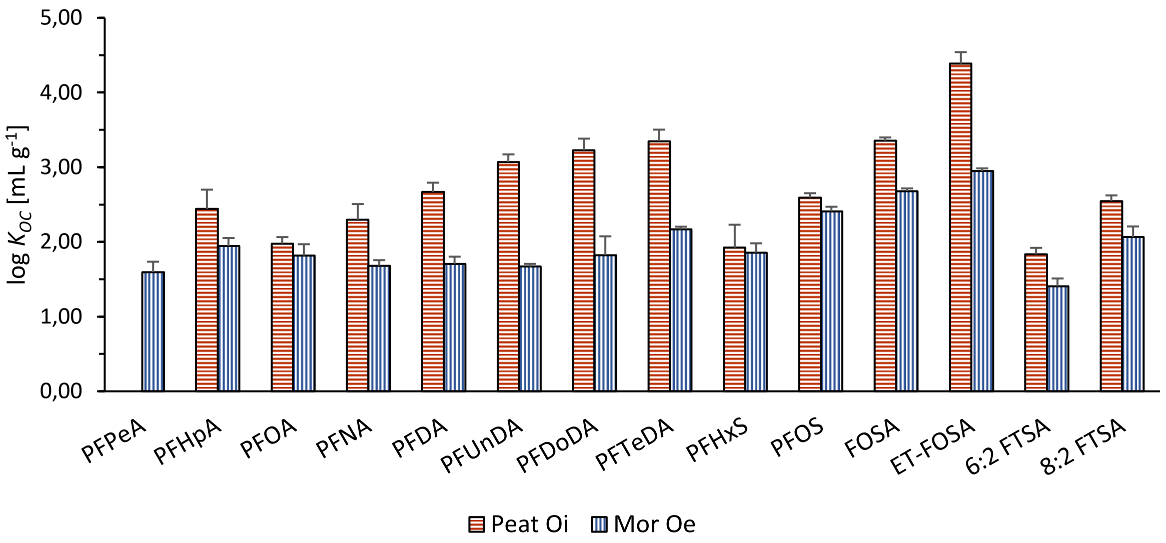

Figure 10 Average log K_{OC} *distribution coefficient (mL* g^{-1}*) of PFASs for the soils Paskalampa peat Oi and Paskalmapa mor Oe in the isotherm sorption experiment. Average values are based on data points S3 and S4, to refer to similar spiking concentrations as in the pH-dependent experiment.*

4.3.2. Sorption reversibility of PFASs

It is expected that strongly sorbing PFASs show a more pronounced sorption irreversibility suggesting for instance decreasing desorption with increasing chain length (Chen et al., 2016; Zhao et al., 2012). Such a trend, taking the highest initial concentration as a starting point (S8), could be observed for PFOA (desorption yield 70 %) > PFDA (68 %) > PFUnDA (23 %) > PFDoDA (5 %), PFTeDA (1 %) and for PFHxS (77 %) > PFOS (35 %) and 6:2 FTSA (90 %) > 8:2 FTSA (34 %), in soil POi (Figure A 9). PFHpA posed an exception with a lower desorption (33 %) as compared to PFOA.

In MOe, PFHpA (desorption yield 8 %) was again more irreversible than PFCAs with a longer chain length such as PFOA (77 %) (Figure A 8). However, PFCAs $C_8 – C_{11}$ showed a sorption reversibility of 100 % at lower and higher initial concentrations which is exemplified in Figure A 12. A similar desorption pattern was also observed for PFNA in soil POi. This non-expected sorption behavior as regards the most long-chain PFCAs may be explained by experimental difficulties resulting from non-settling particles (Kan et al., 1994), which in particular were present in the suspensions of soil MOe. This would lead to a substantial reduction of PFASs on soil and was reflected in the results from the successive dilution equations. An explanation why mainly long-chain PFCAs are affected could be partly derived from the chain rigidity observed by Ellis et al. (2004), which increases as a function of chain length and could lead to steric hindrance affecting the sorption to SOM. Contrasting to POi, PFHxS (31 %) showed a weaker desorption as compared to PFOS (49 %), what was also observed for FTSAs. Additionally, FOSA (36 %) yielded a higher desorption than Et-FOSA (7 %) what corresponds to the previously identified higher log K_{OC} values of Et-FOSA. The described desorption patterns could be also observed for the starting point at the lower concentration (S4) in both soils (Table A 25). A trend towards higher irreversibility with increasing sorption as seen in POi, was also identified by Chen et al. (21016) for PFCAs. The obtained results indicate moreover higher reversibility at the maximum concentration to which the soil was initially exposed to, which is consistent for all available compounds. Desorption experiments indicated also that PFOS is more irreversible than it´s analog PFNA in POi. However, PFHpA was less reversible than PFHxS in both soils which contrasts with expected stronger reversibility of carboxylates as compared to corresponding sulfonates. In agreement with previous studies (Milinovic et al., 2015), PFOA showed a higher sorption reversibility in both soils as compared to PFOS.

Based on the limited data it is difficult to make a strong statement whether soil POi or MOe show a higher irreversibility of sorption. PFOA, PFOS, FOSA and 8:2 FTSA are desorbed more easily from soil MOe as compared to POi for the desorption starting at the highest spiked concentration. While it is indifferent for the desorption starting at lower concentrations. PFHpA and PFHxS sorbed in general much stronger in soil MOe as compared to POi. The stronger sorption of PFHxS in MOe could be also observed in the pH-dependent experiment.

Implications for the prediction of distribution coefficients and environmental fate of PFASs might be indicated by varying log K_{OC} values derived from sorption and desorption experiments. The desorption experiment in this study yielded on average higher log K_{OC} values than the sorption experiment especially for PFASs that were identified as strongly irreversible (desorption yield < 33 %) such as PFHpA, PFUnDA, PFDoDA and FOSA in POi as well as PFHpA, PFHxS, Et-FOSA, 6:2 FTSA (low initial conc.) and 8:2 FTSA (low initial conc.) in MOe. In MOe, log K_{OC} increased after four desorption treatments for all compounds e.g. by 1.21 log units for PFHpA (from log K_{OC} 1.98 to 3.19) or by 1.05 and 0.86 log units for 6:2 FTSA and PFHxS, respectively. PFOA showed an increase of 0.53 (high initial conc.) and 0.59 log units (low initial conc.) despite being relatively reversible. However, PFOS, being a rather reversibly sorbing compound showed a marginal increase of log K_{OC}, while Et-FOSA showed a similar increase despite being more irreversible. An increased distribution coefficient with each desorption cycle describes hysteretic sorption and can occur even if the sorption isotherm is linear (Pan et al., 2009). A high hysteresis for PFOA and a negligible hysteresis effect for PFOS on peat soil was also observed by Zhi and Liu (2018). Sorption hysteresis involves several implications for the natural attenuation and environmental transport of PFAS as well as for the development of biological and physicochemical remediation strategies. Prediction models are usually based on sorption coefficients derived from sorption isotherms, thus assuming sorption reversibility (Zhi and Liu, 2018). Neglecting a potential hysteresis effect, meaning a higher sorption coefficient computed from the desorption isotherm as compared to the sorption isotherm, could lead to resistance towards remediation treatments. However, it needs to be investigated whether such a sorption/desorption behavior results from experimental artefacts yielding an *apparent* hysteresis or is time invariant and repeatable leading to a *true* hysteresis (Huang et al., 1998; Kan et al., 1994; Zhi and Liu, 2018). Further research is needed as desorption hysteresis of nonionic organic compounds is affected by the rigidity and aromaticity of organic matter (Pignatello et al., 2006), while Jia et al. (2010) reported that the extent of desorption of ionic organic chemicals such as PFASs, is significantly affected by electrostatic interactions between ions in solution with the sorbate and sorbent. The hydrophilic headgroup of PFASs is capable to integrate with water and thus allows the desorption (Zhao et al., 2014). Recent studies also observed an increasing hysteresis effect with an increasing perfluorinated chain-length of PFASs as well as a partially irreversible sorption behavior of PFOS, PFNA and PFDA (c.f. Chen et al., 2016). The long PFAS tails could hinder the diffusion process and lead to entrapment, thus a slower PFAS desorption as compared to the sorption process would be observed (Zhi and Liu, 2018).

The evaluation of the desorption pattern in soil POi reveals that only certain compounds show an increased log K_{OC} (PFOA, PFHpA) with further sequential desorption. Other PFASs show a varying behavior or a decreasing log K_{OC} with further desorption, reaching similar or lower log K_{OC} values as compared to the initial starting concentration for example PFNA, PFDA, PFUnDA, PFDoDA, PFHxS, PFOS, FOSA, 6:2 FTSA, 8:2 FTSA. The results demonstrate that the comparison of distribution coefficients from different sites involves difficulties.

Higher log K_{OC} values derived from the desorption isotherm would indicate a larger retention in organic soil horizons than calculated based on sorption isotherms. Similar observations were made by Chen et al. (2016) for the sorption/desorption of PFOS, PFNA and PFDA in freshwater sediments. PFOS and PFHxS were weakly and reversibly sorbed (Chen et al., 2016) which was also observed in soil POi, while sorption of PFHxS was rather irreversible in soil MOe. Chen et al. (2016) suggested that sorption of long-chain PFASs would consequently not be governed by equilibrium processes, in contrast with other hydrophobic compounds.

Zareitalabad et al. (2013) further investigated field-based and lab-based log K_{OC} for PFOA and PFOS in soils and sediments, finding a potential underestimation of sorption derived from lab-based distribution coefficients. Such an underestimation of sorption may overestimate transport within the soil compartment, leading to overestimated PFAS concentrations in water bodies to which the majority of these contaminants is leaching. Longer residence times in contaminated soils could also increase cumulative transfer of PFASs into other environmental matrices such as crops (Zareitalabad et al., 2013).

4.4. Effect of perfluorocarbon chain length and functional head groups on sorption

PFAS sorption increased in the presence of additional CF_2 units in the perfluorinated chain for PFCAs (C_7, C_{10}, C_{11} and C_{13}), PFSAs (C_4, C_6 and C_8) and FTSAs (C_6, C_8) in all soils. The increase in sorption of PFCAs was highest in soil POi with 0.17 log units K_{OC} per additional CF_2 moiety, followed by 0.10 and 0.07 log units for soils MOe and POe, respectively (Figure 11). Whereas for PFSAs, MOe showed a higher increase of the distribution coefficient per CF_2 moiety by 0.25 log units compared to POe (0.22 log units) and POi (0.19 log units). The strongest increase in log K_{OC} was identified for FTSAs, with a consistent increase in sorption of 0.38 log units per CF_2 moiety in all three soils. The latter suggests similar interactions of the hydrophobic tail with different sorbents (Higgins and Luthy, 2006). Moreover, the varying increase in log K_{OC} with the number of CF_2 moieties suggests that hydrophobic interactions may have been more important for sorption of FTSAs and PFSAs and to a lesser extent for binding of PFCAs, which is confirmed in the isotherm sorption experiment (Figure A 10). Other sorption mechanisms such as electrostatic interactions may influence the PFCA sorption to a greater extent and explain the differences between the soils.

However, the increase in binding strength in this present study is lower compared to previous findings which ranged between 0.50 – 0.75 log units per CF_2 moiety for PFCAs (Ahrens et al., 2010; Campos Pereira et al., 2018; Higgins and Luthy, 2006) and 0.40 – 0.83 log units per CF_2 moiety for PFSAs in similar environmental matrices (Campos Pereira et al., 2018; Higgins and Luthy, 2006; Milinovic et al., 2015). Especially the comparison of the soil MOe with the results of Campos Pereira et al. (2018) showed a weaker effect of the perfluorocarbon chain length in the present study despite very similar soil characteristics. Differences in the magnitude of the chain length effect on sorption could be attributed not only to sorbent characteristics but also to differences in the experimental design. This assumption is emphasized by the results from the isotherm experiment (see 4.3) showing an increase in sorption of 0.44 log units (POi) and 0.37 log units (MOe) per additional CF_2 moiety for PFSAs (Appendix XVII). A stronger impact of the chain length could be also observed for PFCAs in POi (0.27 log units) and a weaker effect in MOe with 0.07 log units. Whereas similar to the pH-dependent experiment, sorption per additional CF_2 moiety increased by approximately 0.38 log units for FTSAs in both soils.

The results indicate an increased partitioning to soil organic matter with increasing perfluorocarbon chain length which is consistent with previous studies (Chen et al., 2016; Higgins and Luthy, 2006; Li et al., 2019). The observed differences in log K_{OC} values per CF_2 moiety were expected due to stronger hydrophobicity associated with increasing perfluorocarbon chain length which can also be observed for the most long-chained PFCAs. Additionally, a larger molecule size enhances the probability of contacting with active sites of sorbents, hence increasing the sorption affinity within a homologous group (Zhao et al., 2014).

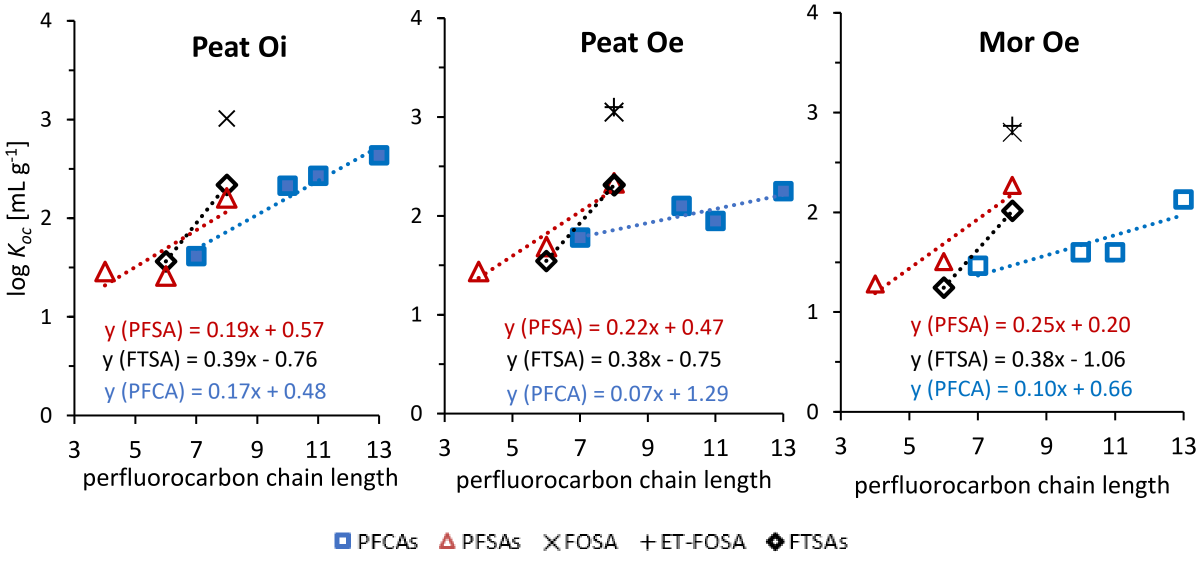

Figure 11 Relationship between average log K_{OC} [mL g^{-1}] and perfluorocarbon chain length in the pH-dependent sorption experiment. Closed markers indicate statistically significant relationship ($p \leq 0.05$).

In addition, differences in log K_{OC} were identified for PFASs of the same perfluorinated chain length but with different functional head group such as for the analogues PFHxS and 6:2 FTSA (C_6) as well as FOSA, Et-FOSA, PFOS and 8:2 FTSA (C_8). The sorption of both FTSAs was higher than sorption of the analogue PFSAs in POi while it was the lower in MOe (Figure 5). Sorption of FOSA and Et-FOSA differed from each other only marginally in the pH-dependent sorption experiment and the compounds are distinguished by the additional ethyl spacer–group (Et-FOSA) which is leading to a higher sorption of Et-FOSA, which became more evident in the sorption isotherm experiment. Both compounds were binding stronger as compared to PFOS and 8:2 FTSA in all soils due to the presence of uncharged sulfonamide head group as compared to its anionic analogues. The sorption difference of FOSA and Et-FOSA to PFOS increased in the order of MOe < POe < POi whereas an opposite pattern was observed for the sorption difference to 8:2 FTSA. A direct comparison of PFSAs and PFCAs of equal chain length was not possible in the pH-dependent experiment. However, in the isotherm experiment, PFASs showed a sorption affinity in the order of Et-FOSA > FOSA > PFOS > 8:2 FTSA > PFNA for both soils (POi, MOe) under study. Differences based on different hydrophilic head groups were more pronounced in soil POi as compared to MOe for FOSA/Et-FOSA and its analogous PFSAs and PFCAs, whereas the sorption difference between PFOS and PFNA was larger in MOe as compared to POi. Consequently, trends presented in Figure 11 indicating a higher sorption of PFSAs as compared to PFCAs of the same chain length (C_8) could be confirmed in the isotherm experiment for PFOS *vs* PFNA which is in agreement with previous studies (Campos Pereira et al., 2018; Higgins and Luthy, 2006). However, the isotherm experiments showed that the presence of a sulfonate functional group did not lead to increased sorption for the analog PFHxS as compared to PFHpA in POi as well as MOe. Instead, PFHpA was binding stronger and a larger difference between C_6 analogs was identified in POi rather than MOe.

Observed differences in sorption affinity between PFASs of the same perfluorocarbon chain length but with different functional head groups show that both hydrophobic and hydrophilic structural properties of PFASs are relevant for sorption to soil organic matter. The proposed larger size of the sulfonate moiety as compared to the carboxylate moiety might enhance the hydrophobicity of the compounds (Higgins and Luthy, 2006). Moreover, specific electrostatic interactions between the moieties with the sorbent could further promote sorption, as nonselective interactions alone would not explain the magnitude of the observed differences (Higgins and Luthy, 2006). According to Barzen-Hanson et al. (2017), electrostatic interactions are more thermodynamically favorable and would therefore overrule hydrophobic interactions. The results showed that differences in log K_{OC} values between perfluorosulfonates and perluorocarboxylates of equal chain length were not consistent within soils and also differed between soils.

4.5. Future perspectives

Despite limitations in the production and use of PFASs, it is necessary to understand their environmental chemistry due to their long persistence in the environment and current knowledge gaps in terms of environmental risk assessment. This study evaluated the sorption and desorption behaviour of selected PFASs to organic matter under consideration of the soil chemical composition and physcio-chemical properties of PFASs. Soils pose a potential source for environmental and human exposure to PFASs, thus leaching of PFASs from soils and sediments requires further assessment. Future work should focus on the identification of the fractions of organic matter relevant for PFAS sorption, especially for short-chain compounds as these have a higher mobility in the environment and under consideration of potential sorption preferences of chemical-specific characteristics. Hereby, various types of organic matter should be investigated and other methods should be tested to be able to develop standardized methods for PFAS assessment. Moreover, further kinetic experiments would be necessary to identify potential discrepancies between sorption and desorption equilibria. Consequently, a better understanding of PFAS sorption, its reversibility and irreversibility, is the key for improving the prediction and modelling of the environmental fate and transport of these contaminants. This plays a crucial role for already existing as well as newly emerging PFASs and their replacement compounds.

5. Conclusions

The findings of the conducted sorption experiments in laboratory scale imply that PFAS sorption mechanisms are dependent on the composition and properties of soil organic matter, as well as on the physico-chemical characteristics of the studied compounds. PFASs were bound stronger to peat soils as compared to the mor horizon which was especially more pronounced for the most long-chain PFASs, demonstrating the importance of soil organic matter composition.

The main sorption processes were attributed to electrostatic and hydrophobic interactions between PFASs and organic matter of the soils. The presence of electrostatic interactions was verified by the observed effect of cation additions and solution pH. The addition of Al^{3+} and Ca^{2+} increased PFAS sorption as compared to the addition of Na^{+} in all soils. Moreover, PFAS sorption was inversely related to the pH value in all three soils. This indicates that PFAS sorption likely was inversely related to the net negative surface charge of soils.

Hydrophobic interactions were observed due to the enhanced sorption with increasing length of the perluorinated carbon chain. Differences between the soils in the isotherm experiment were also more pronounced with increasing hydrophobicity of the sorbate. Moreover, the soil hydrophobicity index and humin content were positively related to PFAS sorption. Humic and fulvic acids on the other hand did not contribute to any significant extent to PFAS sorption. Sorption was further affected by the type of PFAS hydrophilic head group, resulting in a stronger sorption of perfluorosulfonates as compared to perfluorocarboxylates. Consequently, both the type of functional head group and the length of the perfluorinated carbon chain influenced PFAS sorption to soil organic matter. The magnitude of the effect of the head group and the length of the perfluorocarbon chain varied between the soils.

Selective binding mechanisms of PFASs to soil organic matter could not be observed in this present study. The sorption isotherms onto peat and mor horizons were overall linear, which, together with the previously observed sorption in the pH-experiment, suggesting the observation of nonspecific PFAS binding. Sorption reversibility was observed to be concentration-dependent and in general negatively related to the compound hydrophobicity. Moreover, sorption coefficients derived from the sorption and desorption isotherms differ from each other, indicating that lab-derived binding parameters should be chosen with care when used for risk management.

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Appendix

Appendix I

Table A 1 Dissolved organic carbon (mg L^{-1}) in the soils Paskalampa Peat Oi, Peat Oe and Mor Oe. Blanks were prepared in 10 mM $NaNO_3$ electrolyte background.

	Dissolved organic carbon [mg L^{-1}]		
	POi	POe	MOe
Al pH 3	41.15	48.39	128.60
Al pH 4	33.58	56.86	158.70
Al pH 5	41.43	60.46	220.50
Al pH 6	45.53	72.08	231.80
Ca pH 3	35.70	47.70	135.70
Ca pH 4	34.79	37.76	183.30
Ca pH 5	39.05	72.77	209.70
Ca pH 6	54.37	75.05	219.90
Na pH 3	32.98	52.89	121.00
Na pH 4	29.88	54.04	190.80
Na pH 5	35.96	56.60	226.30
Na pH 6	48.37	73.00	284.90
Blank ($NaNO_3$)	39.70	67.79	149.00
Blank ($NaNO_3$)	35.94	60.14	143.00

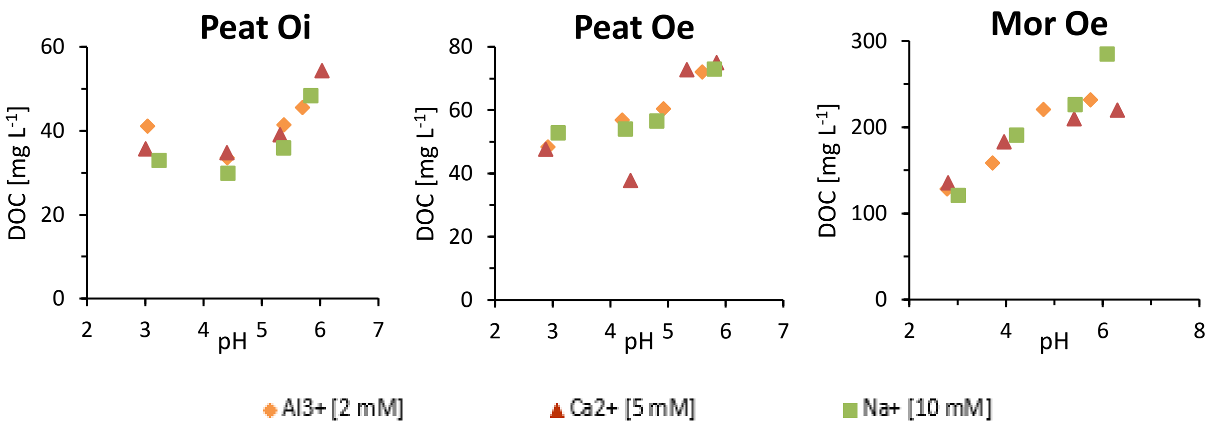

Figure A 1 Concentrations of dissolved organic carbon (mg L^{-1}) in the pH sorption experiment as a function of pH and cation additions.

Appendix II

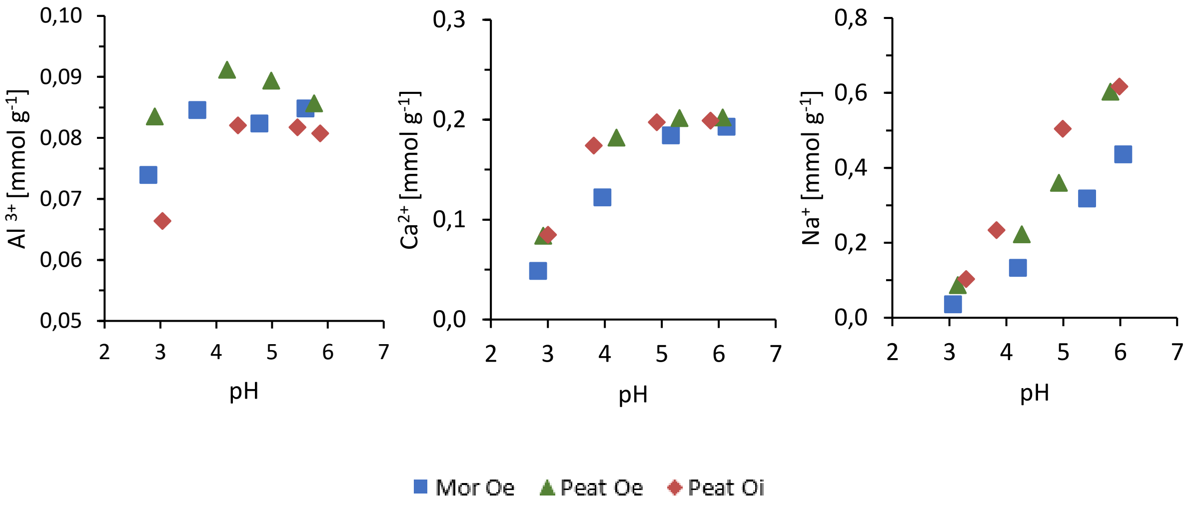

Figure A 2 Total concentration of Al^{3+}, Ca^{2+} and Na^{+} in soils after cation additions and followed equilibration in the pH-dependent sorption experiment.

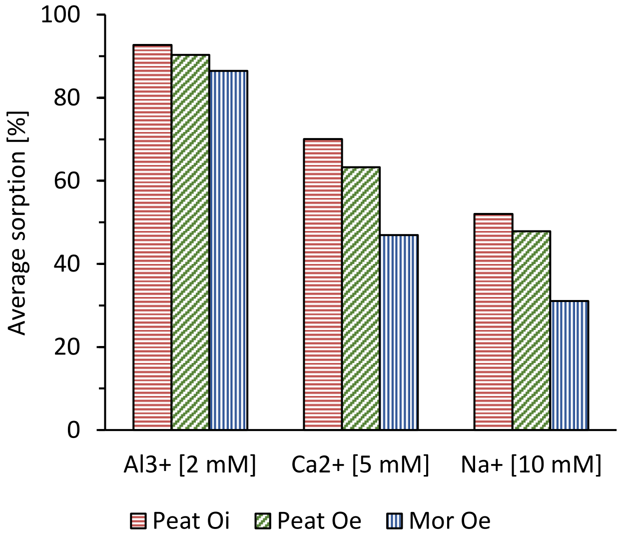

Figure A 3 Average sorption of Al^{3+}, Ca^{2+} and Na^{+} cation additions after equilibration in the three soils under study.

Appendix III

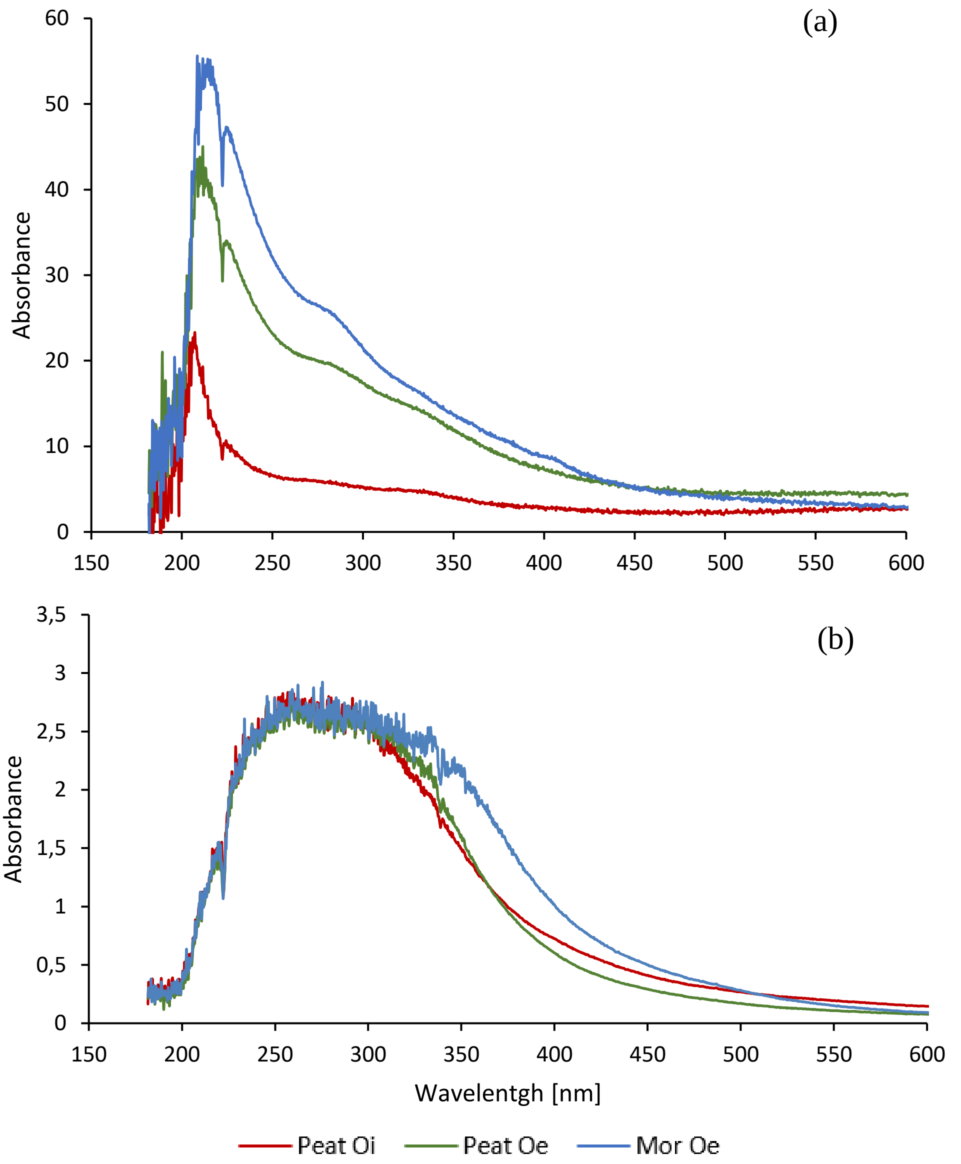

Figure A 4 UV absorbance spectra of humic acids (a) and fulvic acids (b) extractions of Paskalampa Peat Oi, Paskalampa peat Oe and Paskalampa mor Oe.

Table A 2 Calculated specific ultraviolet absorbance SUVA at 254 nm wavelength.

	Peat Oi	Peat Oe	Mor Oe
		Humic acid extractions	
SUVA_{254} [L cm^{-1} mg^{-1}]	3.44	6.21	5.01
		Fulvic acid extraction	
SUVA_{254} [L cm^{-1} mg^{-1}]	1.11	0.74	0.53

Appendix IV

Table A 3 Measured aqueous concentration of PFASs in the soil Paskalampa Peat Oi in the pH-dependent sorption experiment. Concentrations in strikethrough style were below the respective LoQ and therefore excluded from further analysis. No native PFASs were detected in negative blanks.

Aqueous PFAS concentrations in POi [ng mL^{-1}]													
Sample	dupl.	pH	PFOA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	FOSA	Et-FOSA	6:2 FTSA	8:2 FTSA
LoQ			0.07	0.06	0.06	0.07	0.07	0.07	0.013	0.04	0.50	0.12	0.14
Blank. neg (n=3).		n.d.	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Blank. pos.	a	n.d.	16.13	6.08	4.23	1.65	17.29	18.22	23.41	15.97	18.62	9.06	9.88
Blank. pos.	b	n.d.	19.07	6.82	5.02	1.82	20.02	19.55	25.28	18.11	21.59	10.26	11.36
Blank. pos.	c	n.d.	17.73	6.46	4.40	1.82	19.27	19.98	24.65	17.16	20.12	9.77	11.61
Al pH 3	a	3.04	6.38	0.14	0.07	0.28	14.45	10.14	1.80	0.39	~~0.09~~	5.48	0.78
Al pH 3	b	3.02	5.70	0.37	0.19	0.14	13.80	8.19	1.63	0.53	~~0.29~~	4.27	0.78
Al pH 4	a	4.29	11.93	0.75	0.23	0.11	15.61	14.64	5.54	0.59	~~0.07~~	6.52	1.32
Al pH 4	b	4.49	10.71	0.80	0.36	0.14	13.09	12.79	5.05	0.69	~~0.26~~	5.98	2.42
Al pH 5	a	5.32	13.63	3.90	1.46	0.37	15.01	15.68	11.45	2.44	0.71	6.14	3.55
Al pH 5	b	5.59	13.86	3.59	0.71	0.23	15.07	15.51	12.04	1.36	~~0.26~~	7.01	4.89
Al pH 6	a	5.84	14.06	4.74	1.79	0.46	16.29	16.52	12.52	2.33	0.67	7.67	4.80
Al pH 6	b	5.88	13.93	8.64	3.26	0.49	14.69	17.90	15.21	3.82	0.90	8.35	5.81
Ca pH 3	a	3.00	7.04	0.23	0.15	0.09	13.40	10.42	1.84	0.40	~~0.10~~	5.18	0.76
Ca pH 3	b	3.01	6.28	0.21	0.06	0.07	13.79	9.94	1.77	0.49	~~0.08~~	5.44	0.58
Ca pH 4	a	4.61	11.62	1.44	0.24	0.08	13.88	14.31	7.53	0.90	~~0.09~~	6.02	2.93
Ca pH 4	b	4.36	11.54	1.32	0.65	0.18	12.96	14.12	6.97	1.29	~~0.23~~	7.00	1.93
Ca pH 5	a	5.47	13.82	9.22	4.50	0.50	14.67	15.29	16.49	5.53	0.82	7.14	5.52
Ca pH 5	b	5.27	14.48	3.86	1.47	0.31	14.43	16.20	14.33	2.05	~~0.25~~	6.24	5.23
Ca pH 6	a	6.44	15.42	5.92	3.08	0.54	15.92	17.69	15.99	2.52	0.97	8.61	7.60
Ca pH 6	b	6.21	13.74	6.56	3.25	0.40	13.85	16.53	15.39	2.48	0.76	8.32	6.47
Na pH 3	a	3.29	8.46	0.38	0.22	0.18	13.26	10.92	3.27	0.52	~~0.12~~	6.32	1.62
Na pH 3	b	3.31	8.57	0.42	0.24	0.15	14.36	11.86	2.87	0.45	~~0.21~~	5.76	1.51
Na pH 4	a	4.34	11.83	2.32	0.74	0.17	13.92	13.62	9.07	1.52	~~0.15~~	6.74	3.54
Na pH 4	b	4.34	12.06	1.63	0.55	0.19	11.92	13.38	8.90	1.11	~~0.08~~	6.18	3.10
Na pH 5	a	5.64	14.17	4.54	1.96	0.48	13.63	15.54	13.57	1.61	0.76	7.78	5.07
Na pH 5	b	5.79	14.30	5.19	1.84	0.36	13.14	16.02	14.47	1.87	~~0.41~~	7.47	4.53
Na pH 6	a	6.18	14.77	12.52	6.66	0.98	14.65	16.92	18.26	7.03	1.67	7.97	7.48
Na pH 6	b	6.10	14.09	6.13	2.57	0.51	14.97	18.78	18.69	2.43	0.62	8.22	5.62

n.d. not determined

Table A 4 Measured aqueous concentration of PFASs in the soil Paskalampa Peat Oe in the pH-dependent sorption experiment. No native PFASs were detected in negative blanks.

Aqueous PFAS concentrations in POe [ng mL^{-1}]													
Sample	dupl.	pH	PFOA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	FOSA	Et-FOSA	6:2 FTSA	8:2 FTSA
LoQ			0.06	0.06	0.13	0.07	0.45	0.07	0.06	0.02	0.11	0.08	0.10
Blank, neg (n=3).		n.d.	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Blank, pos.	a	n.d.	16.13	6.08	4.23	1.65	17.29	18.22	23.41	15.97	18.62	9.06	9.88
Blank, pos.	b	n.d.	19.07	6.82	5.02	1.82	20.02	19.55	25.28	18.11	21.59	10.26	11.36
Blank, pos.	c	n.d.	17.73	6.46	4.40	1.82	19.27	19.98	24.65	17.16	20.12	9.77	11.61
Al pH 3	a	2.92	3.48	0.49	0.43	0.27	13.59	5.99	1.50	0.36	0.36	3.78	0.55
Al pH 3	b	2.88	3.78	0.46	0.43	0.21	13.35	6.04	1.39	0.29	0.32	3.97	0.80
Al pH 4	a	4.17	8.86	1.74	1.56	0.48	14.06	12.26	5.36	1.07	1.16	6.61	2.75
Al pH 4	b	4.22	10.11	2.20	1.75	0.40	15.02	12.57	5.99	1.25	1.26	7.32	2.95
Al pH 5	a	5.03	12.65	3.73	2.33	0.51	14.76	14.14	9.81	1.39	1.53	7.20	4.32
Al pH 5	b	4.93	12.83	4.31	2.78	0.72	15.65	13.69	9.62	1.73	1.94	8.12	4.05
Al pH 6	a	5.79	13.19	5.87	3.53	0.84	14.71	14.24	12.23	2.12	2.11	7.72	5.35
Al pH 6	b	5.71	13.57	5.85	3.39	0.82	15.65	15.04	11.77	1.86	2.13	7.93	5.47
Ca pH 3	a	2.92	4.30	0.62	0.50	0.28	13.05	7.00	1.67	0.44	0.38	4.62	0.69
Ca pH 3	b	2.91	4.29	0.54	0.53	0.26	12.96	7.07	2.03	0.39	0.43	4.49	0.99
Ca pH 4	a	4.24	9.90	2.06	1.64	0.49	13.86	11.80	5.86	1.11	1.14	6.47	2.64
Ca pH 4	b	4.17	10.47	2.24	1.82	0.48	14.47	11.81	5.88	1.21	1.31	7.16	3.09
Ca pH 5	a	5.35	13.23	4.74	3.14	0.69	15.05	15.09	11.07	1.83	1.97	7.56	5.16
Ca pH 5	b	5.26	13.03	5.09	3.37	0.77	15.21	14.49	10.71	1.83	2.25	8.24	4.79
Ca pH 6	a	6.06	14.23	7.05	4.23	0.98	15.02	13.97	13.08	2.15	2.24	7.63	5.68
Ca pH 6	b	6.07	13.77	7.35	4.17	0.99	14.86	14.62	13.76	2.14	2.06	8.10	6.14
Na pH 3	a	3.15	4.89	0.95	0.77	0.36	11.91	8.81	2.24	0.77	0.84	5.09	1.34
Na pH 3	b	3.15	5.32	1.17	0.95	0.30	11.78	9.03	2.37	0.90	0.93	5.02	1.64
Na pH 4	a	4.27	10.72	2.59	1.99	0.58	14.30	12.48	7.36	1.40	1.41	7.05	3.33
Na pH 4	b	4.28	11.07	2.48	1.92	0.60	15.51	11.92	7.46	1.33	1.57	7.38	3.00
Na pH 5	a	4.91	12.17	4.58	2.88	0.78	13.94	14.21	10.87	1.73	1.83	7.61	4.59
Na pH 5	b	4.94	12.70	4.03	2.72	0.81	14.91	14.16	10.73	1.79	1.94	7.58	4.93
Na pH 6	a	5.85	13.16	7.59	4.32	0.92	13.28	14.00	13.81	2.19	2.02	7.16	6.45
Na pH 6	b	5.81	14.85	7.47	4.62	1.04	14.78	15.87	15.66	2.19	2.34	7.97	6.95

n.d. not determined

Table A 5 Measured aqueous concentration of PFASs in the soil Paskalampa Mor Oe in the pH-dependent sorption experiment. No native PFASs were detected in negative blanks.

Aqueous PFAS concentrations in MOe [ng mL^{-1}]													
Sample	dupl.	pH	PFOA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	FOSA	Et-FOSA	6:2 FTSA	8:2 FTSA
LoQ			0.07	0.06	0.02	0.02	0.02	0.07	0.06	0.02	0.03	0.56	0.07
Blank, neg (n=3).		n.d.	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Blank, pos.	a	n.d.	19.38	7.23	5.34	1.86	21.45	23.65	28.36	19.34	21.53	9.57	9.99
Blank, pos.	b	n.d.	19.10	6.90	5.01	1.98	20.98	23.38	27.75	19.61	20.43	9.36	10.09
Blank, pos.	c	n.d.	21.00	6.52	4.92	1.92	21.72	24.15	29.37	20.14	21.73	10.08	9.82
Al pH 3	a	2.78	5.81	2.21	1.59	0.45	17.61	9.49	3.30	1.60	1.47	4.92	2.10
Al pH 3	b	2.78	5.37	1.45	1.10	0.39	17.81	9.21	2.90	1.18	1.02	4.86	1.28
Al pH 4	a	3.64	11.51	3.68	2.60	0.56	18.73	16.69	6.83	2.26	1.56	7.69	3.12
Al pH 4	b	3.67	10.91	2.62	1.92	0.48	19.08	15.30	5.22	1.48	1.49	7.34	2.26
Al pH 5	a	4.80	17.07	4.92	3.47	0.74	18.73	20.03	11.15	2.13	2.12	9.23	3.96
Al pH 5	b	4.74	16.51	5.49	3.41	0.71	18.46	17.48	10.94	1.91	1.70	8.85	4.32
Al pH 6	a	5.61	18.49	6.48	4.34	0.91	17.25	20.20	13.12	2.87	2.52	10.55	6.33
Al pH 6	b	5.58	18.07	6.17	3.47	0.80	16.98	19.65	13.07	2.33	2.11	10.01	6.06
Ca pH 3	a	2.83	5.54	1.58	1.13	0.47	13.51	8.40	2.90	1.40	1.34	5.13	2.29
Ca pH 3*	b	2.83											
Ca pH 4*	a	3.98											
Ca pH 4	b	3.94	10.29	3.18	2.43	0.56	14.92	13.94	5.15	1.52	1.51	7.16	2.97
Ca pH 5	a	5.26	15.05	4.83	3.22	0.76	16.67	18.03	9.28	2.15	1.82	8.71	4.35
Ca pH 5	b	5.06	16.00	5.37	4.04	0.90	19.06	18.45	9.49	2.42	2.18	9.30	5.06
Ca pH 6	a	6.20	17.26	7.41	4.85	0.96	17.56	18.84	13.84	2.85	2.55	9.84	5.92
Ca pH 6	b	6.07	16.68	6.97	4.23	0.82	16.61	18.38	13.05	2.68	2.74	10.26	6.13
Na pH 3	a	3.06	6.85	1.70	1.38	0.47	15.56	10.76	3.41	1.56	1.76	6.15	2.60
Na pH 3	b	3.06	7.39	2.86	2.49	0.56	15.75	11.61	3.53	2.33	2.34	6.45	2.33
Na pH 4	a	4.21	13.23	4.11	3.07	0.63	16.37	15.87	7.33	1.99	2.06	8.51	4.13
Na pH 4	b	4.20	13.47	4.12	3.12	0.67	15.93	16.21	7.77	2.21	2.11	7.97	3.36
Na pH 5	a	5.28	15.68	5.25	3.12	0.78	15.21	19.30	10.39	2.06	2.24	8.87	6.04
Na pH 5	b	5.56	19.22	7.73	5.04	1.00	17.56	19.67	13.85	3.12	2.66	10.64	6.58
Na pH 6	a	6.09	16.58	6.11	3.60	0.81	14.83	19.18	14.12	2.55	2.51	9.76	6.17
Na pH 6	b	6.01	17.07	6.75	4.20	0.92	16.62	19.49	14.23	2.42	2.35	9.67	7.30

* omitted from results; n.d. not determined

Appendix V

Table A 6 Calculated sorbed PFAS concentrations (ng g^{-1} dw soil) in the soil sample Paskalampa Peat Oi. Concentrations below the LoQ were omitted for the determination of sorbed concentrations and are therefore strikethrough.

Calculated sorbed PFAS concentrations in POi [ng g^{-1} dw]

Sample	dupl.	pH	PFOA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	FOSA	Et-FOSA*	6:2 FTSA	8:2 FTSA
Al pH 3	a	3.04	450.29	252.69	179.28	59.17	176.51	364.40	906.08	667.65	~~800.67~~	168.69	406.93
Al pH 3	b	3.02	477.81	243.49	174.32	64.77	202.43	442.40	912.88	662.21	~~792.75~~	216.93	406.93
Al pH 4	a	4.29	228.61	228.29	172.72	66.29	130.27	184.24	756.48	659.81	~~801.63~~	127.01	385.25
Al pH 4	b	4.49	277.25	225.97	167.44	64.93	230.91	258.32	776.08	655.49	~~794.11~~	148.77	341.17
Al pH 5	a	5.32	160.29	102.29	123.68	55.89	154.03	142.96	519.76	585.73	775.87	142.37	296.13
Al pH 5	b	5.59	151.33	114.61	153.52	61.17	151.79	149.44	496.40	628.69	~~794.03~~	107.57	242.29
Al pH 6	a	5.84	143.09	68.53	110.24	51.97	103.07	109.28	477.20	590.21	777.47	81.01	245.97
Al pH 6	b	5.88	148.61	0.00	51.68	50.77	166.83	53.84	369.60	530.45	768.59	53.81	205.41
Ca pH 3	a	3.00	424.05	249.01	175.92	66.77	218.43	353.36	904.24	667.09	~~800.27~~	180.61	407.73
Ca pH 3	b	3.01	454.37	249.65	179.44	67.89	202.75	372.32	907.28	663.57	~~801.07~~	170.29	414.93
Ca pH 4	a	4.61	241.01	200.37	172.48	67.49	199.23	197.44	676.64	647.17	~~800.67~~	146.93	320.93
Ca pH 4	b	4.36	244.05	205.41	155.76	63.25	235.95	205.36	699.04	631.81	~~795.23~~	107.89	360.93
Ca pH 5	a	5.47	152.85	0.00	2.00	50.37	167.79	158.56	318.16	462.05	771.79	102.13	217.01
Ca pH 5	b	5.27	126.29	103.73	122.96	58.13	177.31	122.16	404.88	601.33	~~794.35~~	138.37	228.69
Ca pH 6	a	6.44	88.93	21.49	58.80	48.93	117.71	62.32	338.24	582.29	765.47	43.49	134.13
Ca pH 6	b	6.21	156.13	0.00	52.08	54.45	200.59	108.88	362.48	584.21	773.95	55.17	179.25
Na pH 3	a	3.29	367.25	242.93	173.20	63.33	224.27	333.12	847.20	662.29	~~799.71~~	134.93	373.17
Na pH 3	b	3.31	362.85	241.25	172.24	64.53	180.11	295.68	863.28	665.25	~~795.95~~	157.33	377.65
Na pH 4	a	4.34	232.37	165.17	152.16	63.89	197.87	225.12	615.28	622.61	~~798.35~~	118.37	296.29
Na pH 4	b	4.34	223.17	193.01	159.84	62.93	277.71	234.96	622.08	639.01	~~801.07~~	140.53	313.81
Na pH 5	a	5.64	139.01	76.45	103.60	51.49	209.47	148.56	435.20	618.77	773.95	76.69	235.25
Na pH 5	b	5.79	133.65	50.61	108.24	55.97	228.91	129.20	398.96	608.45	~~787.87~~	89.25	256.69
Na pH 6	a	6.18	114.93	0.00	0.00	31.41	168.59	93.28	247.36	402.05	737.47	69.25	138.93
Na pH 6	b	6.10	142.13	12.77	79.20	50.05	155.63	18.96	230.48	586.21	779.63	58.93	213.33

*omitted from results

Table A 7 Calculated sorbed PFAS concentrations (ng g^{-1} dw soil) in the soil sample Paskalampa Peat Oe.

Calculated sorbed PFAS concentrations in POe [ng g^{-1} dw]													
Sample	dupl.	pH	PFOA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	FOSA	Et-FOSA	6:2 FTSA	8:2 FTSA
Al pH 3	a	2.92	566.29	238.69	164.56	59.65	210.99	530.56	918.08	668.93	789.87	236.77	415.89
Al pH 3	b	2.88	554.45	239.89	164.80	62.13	220.51	528.48	922.16	671.65	791.55	228.93	405.89
Al pH 4	a	4.17	351.33	188.45	119.60	51.33	192.27	279.68	763.68	640.53	758.03	123.49	327.89
Al pH 4	b	4.22	301.25	170.29	111.84	54.37	153.71	267.20	738.40	633.33	754.19	95.25	319.97
Al pH 5	a	5.03	199.81	108.93	88.80	49.97	164.03	204.40	585.36	627.65	743.39	99.89	265.25
Al pH 5	b	4.93	192.29	85.81	70.64	41.81	128.43	222.56	593.12	614.13	726.67	63.25	276.13
Al pH 6	a	5.79	177.89	23.49	40.64	36.77	165.95	200.40	488.56	598.37	720.11	78.93	224.05
Al pH 6	b	5.71	162.85	23.97	46.24	37.57	128.59	168.32	507.20	608.85	719.31	70.77	219.01
Ca pH 3	a	2.92	533.73	233.17	161.92	59.25	232.51	490.16	911.20	665.57	789.07	203.01	410.45
Ca pH 3	b	2.91	533.97	236.69	160.80	60.13	236.19	487.28	896.56	667.81	787.39	208.29	398.37
Ca pH 4	a	4.24	309.49	175.65	116.32	51.01	200.19	298.08	743.68	638.85	758.83	129.25	332.37
Ca pH 4	b	4.17	287.01	168.61	109.04	51.25	175.55	297.76	742.56	635.01	751.95	101.41	314.45
Ca pH 5	a	5.35	176.29	68.37	56.16	43.09	152.43	166.40	535.28	610.05	725.63	85.33	231.65
Ca pH 5	b	5.26	184.45	54.61	47.28	39.65	145.95	190.48	549.60	610.13	714.51	58.37	246.29
Ca pH 6	a	6.06	136.45	0.00	12.72	31.41	153.55	211.28	454.72	597.25	714.91	82.61	210.61
Ca pH 6	b	6.07	154.93	0.00	15.28	31.09	159.95	185.04	427.52	597.49	721.95	63.81	192.53
Na pH 3	a	3.15	510.13	220.13	151.12	56.21	277.95	417.60	888.16	652.29	770.91	184.29	384.45
Na pH 3	b	3.15	492.85	211.25	144.08	58.53	283.31	408.72	882.96	647.09	767.31	186.93	372.29
Na pH 4	a	4.27	276.93	154.37	102.40	47.17	182.43	270.72	683.44	627.09	748.03	105.97	304.77
Na pH 4	b	4.28	262.93	158.85	105.12	46.69	134.11	293.12	679.52	629.97	741.47	92.77	317.81
Na pH 5	a	4.91	218.77	75.09	66.88	39.41	196.75	201.68	543.12	613.97	731.31	83.33	254.53
Na pH 5	b	4.94	197.81	96.93	73.04	38.29	158.19	203.60	548.64	611.49	726.91	84.61	240.77
Na pH 6	a	5.85	179.17	0.00	9.04	33.81	223.47	210.16	425.44	595.57	723.55	101.57	180.05
Na pH 6	b	5.81	111.65	0.00	0.00	28.93	163.31	135.12	351.44	595.65	710.99	68.93	159.97

Table A 8 Calculated sorbed PFAS concentrations (ng g^{-1} dw soil) in the soil sample Paskalampa Mor Oe.

Calculated sorbed PFAS concentrations in MOe [ng g^{-1} dw]													
Sample	dupl.	pH	PFOA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	FOSA	Et-FOSA	6:2 FTSA	8:2 FTSA
Al pH 3	a	2.78	560.88	187.15	140.11	58.80	150.93	569.63	1007.71	723.84	790.53	190.24	314.88
Al pH 3	b	2.78	578.24	217.55	159.63	60.96	142.77	580.83	1023.55	740.64	808.37	192.32	347.60
Al pH 4	a	3.64	332.64	128.27	99.71	54.48	105.97	281.31	866.59	697.44	786.69	79.36	273.92
Al pH 4	b	3.67	356.80	170.51	126.91	57.68	91.97	337.07	930.99	728.64	789.41	93.12	308.32
Al pH 5	a	4.80	110.40	78.67	64.91	46.96	106.13	148.03	693.71	702.40	764.53	17.68	240.32
Al pH 5	b	4.74	132.72	55.95	67.15	48.24	116.77	249.79	702.11	711.36	781.17	32.96	226.00
Al pH 6	a	5.61	53.60	16.35	30.19	40.32	165.41	141.07	614.91	673.04	748.37	0.00	145.44
Al pH 6	b	5.58	70.56	28.59	64.99	44.80	176.29	163.23	616.91	694.56	764.93	0.00	156.24
Ca pH 3	a	2.83	571.44	212.03	158.51	57.76	315.09	613.23	1023.79	731.76	795.57	181.52	307.28
Ca pH 3*	b	2.83											
Ca pH 4*	a	3.98											
Ca pH 4	b	3.94	381.52	148.11	106.59	54.24	258.37	391.31	933.87	727.04	788.85	100.32	279.76
Ca pH 5	a	5.26	191.20	82.11	74.91	46.16	188.69	227.79	768.67	701.68	776.21	38.64	224.64
Ca pH 5	b	5.06	153.28	60.43	41.95	40.80	93.09	211.23	760.03	690.88	762.13	15.04	196.48
Ca pH 6	a	6.20	102.72	0.00	9.47	38.40	153.01	195.31	586.11	673.84	747.17	0.00	161.76
Ca pH 6	b	6.07	125.92	0.00	34.27	43.76	190.85	213.95	617.63	680.72	739.57	0.00	153.60
Na pH 3	a	3.06	519.20	207.23	148.43	57.92	233.09	518.83	1003.47	725.52	778.69	140.72	294.88
Na pH 3	b	3.06	497.52	160.83	104.11	54.32	225.49	484.67	998.67	694.40	755.57	128.80	305.68
Na pH 4	a	4.21	264.08	111.15	80.83	51.36	200.69	314.27	846.35	708.24	766.93	46.64	233.68
Na pH 4	b	4.20	254.56	110.51	78.83	50.08	218.21	300.51	828.99	699.44	764.77	67.92	264.16
Na pH 5	a	5.28	165.84	65.39	78.91	45.52	246.93	177.23	724.27	705.20	759.73	32.08	157.28
Na pH 5	b	5.56	24.24	0.00	2.03	36.88	152.93	162.27	585.79	662.88	742.85	0.00	135.44
Na pH 6	a	6.09	129.84	31.07	59.79	44.16	262.21	181.79	574.99	685.84	748.85	0.00	151.84
Na pH 6	b	6.01	110.40	5.31	35.63	40.00	190.37	169.31	570.35	691.04	755.01	0.00	106.88

*omitted from results

Appendix VI

Table A 9 Log K_{OC} (mL g^{-1} dw soil) values obtained from pH sorption experiment for the soil Paskalampa Peat Oi. Concentrations below the LoQ were omitted in the determination of the respective partitioning coefficient.

Log K_{OC} [mL g^{-1} dw] for POi													
Sample	dupl.	pH	PFOA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	FOSA	Et-FOSA*	6:2 FTSA	8:2 FTSA
Al pH 3	a	3.04	2.20	3.62	3.78	2.67	1.43	1.90	3.05	3.58		1.84	3.07
Al pH 3	b	3.02	2.27	3.17	3.31	3.00	1.51	2.08	3.10	3.45		2.05	3.07
Al pH 4	a	4.29	1.63	2.83	3.22	3.14	1.27	1.45	2.48	3.40		1.64	2.81
Al pH 4	b	4.49	1.76	2.80	3.01	3.01	1.59	1.65	2.53	3.32		1.74	2.50
Al pH 5	a	5.32	1.42	1.77	2.28	2.53	1.36	1.31	2.00	2.73		1.71	2.27
Al pH 5	b	5.59	1.39	1.85	2.68	2.77	1.35	1.33	1.96	3.01		1.53	2.04
Al pH 6	a	5.84	1.36	1.51	2.14	2.40	1.15	1.17	1.93	2.75		1.37	2.06
Al pH 6	b	5.88	1.38		1.55	2.36	1.40	0.83	1.73	2.49		1.16	1.90
Ca pH 3	a	3.00	2.13	3.39	3.42	3.20	1.56	1.88	3.04	3.57		1.89	3.08
Ca pH 3	b	3.01	2.21	3.42	3.81	3.36	1.52	1.92	3.06	3.48		1.84	3.21
Ca pH 4	a	4.61	1.66	2.49	3.21	3.30	1.50	1.49	2.30	3.20		1.73	2.39
Ca pH 4	b	4.36	1.67	2.54	2.72	2.89	1.61	1.51	2.35	3.04		1.54	2.62
Ca pH 5	a	5.47	1.39			2.35	1.41	1.36	1.63	2.27		1.50	1.94
Ca pH 5	b	5.27	1.29	1.78	2.27	2.62	1.44	1.23	1.80	2.82		1.69	1.99
Ca pH 6	a	6.44	1.11	0.91	1.63	2.30	1.22	0.89	1.67	2.71		1.05	1.59
Ca pH 6	b	6.21	1.40		1.55	2.48	1.51	1.17	1.72	2.72		1.17	1.79
Na pH 3	a	3.29	1.99	3.15	3.25	2.89	1.58	1.83	2.76	3.45		1.68	2.71
Na pH 3	b	3.31	1.97	3.10	3.20	2.98	1.45	1.74	2.83	3.52		1.78	2.75
Na pH 4	a	4.34	1.64	2.20	2.66	2.93	1.50	1.57	2.18	2.96		1.59	2.27
Na pH 4	b	4.34	1.61	2.42	2.81	2.87	1.72	1.59	2.19	3.11		1.70	2.35
Na pH 5	a	5.64	1.34	1.57	2.07	2.38	1.53	1.33	1.85	2.93		1.34	2.01
Na pH 5	b	5.79	1.32	1.34	2.12	2.53	1.59	1.25	1.79	2.86		1.43	2.10
Na pH 6	a	6.18	1.24			1.85	1.41	1.09	1.48	2.11	2.99	1.29	1.62
Na pH 6	b	6.10	1.35	0.67	1.84	2.34	1.36	0.35	1.44	2.73		1.20	1.93
Average			1.61	2.33	2.66	2.72	1.46	1.41	2.20	3.01	n.d.	1.56	2.34

* omitted from results
n.d. not determined

Table A 10 Log K_{OC} (mL g^{-1} dw soil) values obtained from pH sorption experiment for the soil Paskalampa Peat Oe. Concentrations below the LoQ were omitted in the determination of the respective partitioning coefficient.

Log K_{OC} [mL g^{-1} dw] for POe													
Sample	dupl.	pH	PFOA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	FOSA	Et-FOSA	6:2 FTSA	8:2 FTSA
Al pH 3	a	2.92	2.54	3.02	2.91	2.67	1.52	2.28	3.12	3.60	3.67	2.13	3.21
Al pH 3	b	2.88	2.50	3.05	2.92	2.80	1.55	2.27	3.15	3.70	3.72	2.09	3.04
Al pH 4	a	4.17	1.93	2.37	2.22	2.36	1.47	1.69	2.49	3.11	3.15	1.60	2.41
Al pH 4	b	4.22	1.81	2.22	2.14	2.46	1.34	1.66	2.42	3.04	3.11	1.45	2.37
Al pH 5	a	5.03	1.53	1.80	1.91	2.32	1.38	1.49	2.11	2.99	3.02	1.47	2.12
Al pH 5	b	4.93	1.51	1.63	1.74	2.10	1.25	1.54	2.12	2.88	2.90	1.22	2.17
Al pH 6	a	5.79	1.46	0.93	1.39	1.97	1.38	1.48	1.93	2.78	2.87	1.34	1.95
Al pH 6	b	5.71	1.41	0.94	1.47	1.99	1.25	1.38	1.97	2.85	2.86	1.28	1.93
Ca pH 3	a	2.92	2.43	2.90	2.84	2.65	1.58	2.18	3.07	3.51	3.64	1.97	3.11
Ca pH 3	b	2.91	2.43	2.98	2.82	2.70	1.59	2.17	2.98	3.57	3.60	2.00	2.94
Ca pH 4	a	4.24	1.83	2.26	2.18	2.35	1.49	1.73	2.44	3.09	3.15	1.63	2.43
Ca pH 4	b	4.17	1.77	2.21	2.11	2.36	1.42	1.73	2.43	3.05	3.09	1.48	2.34
Ca pH 5	a	5.35	1.46	1.49	1.58	2.13	1.34	1.37	2.02	2.85	2.90	1.38	1.98
Ca pH 5	b	5.26	1.48	1.36	1.48	2.04	1.31	1.45	2.04	2.86	2.83	1.18	2.04
Ca pH 6	a	6.06	1.31		0.81	1.84	1.34	1.51	1.87	2.78	2.84	1.37	1.90
Ca pH 6	b	6.07	1.38		0.90	1.83	1.36	1.43	1.82	2.78	2.88	1.23	1.83
Na pH 3	a	3.15	2.35	2.70	2.62	2.53	1.70	2.01	2.93	3.26	3.30	1.89	2.79
Na pH 3	b	3.15	2.30	2.59	2.51	2.62	1.71	1.99	2.90	3.19	3.25	1.90	2.69
Na pH 4	a	4.27	1.74	2.11	2.04	2.24	1.44	1.67	2.30	2.98	3.06	1.51	2.29
Na pH 4	b	4.28	1.71	2.14	2.07	2.23	1.27	1.72	2.29	3.01	3.00	1.43	2.36
Na pH 5	a	4.91	1.59	1.55	1.70	2.04	1.48	1.48	2.03	2.88	2.93	1.37	2.08
Na pH 5	b	4.94	1.52	1.71	1.76	2.01	1.36	1.49	2.04	2.86	2.91	1.38	2.02
Na pH 6	a	5.85	1.47		0.65	1.90	1.56	1.51	1.82	2.77	2.89	1.48	1.78
Na pH 6	b	5.81	1.21			1.78	1.37	1.26	1.68	2.77	2.82	1.27	1.69
Average			1.78	2.10	1.95	2.25	1.44	1.69	2.33	3.05	3.10	1.54	2.31

Table A 11 Log K_{OC} (mL g^{-1} dw soil) values obtained from pH sorption experiment for the soil Paskalampa Mor Oe.

Log K_{OC} [mL g^{-1} dw] for MOe													
Sample	dupl.	pH	PFOA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	FOSA	Et-FOSA	6:2 FTSA	8:2 FTSA
Al pH 3	a	2.78	2.26	2.20	2.22	2.39	1.20	2.05	2.76	2.93	3.00	1.86	2.45
Al pH 3	b	2.78	2.30	2.45	2.43	2.46	1.17	2.07	2.82	3.07	3.17	1.87	2.71
Al pH 4	a	3.64	1.73	1.81	1.85	2.26	1.02	1.50	2.37	2.76	2.97	1.28	2.21
Al pH 4	b	3.67	1.79	2.08	2.09	2.35	0.95	1.61	2.52	2.96	2.99	1.37	2.41
Al pH 5	a	4.80	1.08	1.47	1.54	2.07	1.02	1.14	2.06	2.79	2.83	0.55	2.05
Al pH 5	b	4.74	1.18	1.28	1.56	2.10	1.07	1.43	2.08	2.84	2.93	0.84	1.99
Al pH 6	a	5.61	0.73	0.67	1.11	1.92	1.25	1.11	1.94	2.64	2.74		1.63
Al pH 6	b	5.58	0.86	0.94	1.54	2.02	1.29	1.19	1.94	2.75	2.83		1.68
Ca pH 3	a	2.83	2.28	2.40	2.42	2.36	1.64	2.13	2.82	2.99	3.04	1.82	2.40
Ca pH 3*	b	2.83											
Ca pH 4*	a	3.98											
Ca pH 4	b	3.94	1.84	1.94	1.91	2.26	1.51	1.72	2.53	2.95	2.99	1.42	2.24
Ca pH 5	a	5.26	1.37	1.50	1.64	2.05	1.32	1.37	2.19	2.78	2.90	0.92	1.98
Ca pH 5	b	5.06	1.25	1.32	1.29	1.93	0.96	1.33	2.17	2.73	2.82	0.48	1.86
Ca pH 6	a	6.20	1.05		0.56	1.87	1.21	1.29	1.90	2.64	2.74		1.71
Ca pH 6	b	6.07	1.15		1.18	2.00	1.33	1.34	1.95	2.68	2.70		1.67
Na pH 3	a	3.06	2.15	2.36	2.30	2.36	1.45	1.95	2.74	2.94	2.92	1.63	2.33
Na pH 3	b	3.06	2.10	2.02	1.89	2.26	1.43	1.89	2.72	2.74	2.78	1.57	2.39
Na pH 4	a	4.21	1.57	1.70	1.69	2.18	1.36	1.57	2.33	2.82	2.84	1.01	2.02
Na pH 4	b	4.20	1.55	1.70	1.67	2.15	1.41	1.54	2.30	2.77	2.83	1.20	2.17
Na pH 5	a	5.28	1.30	1.37	1.67	2.04	1.48	1.23	2.11	2.80	2.80	0.83	1.69
Na pH 5	b	5.56	0.37		-0.12	1.84	1.21	1.19	1.90	2.60	2.72		1.58
Na pH 6	a	6.09	1.16	0.98	1.49	2.01	1.52	1.25	1.88	2.70	2.75		1.66
Na pH 6	b	6.01	1.08	0.17	1.20	1.91	1.33	1.21	1.87	2.73	2.78		1.44
Average			1.46	1.60	1.60	2.13	1.28	1.51	2.27	2.80	2.87	1.24	2.01

* omitted from results

Table A 12 Sorbed fraction of target PFASs to the soil compartment in all soils under study. Values represent the average sorption of all available data points in the pH-dependent experiment

	Sorbed fraction [%]										
	PFOA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	FOSA	Et-FOSA	6:2 FTSA	8:2 FTSA
Peat Oi	33.30	52.42	68.54	81.01	24.73	25.78	60.01	89.18		30.47	66.58
Peat Oe	41.76	47.35	48.98	65.55	24.52	37.17	67.24	91.83	92.65	30.48	66.65
Mor Oe	34.88	36.88	41.60	64.39	22.21	33.53	70.33	89.44	90.78	17.65	58.24

Appendix VII

Table A 13 Generalized linear mixed model for testing significance ($p \leq 0.05$) of differences in log K_{OC} averages between three different cation treatments in the pH-dependent sorption experiment. Log K_{OC} values followed roughly log-normal distributions. Blank cells correspond to non-significant differences.

Tested hypothesis	log K_{OC} (Al^{3+} [2 mM] > Ca^{2+} [5 mM])	log K_{OC} (Al^{3+} [2 mM] > Na^{+} [10 mM])	log K_{OC} (Ca2^{+} [5 mM] > Na^{+} [10 mM])
	POi		
PFOA		0.027	
PFUnDA			
PFDoDA			
PFTeDA			
PFBS		0.007	
PFHxS			
PFOS		0.017	
FOSA			
Et-FOSA	n.d.	n.d.	n.d.
6:2 FTSA			
8:2 FTSA		0.049	
	POe		
PFOA			
PFUnDA			
PFDoDA			
PFTeDA	0.008	0.000	0.037
PFBS		0.026	
PFHxS			
PFOS	0.042	0.007	0.037
FOSA		0.014	
Et-FOSA		0.030	
6:2 FTSA			
8:2 FTSA		0.016	
	MOe		
PFOA			
PFUnDA			
PFDoDA			
PFTeDA		0.017	
PFBS	0.038	0.003	
PFHxS			0.020
PFOS			0.016
FOSA			
Et-FOSA	0.004		
6:2 FTSA			
8:2 FTSA		0.003	0.019

n.a. not determined

Appendix VIII

Table A 14 Generalized linear mixed model for testing significance ($p \leq 0.05$) of differences in log K_{OC} averages between three different soils in the pH-dependent sorption experiment. Log K_{OC} values followed roughly log-normal distributions. Blank cells correspond to non-significant differences.

Tested hypothesis	log K_{OC} (POi > POe)	log K_{OC} (POi > MOe)	log K_{OC} (POe > MOe)
PFOA	0.020		0.002
PFUnDA			
PFDoDA	0.041	0.022	
PFTeDA	0.000	0.000	0.051
PFBS		0.000	0.000
PFHxS	0.000	0.027	0.004
PFOS	0.017	0.044	
FOSA		0.006	0.001
Et-FOSA	n.d.	n.d.	0.000
6:2 FTSA		0.000	0.000
8:2 FTSA		0.001	0.001

n.a. not determined

Appendix IX

Table A 15 Linear regression analysis describing the relationship between log K_{OC} and the sorption predictor pH using Pearson r^2 values, significance, regression slopes and intercept

Compound	r^2 (log K_{OC} vs pH)	Significance (p-value)	Slope (Δ log K_{OC} /ΔpH)	Intercept
	POi			
PFOA	0.93	<0.001	-0.28	2.96
PFUnDA	0.93	<0.001	-0.73	5.65
PFDoDA	0.57	<0.001	-0.58	5.25
PFTeDA	0.60	<0.001	-0.22	3.74
PFBS	0.19	0.03	-0.05	1.69
PFHxS	0.79	<0.001	-0.30	2.85
PFOS	0.93	<0.001	-0.44	4.31
FOSA	0.75	<0.001	-0.30	4.46
Et-FOSA	n.d.	n.d.	n.d.	n.d.
6:2 FTSA	0.77	<0.001	-0.20	2.50
8:2 FTSA	0.92	<0.001	-0.39	4.21
	POe			
PFOA	0.93	<0.001	-0.37	3.44
PFUnDA	0.96	<0.001	-0.66	4.90
PFDoDA	0.94	<0.001	-0.58	4.56
PFTeDA	0.93	<0.001	-0.27	3.46
PFBS	0.46	<0.001	-0.08	1.80
PFHxS	0.88	<0.001	-0.26	2.86
PFOS	0.96	<0.001	-0.41	4.19
FOSA	0.86	<0.001	-0.24	4.14
Et-FOSA	0.84	<0.001	-0.24	4.19
6:2 FTSA	0.81	<0.001	-0.24	2.63
8:2 FTSA	0.94	<0.001	-0.39	4.07
	MOe			
PFOA	0.81	<0.001	-0.41	3.32
PFUnDA	0.87	<0.001	-0.51	3.81
PFDoDA	0.63	<0.001	-0.40	3.41
PFTeDA	0.88	<0.001	-0.15	2.80
PFBS	0.00	0.83	-0.01	1.31
PFHxS	0.83	<0.001	-0.25	2.65
PFOS	0.95	<0.001	-0.28	3.53
FOSA	0.64	<0.001	-0.08	3.18
Et-FOSA	0.63	<0.001	-0.08	3.24
6:2 FTSA	0.88	<0.001	-0.47	3.09
8:2 FTSA	0.90	<0.001	-0.28	3.28

n.d. not determined

Appendix X

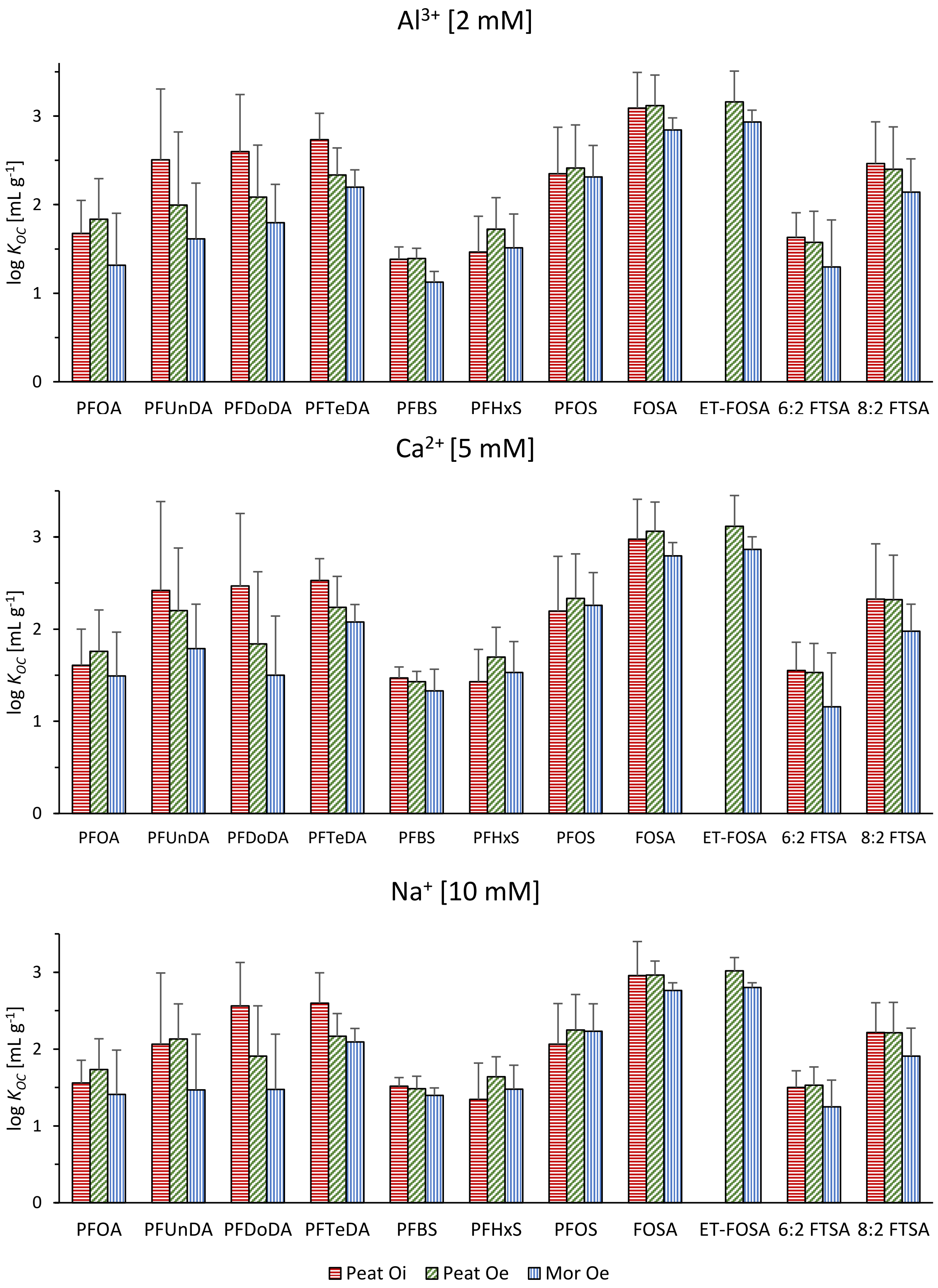

Figure A 5 Comparison of the soils under study based on average log K_{OC} (mL g^{-1}) across all measured pH-values for all target compounds within respective Al^{3+}, Ca^{2+} and Na^{+} treatments.

Appendix XI

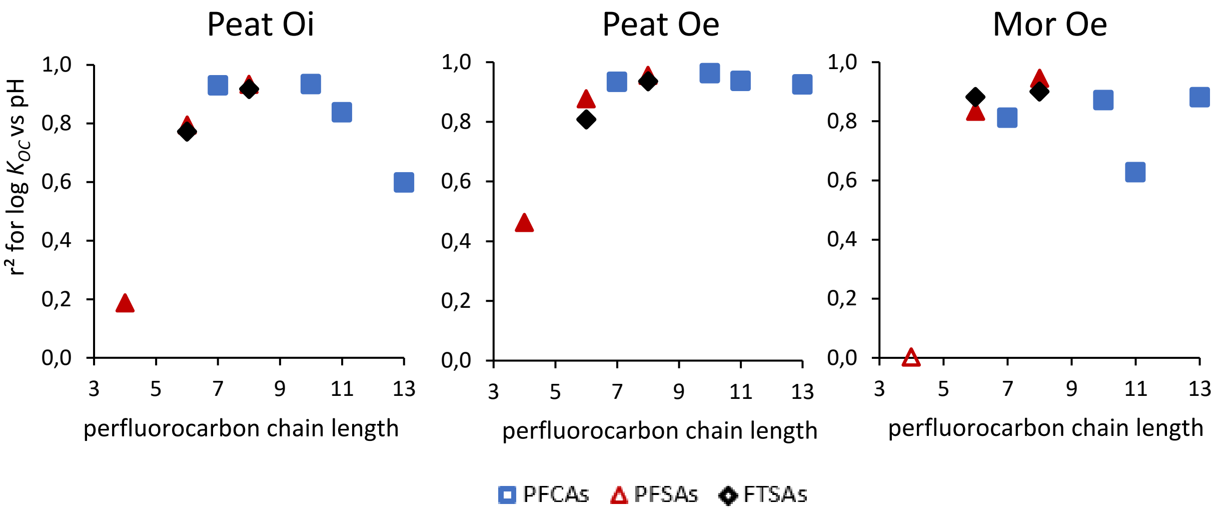

Figure A 6 Pearson r² value for log K_{OC} vs. pH as influenced by the perfluorocarbon chain length. Closed markers represent significant relationship between log K_{OC} and pH ($p \leq 0.05$).

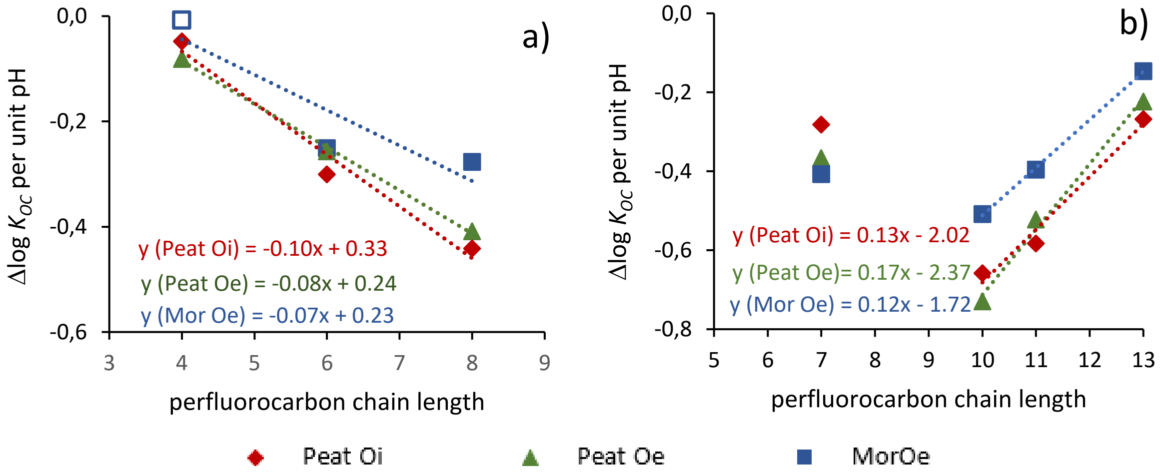

Figure A 7 Δlog K_{OC} per unit pH with respect to chain length of PFSAs (a)) and PFCAs (b)). Closed markers represent significant relationships between log K_{OC} and pH ($p \leq 0.05$).

Appendix XII

Table A 16 Aqueous concentrations of spiked PFAS standard stock solution in positive blanks (100% MeOH) in the sorption isotherm experiment. S1 represent the lowest spiked and S8 respectively the highest spiked concentration.

	Aqueous PFAS concentrations in positive blanks [ng mL^{-1}]													
Positive Blank (n=3)	PFPeA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFHxS	PFOS	FOSA	ET-FOSA	6:2 FTSA	8:2 FTSA
S1	2.54	3.78	4.40	1.96	1.52	1.51	1.09	0.45	5.94	6.47	4.35	5.49	2.17	2.52
S2	5.07	7.57	8.81	3.92	3.03	3.02	2.19	0.91	11.87	12.94	8.71	10.98	4.33	5.03
S3	7.46	11.13	12.95	5.76	4.46	4.44	3.22	1.34	17.46	19.02	12.81	16.14	6.37	7.40
S4	12.68	18.92	22.02	9.79	7.58	7.55	5.47	2.27	29.68	32.34	21.77	27.44	10.83	12.58
S5	20.52	30.60	35.62	15.84	12.26	12.22	8.86	3.67	48.01	52.31	35.22	44.39	17.51	20.35
S6	35.44	52.86	61.53	27.37	21.18	21.10	15.30	6.34	82.93	90.36	60.84	76.68	30.25	35.15
S7	55.95	83.46	97.15	43.21	33.44	33.32	24.15	10.02	130.94	142.67	96.06	121.07	47.76	55.50
S8	74.60	111.28	129.53	57.61	44.58	44.43	32.20	13.36	174.59	190.23	128.09	161.43	63.68	74.00

Table A 17 Measured aqueous concentration of PFASs in the soil Paskalampa Peat Oi in the isotherm sorption and desorption experiment. Concentrations in strikethrough style were below the respective LoQ and therefore excluded from further analysis.

Aqueous PFAS concentrations in POi [ng mL^{-1}]																
Sample	dupl.	pH	PFPeA*	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFHxS	PFOS	FOSA	ET-FOSA	6:2 FTSA	8:2 FTSA
LoQ				0.57	0.07	0.04	0.06	0.05	0.06	0.04	0.05	0.05	0.01	0.05	0.01	0.88
S 1	a	3.70		1.30	2.00	1.00	0.47	0.22	0.27	0.09	5.08	0.82	0.46	~~0.04~~	1.26	~~0.37~~
S 1	b	3.69		1.43	2.00	0.95	0.22	0.17	0.14	0.07	2.65	0.68	0.22	~~0.02~~	1.31	~~0.37~~
S 2	a	3.73		3.41	4.50	2.55	1.03	0.41	0.24	0.08	7.48	2.89	0.46	0.05	2.56	1.16
S 2	b	3.72		3.64	4.43	1.96	0.68	0.31	0.16	0.05	9.20	1.96	0.36	~~0.04~~	2.75	1.19
S 3	a	3.74		2.45	6.23	1.87	0.85	0.38	0.22	0.06	7.59	3.22	0.47	0.06	3.50	1.33
S 3	b	3.73		2.21	5.30	1.50	0.64	0.31	0.17	0.05	8.21	3.54	0.46	~~0.04~~	3.36	1.70
S 4	a	3.75		5.08	11.51	2.63	1.04	0.47	0.19	0.06	19.83	6.28	0.97	0.06	6.50	2.37
S 4	b	3.74		5.59	11.57	3.82	1.27	0.51	0.28	0.10	14.50	6.18	0.76	0.13	6.37	2.64
S 5	a	3.70		15.41	17.42	7.48	2.73	0.99	0.36	0.12	23.68	7.17	0.95	0.14	10.20	3.45
S 5	b	3.72		13.99	17.71	8.53	3.52	1.73	0.61	0.14	31.60	9.70	1.25	0.22	10.87	4.40
S 6*	a	3.73														
S 6*	b	3.71														
S 7	a	3.73		39.05	56.00	24.17	11.36	4.41	0.76	0.09	82.31	32.58	3.12	0.53	33.44	11.57
S 7	b	3.72		31.12	56.44	25.48	10.36	3.97	1.23	0.21	95.65	33.06	2.97	0.69	32.80	12.90
S 8	a	3.72		51.54	71.25	35.26	14.43	6.21	1.85	0.43	110.82	41.95	4.16	0.95	41.76	17.20
S 8	b	3.74		48.95	68.71	34.02	13.30	4.55	0.91	0.11	105.53	39.63	3.24	0.50	42.35	13.24
D 4 low	a	3.80		0.98	2.91	1.39	0.82	0.33	0.22	0.07	5.44	4.88	0.41	~~0.02~~	1.32	1.61
D 4 low	b	3.78		1.14	2.77	1.76	1.02	0.52	0.24	0.10	3.58	4.05	0.41	~~0.04~~	1.25	0.96
D 3 low	a	3.86		1.66	4.00	1.72	0.69	0.42	0.09	0.12	5.53	3.80	0.48	0.52	2.12	0.88
D 3 low	b	3.84		1.58	3.91	1.59	0.95	0.51	0.14	0.08	7.25	2.60	0.51	~~0.04~~	1.93	1.09
D 2 low	a	3.86		2.37	5.80	1.81	0.65	0.18	0.08	0.07	10.76	4.24	0.15	~~0.01~~	2.60	1.60
D 2 low	b	3.85		3.22	6.43	2.24	0.96	0.33	0.11	0.07	6.78	4.03	0.16	~~0.00~~	2.40	1.38
D 1 low	a	3.95		3.83	7.86	2.28	0.61	0.17	0.16	0.09	11.31	3.38	0.14	~~0.01~~	4.96	1.01
D 1 low	b	3.95		4.55	9.25	3.00	1.49	0.66	0.08	~~0.03~~	11.02	4.32	0.32	~~0.01~~	4.34	2.19
D 4 high	a	3.92		8.95	17.16	17.67	15.48	9.21	1.95	0.11	22.92	33.24	5.37	0.30	7.72	12.03
D 4 high	b	3.94		9.08	18.50	16.39	10.65	4.44	0.95	0.13	23.51	25.15	2.08	0.25	7.78	10.08
D 3 high	a	3.82		13.17	24.90	19.38	8.95	3.47	0.65	0.22	30.90	25.80	2.03	0.22	12.26	8.80
D 3 high	b	3.85		14.21	26.76	17.71	8.15	3.29	0.85	0.23	31.49	24.67	1.90	0.29	11.64	6.95
D 2 high	a	3.82		25.68	40.29	22.95	11.30	3.93	0.50	0.04	42.59	33.41	1.43	0.05	20.32	12.04
D 2 high	b	3.85		21.48	37.69	22.54	9.63	2.66	0.54	0.09	56.39	23.11	1.26	0.07	22.30	11.93
D 1 high	a	3.76		36.03	51.81	30.28	12.10	3.45	0.50	0.08	92.21	34.73	1.30	0.33	36.70	15.18
D 1 high	b	3.79		34.90	53.75	23.40	9.39	2.82	0.21	0.07	74.33	33.45	0.60	~~0.01~~	27.30	12.07

* omitted from results

Table A 18 Measured aqueous concentration of PFASs in the soil Paskalampa Mor Oe in the isotherm sorption and desorption experiment. Concentrations in strikethrough style were below the respective LoQ and therefore excluded from further analysis.

Aqueous PFAS concentrations in MOe [ng mL^{-1}]

Sample	dupl.	pH	PFPeA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFHxS	PFOS	FOSA	ET-FOSA	6:2 FTSA	8:2 FTSA
LoQ			0.38	0.54	0.09	0.05	0.13	0.06	0.01	0.05	0.13	0.08	0.05	0.15	0.08	0.05
S 1	a	3.49	3.61	2.67	2.28	1.72	1.18	1.14	0.77	0.17	5.62	1.60	0.87	0.67	1.76	1.06
S 1	b	3.52	2.70	2.97	2.55	1.83	1.16	1.29	0.71	0.23	4.58	1.93	0.81	0.76	1.69	1.46
S 2	a	3.52	5.99	4.84	5.33	3.06	2.08	2.29	1.38	0.35	7.97	3.24	1.75	1.15	3.28	2.84
S 2	b	3.51	6.88	4.92	5.37	3.48	2.58	2.55	1.67	0.40	6.33	3.83	1.74	1.25	3.65	2.26
S 3	a	3.52	4.98	4.42	6.13	3.39	2.36	2.83	1.14	0.45	7.64	4.53	1.62	1.12	4.44	2.35
S 3	b	3.50	5.22	4.74	5.90	3.84	2.75	2.61	1.93	0.45	8.16	3.62	1.63	1.29	4.76	2.84
S 4	a	3.54	8.91	10.13	14.12	5.64	4.37	4.66	3.70	0.71	15.92	7.76	3.19	2.13	8.71	6.34
S 4	b	3.49	6.91	9.01	12.20	5.93	4.95	4.67	2.64	0.82	17.68	7.51	3.04	2.26	7.92	4.59
S 5	a	3.52	13.86	17.72	22.81	11.83	8.74	9.43	7.52	1.62	26.64	11.82	8.39	6.09	14.40	9.25
S 5	b	3.53	17.56	16.16	20.21	10.44	7.63	7.58	5.48	1.26	26.93	9.17	5.17	2.69	14.30	6.08
S 6	a	3.53	25.28	25.86	35.50	15.92	11.96	14.53	10.72	2.44	58.39	18.98	10.65	5.57	24.32	15.14
S 6	b	3.50	27.94	32.79	40.62	22.13	16.12	18.70	13.13	2.63	45.50	19.93	15.26	8.69	25.00	15.99
S 7	a	3.48	29.83	24.20	63.91	33.14	21.82	23.19	16.98	3.55	86.69	51.37	11.97	9.10	41.14	22.15
S 7	b	3.50	29.99	38.81	55.53	31.37	20.18	22.85	16.51	3.27	89.52	44.66	11.88	8.85	34.05	19.83
S 8	a	3.52	50.32	80.07	88.37	44.90	30.63	36.17	24.71	5.12	121.22	67.27	19.49	14.11	58.65	33.18
S 8	b	3.52	70.13	73.74	95.18	44.76	32.25	40.24	28.60	5.89	141.59	71.44	22.43	15.19	59.24	34.28
D 4 low	a	3.90	~~-2.54~~	~~-0.02~~	1.15	1.27	1.52	2.46	1.95	0.28	0.62	2.94	2.92	0.60	0.35	0.92
D 4 low	b	3.86	~~-2.52~~	~~0.00~~	1.13	1.26	1.76	2.45	2.61	0.42	0.90	3.63	3.60	0.81	0.20	0.90
D 3 low	a	3.78	~~-2.24~~	~~0.16~~	1.93	1.71	1.95	1.32	0.61	0.18	1.39	4.31	1.24	0.45	0.61	1.22
D 3 low	b	3.76	~~-2.38~~	~~0.22~~	1.87	2.03	1.67	1.46	0.92	0.30	1.21	4.97	1.30	0.53	0.50	1.68
D 2 low	a	3.74	~~-1.90~~	0.91	3.24	2.62	2.02	1.80	1.18	0.16	3.72	4.46	1.29	0.60	1.24	1.67
D 2 low	b	3.72	~~-1.83~~	1.23	3.26	2.12	2.02	1.69	0.98	0.17	4.38	4.13	1.17	0.60	0.93	1.31
D 1 low	a	3.63	~~0.02~~	2.93	7.06	3.92	2.77	2.87	2.10	0.48	7.47	6.86	2.42	1.21	4.02	2.69
D 1 low	b	3.59	~~0.38~~	3.04	6.60	4.30	2.92	2.81	1.66	0.31	7.39	6.60	1.92	1.19	2.93	3.14
D 4 high	a	3.89	~~-1.90~~	1.82	6.23	9.44	10.67	17.07	16.86	1.89	4.38	19.07	22.37	3.66	1.56	7.63
D 4 high	b	3.88	~~-2.16~~	1.27	5.78	8.44	11.34	15.19	13.99	1.63	4.56	22.33	19.20	3.50	1.54	6.84
D 3 high	a	3.78	~~-0.62~~	3.31	10.50	13.69	12.84	13.56	8.74	1.43	10.53	23.27	9.75	3.97	3.26	7.67
D 3 high	b	3.79	~~-1.18~~	3.35	11.14	13.06	12.26	12.67	7.01	1.45	9.13	24.73	10.54	4.64	3.21	6.63
D 2 high	a	3.73	4.97	10.88	23.15	20.19	15.86	16.57	11.36	1.43	25.61	28.70	10.96	4.05	8.33	11.68
D 2 high	b	3.72	1.70	9.72	20.55	18.80	12.61	14.23	10.31	1.56	22.14	24.26	11.11	4.67	8.14	10.69
D 1 high	a	3.60	17.75	27.94	48.89	28.58	24.99	21.61	15.41	2.96	39.39	43.70	17.99	9.37	18.83	19.99
D 1 high	b	3.62	12.82	24.81	47.14	30.58	19.82	21.06	14.09	2.76	51.13	39.46	14.99	5.88	25.04	18.84

*omitted from results

Appendix XIII

Table A 19 Calculated sorbed PFAS concentrations (ng g^{-1} dw soil) in the soil sample Paskalampa Peat Oi in the isotherm sorption and desorption experiment. Concentrations below the LoQ were omitted in the determination of sorbed concentrations.

Calculated sorbed PFAS concentrations in POi [ng g^{-1} dw]															
Sample	dupl.	pH	PFPeA*	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFHxS	PFOS	FOSA	ET-FOSA	6:2 FTSA	8:2 FTSA
S 1	a	3.70		99.34	96.16	38.27	41.75	51.62	33.16	14.64	34.24	225.91	155.96		36.04	
S 1	b	3.69		94.22	96.08	40.19	51.75	53.54	38.12	15.28	131.28	231.43	165.40		34.28	
S 2	a	3.73		166.36	172.17	54.70	80.07	104.28	77.99	33.05	175.51	401.66	329.83	437.01	70.81	154.87
S 2	b	3.72		157.16	174.97	78.22	94.07	108.52	81.27	34.25	106.71	439.10	334.15		63.05	153.51
S 3	a	3.74		347.12	269.01	155.56	144.17	162.67	120.17	50.94	394.90	632.12	493.70	643.32	114.64	242.63
S 3	b	3.73		356.64	306.29	170.36	152.57	165.47	122.17	51.26	369.94	619.24	493.78		120.24	228.07
S 4	a	3.75		553.58	420.25	286.71	261.49	283.23	211.54	88.50	394.14	1042.36	832.34	1095.24	172.94	408.54
S 4	b	3.74		533.26	418.09	238.95	252.45	281.71	207.86	86.98	607.26	1046.52	840.66	1092.36	178.30	397.58
S 5	a	3.70		607.68	727.96	334.60	381.22	448.95	339.92	141.95	973.24	1805.88	1370.94	1770.05	292.32	675.81
S 5	b	3.72		664.64	716.52	292.52	349.70	419.35	330.00	141.15	656.36	1704.44	1358.78	1767.09	265.76	637.81
S 6*	a	3.73														
S 6*	b	3.71														
S 7	a	3.73		1776.56	1646.10	761.60	883.10	1156.52	935.62	396.90	1945.08	4403.68	3717.68	4821.62	572.96	1757.28
S 7	b	3.72		2093.44	1628.42	709.12	923.10	1174.12	916.74	392.42	1411.48	4384.56	3723.60	4815.30	598.48	1703.92
S 8	a	3.72		2389.60	2331.17	893.87	1206.21	1528.56	1214.29	517.01	2550.45	5931.33	4957.01	6419.36	876.64	2271.89
S 8	b	3.74		2493.12	2432.69	943.79	1251.33	1595.28	1251.89	529.89	2762.29	6024.13	4993.89	6437.36	853.36	2430.29
D 4 low	a	3.80		459.02	181.05	167.27	210.49	264.15	199.86	81.10	21.06	744.36	819.70		56.90	321.82
D 4 low	b	3.78		412.18	146.81	108.15	169.09	241.35	197.02		252.86	788.88	819.50		82.26	318.90
D 3 low	a	3.86		465.02	217.41	188.39	229.61	269.11	206.78	81.62	128.06	863.64	826.74		67.18	368.54
D 3 low	b	3.84		426.30	179.25	146.67	190.93	251.95	203.94		251.14	898.96	825.66		93.82	335.54
D 2 low	a	3.86		483.94	261.37	221.11	244.09	282.19	208.98	84.90	134.14	930.64	842.78		99.94	371.78
D 2 low	b	3.85		425.26	207.13	165.59	209.61	265.63	207.42		405.46	922.28	842.90		122.86	351.50
D 1 low	a	3.95		502.02	336.05	247.95	258.01	285.95	208.94	85.90	338.10	1032.68	845.90		104.74	415.54
D 1 low	b	3.95		462.82	279.53	195.19	218.37	265.59	210.22		456.42	997.24	842.94		132.06	362.86
D 4 high	a	3.92		1564.84	729.85	-559.81	228.61	1067.48	1140.41	514.37	536.25	3561.77	4730.29	6414.44	17.40	1414.49
D 4 high	b	3.94		1697.36	703.09	-304.45	547.73	1333.04	1200.01	518.81	688.37	4185.93	4900.05		164.32	1672.97
D 3 high	a	3.82		1659.52	918.25	-240.73	668.65	1366.48	1205.41	514.41	834.89	4375.21	4904.37	6422.04	80.92	1719.61
D 3 high	b	3.85		1776.36	907.81	-2.93	810.73	1445.00	1220.93	519.53	998.93	4698.69	4945.41		242.72	1937.01
D 2 high	a	3.82		1672.80	1108.49	75.63	800.77	1426.44	1221.21	522.49	1219.05	4739.13	4956.81	6429.64	165.04	1830.89
D 2 high	b	3.85		1915.04	1224.17	254.67	944.25	1523.40	1244.37	527.01	1130.57	5223.09	4996.21		262.12	1976.41
D 1 high	a	3.76		1979.28	1683.81	387.79	1010.93	1514.76	1231.37	522.57	1078.53	5380.97	4988.13	6425.16	243.92	2008.77
D 1 high	b	3.79		2076.16	1656.89	688.11	1141.73	1573.40	1261.61	529.17	1899.81	5478.49	5034.57		608.12	2212.13

*omitted from results

Table A 20 Calculated sorbed PFAS concentrations (ng g^{-1} dw soil) in the soil sample Paskalampa Mor Oe in the isotherm sorption and desorption experiment. Concentrations below the LoQ were omitted in the determination of sorbed concentrations.

Calculated sorbed PFAS concentrations in MOe [ng g^{-1} dw]

Sample	dupl.	pH	PFPeA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFHxS	PFOS	FOSA	ET-FOSA	6:2 FTSA	8:2 FTSA
S 1	a	3.49		44.38	84.80	9.39	13.51	14.74	13.00	11.28	12.64	194.63	139.56	192.58	16.28	58.08
S 1	b	3.52		32.70	74.32	5.15	14.31	8.98	15.48	9.04	54.32	181.35	141.72	189.14	18.92	42.24
S 2	a	3.52		109.16	138.97	34.30	37.91	29.08	32.23	22.25	155.91	387.98	278.23	393.25	42.01	87.51
S 2	b	3.51		105.88	137.69	17.34	17.91	18.68	20.79	20.17	221.67	364.22	278.95	389.09	27.05	110.79
S 3	a	3.52	99.05	268.24	273.09	94.92	83.77	64.59	83.05	35.58	392.90	579.56	447.54	600.92	76.96	201.91
S 3	b	3.50	89.77	255.36	281.97	76.84	68.25	73.15	51.53	35.34	372.10	616.04	447.06	594.04	64.48	182.31
S 4	a	3.54	150.89	351.42	315.85	166.31	128.21	115.87	71.06	62.26	550.38	983.32	743.22	1012.52	84.54	249.66
S 4	b	3.49	231.05	396.30	392.81	154.63	105.01	115.23	113.38	58.10	479.98	993.24	749.22	1007.40	116.06	319.50
S 5	a	3.52	266.13	515.36	512.36	160.44	140.66	111.67	53.36	82.03	854.68	1619.64	1073.50	1531.97	124.40	443.81
S 5	b	3.53	118.13	577.68	616.52	215.96	185.14	185.59	135.12	96.51	843.32	1725.72	1202.14	1668.13	128.64	570.77
S 6	a	3.53	406.39	1079.84	1041.26	457.64	368.60	262.93	182.98	156.15	981.52	2855.08	2007.70	2844.29	237.12	800.27
S 6	b	3.50	299.67	802.64	836.30	209.40	202.28	96.13	86.50	148.55	1497.28	2817.32	1823.30	2719.73	209.84	766.43
S 7	a	3.48	1044.68	2370.32	1329.38	402.80	464.62	405.32	286.98	258.74	1770.04	3652.00	3363.68	4478.90	264.96	1333.84
S 7	b	3.50	1038.60	1786.00	1664.74	473.44	530.30	418.92	305.78	269.78	1656.60	3920.56	3367.20	4488.90	548.24	1426.64
S 8	a	3.52	971.25	1248.48	1646.45	508.59	558.29	330.40	299.65	329.57	2134.45	4918.37	4343.89	5892.96	201.28	1632.61
S 8	b	3.52	178.85	1501.76	1374.05	514.03	493.49	167.52	144.05	298.77	1319.65	4751.49	4226.21	5849.68	177.60	1588.77
D 4 low	a	3.90			131.72					38.90	402.35	552.12	536.74	956.44	30.12	148.52
D 4 low	b	3.86			204.71					34.12	361.31	519.93	530.45	943.56	99.82	160.92
D 3 low	a	3.78			152.09			0.91	8.72	47.64	408.73	612.39	636.95	974.58	36.12	169.24
D 3 low	b	3.76			225.03				39.25	46.76	381.05	598.95	657.19	968.87	101.08	174.33
D 2 low	a	3.74		372.25	186.28	32.02	31.78	29.68	17.44	52.60	414.67	725.43	669.46	984.68	44.12	195.72
D 2 low	b	3.72		397.53	256.23	9.11	10.15	31.66	62.93	56.55	371.02	742.68	693.62	982.15	108.65	224.20
D 1 low	a	3.63		369.48	221.61	84.50	75.73	63.31	36.53	52.74	463.77	812.25	688.93	992.44	39.98	226.57
D 1 low	b	3.59		394.76	291.56	61.59	54.10	65.28	82.02	56.68	420.11	829.51	713.09	989.91	104.52	255.05
D 4 high	a	3.89		1119.71	187.15					1561.52	1561.52	2501.39	2677.25	5470.64	109.47	720.61
D 4 high	b	3.88		1423.87	154.83					827.73	827.73	2452.32	2780.16	5507.09		807.79
D 3 high	a	3.78		1119.71	374.29					1596.27	1596.27	2953.81	3441.89	5564.05	128.43	923.68
D 3 high	b	3.79		1423.87	309.65					888.56	888.56	3015.73	3407.41	5585.36		993.17
D 2 high	a	3.73	970.24	1148.45	483.65					1675.87	1675.87	3502.08	3685.81	5668.96	147.97	1074.88
D 2 high	b	3.72	704.24	1430.00	392.40					958.56	958.56	3681.39	3680.99	5708.56		1115.79
D 1 high	a	3.60	932.35	1135.84	595.01					2175.25	2175.25	4067.23	3884.21	5706.16	229.89	1275.36
D 1 high	b	3.62	601.28	1434.35	564.03					1162.45	1162.45	4125.65	3925.68	5816.83		1292.05

*omitted from results

Appendix XIV

Table A 21 Log K_{OC} (mL g^{-1} dw soil) values obtained from isotherm sorption experiment for the soil Paskalampa Peat Oi. Concentrations below the LoQ were omitted in the determination of the respective partitioning coefficient.

Log K_{OC} [mL g^{-1} dw] for POi															
Sample	dupl.	PFPeA*	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFHxS	PFOS	FOSA	ET-FOSA	6:2 FTSA	8:2 FTSA
S 1	a		2.23	2.03	1.93	2.29	2.72	2.44	2.57	1.18	2.79	2.88		1.80	
S 1	b		2.17	2.03	1.97	2.72	2.84	2.78	2.67	2.04	2.88	3.22		1.77	
S 2	a		2.04	1.93	1.68	2.24	2.75	2.86	2.95	1.72	2.49	3.20	4.27	1.79	2.47
S 2	b		1.98	1.94	1.95	2.49	2.89	3.06	3.17	1.41	2.70	3.32		1.71	2.46
S 3	a		2.50	1.98	2.27	2.58	2.98	3.09	3.26	2.06	2.64	3.37	4.38	1.86	2.61
S 3	b		2.56	2.11	2.40	2.72	3.08	3.21	3.33	2.00	2.59	3.37		1.90	2.48
S 4	a		2.39	1.91	2.39	2.75	3.13	3.40	3.53	1.65	2.57	3.28	4.59	1.77	2.58
S 4	b		2.33	1.91	2.14	2.65	3.09	3.22	3.30	1.97	2.58	3.39	4.26	1.79	2.53
S 5	a		1.94	1.97	2.00	2.49	3.00	3.33	3.41	1.96	2.75	3.51	4.44	1.80	2.64
S 5	b		2.02	1.95	1.88	2.35	2.73	3.08	3.34	1.67	2.59	3.38	4.26	1.74	2.51
S 6*	a														
S 6*	b														
S 7	a		2.01	1.82	1.85	2.24	2.77	3.44	3.97	1.72	2.48	3.42	4.31	1.58	2.53
S 7	b		2.18	1.81	1.79	2.30	2.82	3.22	3.63	1.52	2.47	3.45	4.19	1.61	2.47
S 8	a		2.01	1.86	1.75	2.27	2.74	3.17	3.43	1.71	2.50	3.42	4.18	1.67	2.47
S 8	b		2.05	1.90	1.79	2.32	2.89	3.49	4.04	1.77	2.53	3.54	4.46	1.65	2.61
Average		n.d.	2.17	1.94	1.99	2.46	2.89	3.13	3.40	1.74	2.61	3.34	4.33	1.75	2.53

*omitted from results

n.d. not determined

Table A 22 Log K_{OC} (mL g^{-1} dw soil) values obtained from isotherm sorption experiment for the soil Paskalampa Mor Oe. Concentrations below the LoQ were omitted in the determination of the respective partitioning coefficient.

Log K_{OC} [mL g^{-1} dw] for MOe															
Sample	dupl.	PFPeA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFHxS	PFOS	FOSA	ET-FOSA	6:2 FTSA	8:2 FTSA
S 1	a		1.49	1.84	1.01	1.33	1.38	1.50	2.09	0.62	2.36	2.48	2.73	1.24	2.01
S 1	b		1.31	1.74	0.72	1.36	1.11	1.61	1.87	1.35	2.24	2.51	2.67	1.32	1.73
S 2	a		1.62	1.69	1.32	1.53	1.37	1.64	2.07	1.56	2.35	2.47	2.81	1.38	1.76
S 2	b		1.60	1.68	0.97	1.11	1.14	1.37	1.97	1.82	2.25	2.48	2.76	1.14	1.96
S 3	a	1.57	2.05	1.92	1.72	1.82	1.63	2.13	2.17	1.98	2.38	2.71	3.00	1.51	2.20
S 3	b	1.51	2.00	1.95	1.57	1.67	1.72	1.70	2.16	1.93	2.50	2.71	2.93	1.40	2.08
S 4	a	1.50	1.81	1.62	1.74	1.74	1.67	1.55	2.21	1.81	2.37	2.64	2.95	1.26	1.87
S 4	b	1.80	1.91	1.78	1.69	1.60	1.66	1.90	2.12	1.70	2.39	2.66	2.92	1.44	2.11
S 5	a	1.55	1.73	1.62	1.40	1.48	1.34	1.12	1.97	1.78	2.41	2.38	2.67	1.21	1.95
S 5	b	1.10	1.82	1.76	1.59	1.66	1.66	1.66	2.16	1.77	2.55	2.64	3.06	1.22	2.24
S 6*	a	1.48	1.89	1.74	1.73	1.76	1.53	1.50	2.08	1.50	2.45	2.55	2.98	1.26	1.99
S 6*	b	1.30	1.66	1.58	1.25	1.37	0.98	1.09	2.02	1.79	2.42	2.35	2.77	1.19	1.95
S 7	a	1.82	2.26	1.59	1.36	1.60	1.51	1.50	2.13	1.58	2.12	2.72	2.96	1.08	2.05
S 7	b	1.81	1.93	1.75	1.45	1.69	1.53	1.54	2.19	1.54	2.21	2.72	2.98	1.48	2.13
S 8	a	1.56	1.46	1.54	1.32	1.53	1.23	1.35	2.08	1.52	2.13	2.62	2.89	0.81	1.96
S 8	b	0.68	1.58	1.43	1.33	1.46	0.89	0.97	1.98	1.24	2.09	2.55	2.86	0.75	1.94
Average		1.47	1.76	1.70	1.39	1.54	1.40	1.51	2.08	1.59	2.33	2.57	2.87	1.23	2.00

*omitted from results

n.d. not determined

Appendix XV

Table A 23 Log K_{OC} (mL g^{-1} dw soil) values obtained from isotherm desorption experiment for the soil Paskalampa Peat Oi. Concentrations below the LoQ were omitted in the determination of the respective partitioning coefficient.

Log K_{OC} [mL g^{-1} dw] for POi															
Sample	dupl.	PFPeA*	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFHxS	PFOS	FOSA	ET-FOSA	6:2 FTSA	8:2 FTSA
D 4 low	a		3.02	2.22	2.48	2.79	3.26	3.32	3.40	1.72	2.60	3.65		2.06	2.71
D 4 low	b		2.92	2.16	2.27	2.62	3.03	3.27		2.19	2.69	3.65		2.22	2.89
D 3 low	a		2.81	2.16	2.46	2.90	3.18	3.69	3.20	1.73	2.74	3.60		2.02	2.97
D 3 low	b		2.78	2.07	2.36	2.69	3.07	3.51		2.10	2.90	3.56		2.15	2.86
D 2 low	a		2.67	2.11	2.48	2.95	3.55	3.78	3.42	1.85	2.73	4.10		1.95	2.76
D 2 low	b		2.51	1.99	2.29	2.70	3.26	3.63		2.18	2.74	4.06		2.09	2.77
D 1 low	a		2.51	2.08	2.45	2.98	3.57	3.47	3.32	1.89	2.84	4.11		1.89	2.96
D 1 low	b		2.42	2.00	2.25	2.58	2.98	3.76		2.09	2.73	3.76		1.96	2.61
D 4 high	a		2.59	1.98		1.52		3.12	4.01	1.72	2.38	3.29	4.68	0.70	2.42
D 4 high	b		2.62	1.93		2.06		3.45	3.94	1.81	2.57	3.72		1.67	2.57
D 3 high	a		2.45	1.91		2.22		3.62	3.71	1.78	2.58	3.73	4.82	1.17	2.64
D 3 high	b		2.44	1.88		2.35		3.50	3.70	1.85	2.63	3.76		1.67	2.79
D 2 high	a		2.16	1.79	0.87	2.20		3.73	4.46	1.80	2.50	3.89	5.44	1.26	2.53
D 2 high	b		2.30	1.86	1.40	2.34		3.71	4.12	1.65	2.70	3.95		1.42	2.57
D 1 high	a		2.09	1.86	1.46	2.27		3.74	4.19	1.42	2.54	3.93	4.64	1.17	2.47
D 1 high	b		2.12	1.84	1.82	2.43		4.13	4.21	1.76	2.56	4.27		1.70	2.61

*omitted from results

Table A 24 Log K_{OC} (mL g^{-1} dw soil) values obtained from isotherm desorption experiment for the soil Paskalampa Mor Oe. Concentrations below the LoQ were omitted in the determination of the respective partitioning coefficient.

Log K_{OC} [mL g^{-1} dw] for MOe															
Sample	dupl.	PFPeA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFHxS	PFOS	FOSA	ET-FOSA	6:2 FTSA	8:2 FTSA
D 4 low	a			2.39			-0.16	0.92	2.50	3.09	2.59	2.61	3.48	2.28	2.53
D 4 low	b			2.57				1.45	2.32	2.90	2.49	2.53	3.35	2.98	2.56
D 3 low	a			2.25	1.54	1.48	1.62	1.73	2.74	2.75	2.50	3.00	3.61	2.13	2.48
D 3 low	b			2.41	0.92	1.05	1.61	2.11	2.55	2.76	2.45	3.00	3.54	2.61	2.40
D 2 low	a		2.88	2.11	1.78	1.84	1.82	1.76	2.78	2.37	2.53	3.00	3.49	1.78	2.40
D 2 low	b		2.78	2.22	1.73	1.70	1.86	2.19	2.80	2.25	2.57	3.06	3.49	2.32	2.56
D 1 low	a		2.35	1.92	1.90	1.94	1.88	1.80	2.39	2.14	2.43	2.76	3.19	1.59	2.24
D 1 low	b		2.39	2.05	1.83	1.83	1.88	2.10	2.55	2.08	2.45	2.86	3.20	1.87	2.28
D 4 high	a		3.06	2.05					2.22	2.82	2.39	2.35	3.45	2.12	2.25
D 4 high	b		3.32	2.00					2.26	2.53	2.31	2.43	3.47		2.34
D 3 high	a		2.81	1.93					2.46	2.45	2.37	2.82	3.42	1.87	2.35
D 3 high	b		2.90	1.82					2.42	2.26	2.36	2.78	3.35		2.45
D 2 high	a	2.56	2.29	1.68					2.53	2.09	2.36	2.80	3.42	1.52	2.23
D 2 high	b	2.89	2.44	1.71					2.46	1.91	2.45	2.79	3.36		2.29
D 1 high	a	1.99	1.90	1.52				0.19	2.25	2.01	2.24	2.61	3.06	1.36	2.08
D 1 high	b	1.94	2.05	1.48		1.09			2.26	1.63	2.29	2.69	3.27		2.11

*omitted from results

Appendix XVI

Table A 25 Desorption yield (%) for target PFASs in the soils Paskalampa Peat Oi and Paskalampa Mor Oe. Desorption yield is based on the PFAS concentration in soil after the fourth round of the successive dilution method. D4 and D8 correspond to samples initially spiked with a low and a high PFAS concentration, respectively.

	Desorption yield [%]													
Sample (n=2)	PFPeA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFHxS	PFOS	FOSA	ET-FOSA	6:2 FTSA	8:2 FTSA
	Paskalampa Peat Oi													
D4		19.84	60.89	47.60	26.14	10.52	5.37	7.57	72.65	26.60	2.02		60.38	20.52
D8		33.19	69.92		68.41	23.15	5.10	1.31	76.95	35.20	3.22		89.50	34.34
	Paskalampa Mor Oe													
D4			52.53					39.33	25.88	45.76	28.49	5.94	35.23	45.63
D8		7.51	77.36					48.29	30.83	48.77	36.32	6.51	88.08	52.55

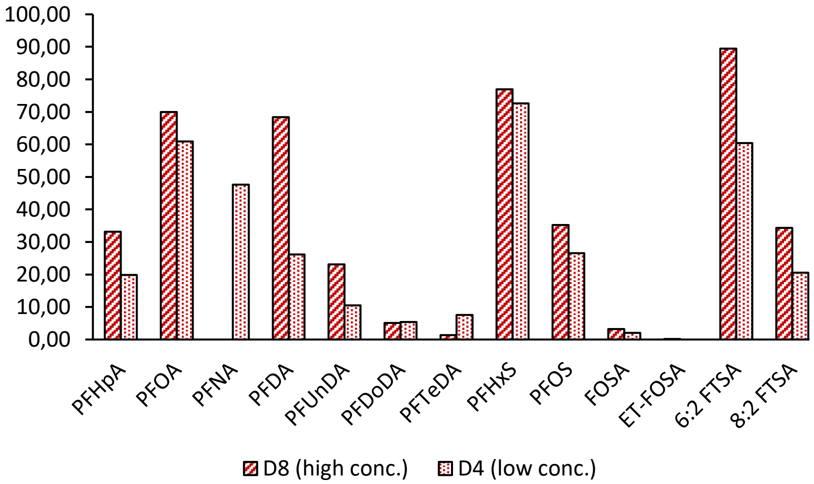

Figure A 9 Desorption yield (%) for the soil Paskalampa Peat Oi.

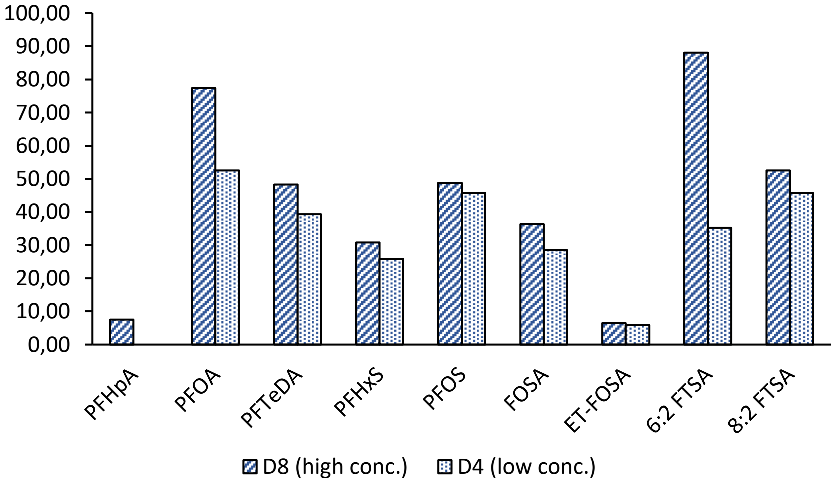

Figure A 8 Desorption yield (%) for the soil Paskalampa Mor Oe.

Appendix XVII

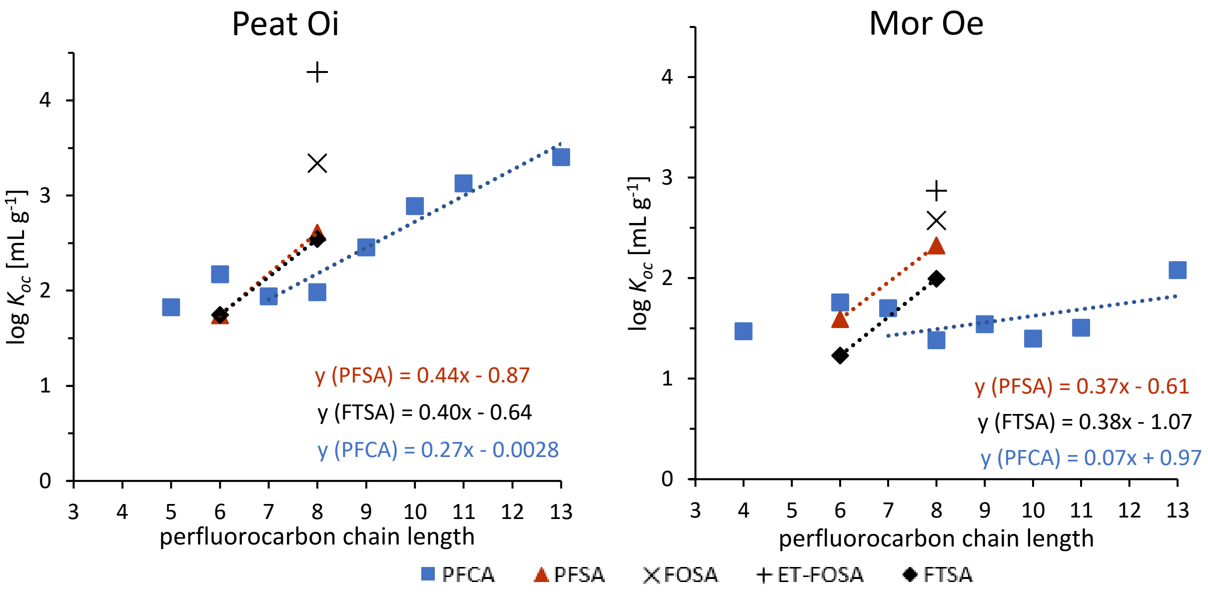

Figure A 10 Relationship between average log K_{OC} [mL g^{-1}] and perfluorocarbon chain length in the isotherm sorption experiment.

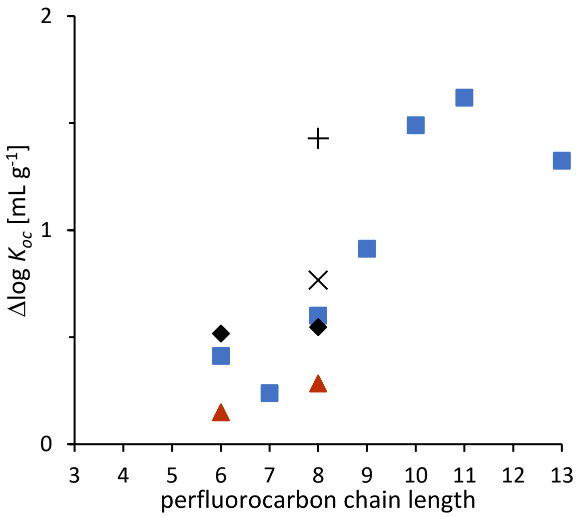

Figure A 11 Δlog K_{OC} of POi to MOe in relation to the chain length. Representation of the higher sorption in POi as compared to MOe for individual target PFASs.

Appendix XVIII

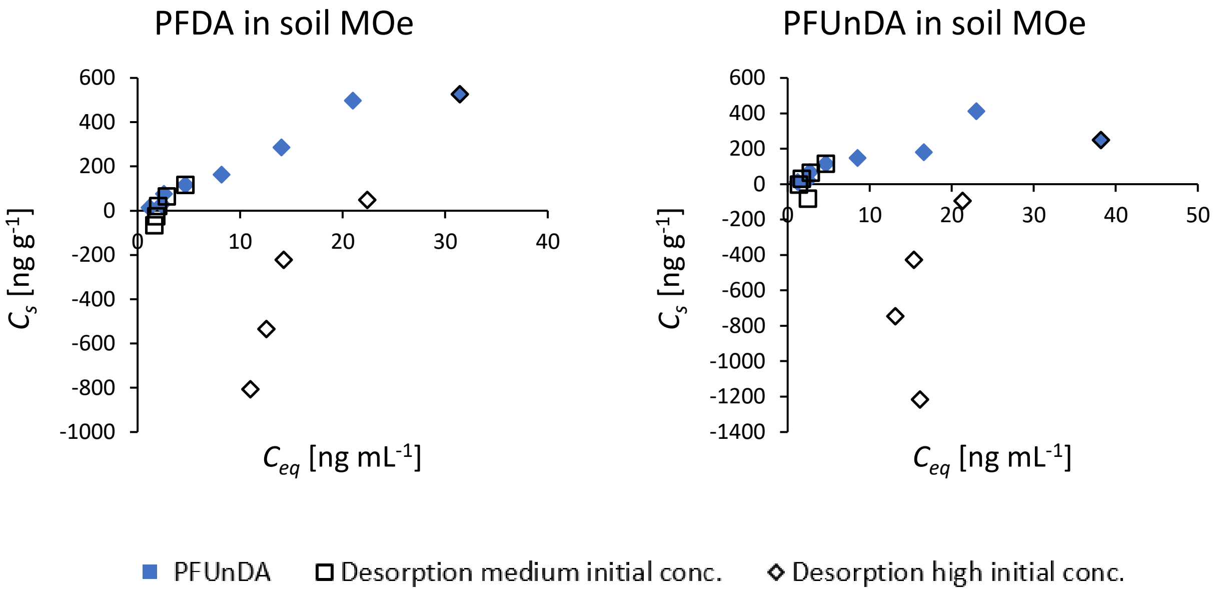

Figure A 12 Sorption and desorption of long chain PFCAs (C_9, C_{10}) in the soil MOe. Presentation of experimental difficulties using the successive dilution method.

Appendix XIX

Table A 26 Absolute recovery and relative recovery for all PFASs under study in the pH sorption (1) and isotherm sorption (2) experiment for the soils Paskalampa Peat Oi, Peat Oe and Mor Oe.

	Absolute recovery [%]														
	PFPeA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	FOSA	ET-FOSA	6:2 FTSA	8:2 FTSA
1	n.d.	n.d.	94.27	33.24	30.37	32.92	23.78	45.39	99.28	105.97	130.66	89.17	102.03	93.64	100.59
2	50.55	87.22	89.21	38.92	30.11	30.01	21.75	45.13	n.d.	117.82	128.51	85.00	109.07	84.26	97.46
	Relative recovery [%]														
	PFPeA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFBS	PFHxS	PFOS	FOSA	ET-FOSA	6:2 FTSA	8:2 FTSA
1	n.d.	n.d.	100.73	101.94	98.38	91.24	73.31	78.92	101.52	104.26	97.57	98.37	307.54	88.20	77.65
2	100.49	97.00	97.00	101.62	105.55	89.36	78.66	75.655	n.d.	99.14	102.61	89.535	629.94	93.015	86.5