BERGISCHE
UNIVERSITÄT
WUPPERTAL

Dissertation im Fach
Geographie

mit dem Titel

Analysis of the sorption and desorption behavior of the surfactants perfluorooctanoic acid (PFOA) and nonylphenol (4-*n*-NP) in soils in relation to physicochemical soil properties with focus on the soil organic carbon content

Zur Erlangung des akademischen Grades
Doktor der Naturwissenschaften (Dr. rer. nat)

durch die Fakultät für Human- und
Sozialwissenschaften
Der Bergischen Universität Wuppertal

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Wuppertal, im Juli 2022

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List of Abbreviations

6:2-FTAB	6:2 fluorotelomer sulfonamido betaine
6:2-FTOH	6:2 flurotelomer alcohol
6:2-FTS	6:2 fluorotelomer sulfonate
AFFF	Aqueous firefighting foams
AP	Alkyl phenol
APEO	Alkyl phenol ethoxylate
BET	Brunauer, Emmett, Teller: a measurement for the soil surface area
$CaCl_2$	Calcium chloride
CEC_{eff}	Effective cation exchange capacity
CMC	Critical micelle concentration
DOC	Dissolved organic carbon
EDC	Endocrine disrupting chemical
et al.	et alii
EtFOSE	N-ethyl perfluorooctane sulfonamidoethanol
FTIR	Fourier transformation infrared
FTOH	Fluorotelomer alcohol
HCl	Hydrochloride acid
HI	Hydrophobicity index
IEP	Isoelectric point of charge
K_D	Soil-to-solution partition coefficient
K_{OW}	Soil-to-solution partition coefficient normalized to soil organic carbon
KOH	Potassium hydroxide
MANOVA	Multivariable analysis of variance
MIR	Mid infrared
n	Numbers of replicates

NaN_3	Sodium azide
NaOH	Caustic soda solution
NP	Nonylphenol
NPEO	Nonylphenol ethoxylates
NRW	North-Rhine Westphalia
OC	Organic carbon
OP	Octyl phenol
p	Level of significance
PAH	Polycyclic aromatic hydrocarbon
PCA	Principal component analysis
PCB	Polychlorinated biphenyl
PFAS	Per- and polyfluorinated substances
PFC	Perfluorochemicals
PFCA	Perfluorocarboxylic acid
PFHxS	Perfluorohexane sulfonic acid
PFOA	Perfluorooctanoic acid
PFOAAmS	Perfluoroctaneamido ammonium iodide
PFOAB	Perfluorooctane amido betaine
PFOS	Perfluorooctane sulfonate acid
PFOSA	Perfluoroalkane sulfonamido
POM	Particulate organic matter
POP	Persistent organic pollutant
PTFE	Fluoropolymer polytetrafluorethylene
PVC	Polyvinyl chloride
R^2	Correlation coefficient
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RSS	Residual sum-of-squares

SNV	Standard normal variate
SOC	Soil organic carbon
SOM	Soil organic matter
TOC	Total organic carbon
UCMR3	Third Unregulated Contaminant Monitoring Rule
USEPA	United States Environmental Protection Agency
WFD	Water framework directive
WWTP	Wastewater treatment plants

Chapter 1

Introduction

Surfactants – a global problem in soils

Surfactants are a diversified group of chemicals known for their wide use in cleaning products (Schick and Oellig, 2019; Ying, 2006). Their main characteristics are high solubility, cleaning abilities and their ability to lower surface or interfacial tension (Li et al., 2018a; Ruczynska et al., 2020). They consist of a polar head-group and a long hydrophobic tail (Idkowiak et al., 2017; Tadros, 2014). Surfactants tend to adsorb between two liquids or between an aqueous solution and the air or soil (Camino and Pilosof, 2011; Camino et al., 2012), and the hydrophilic tail is directed to the aqueous phase at any time (Zafeiri et al., 2017).

The worldwide production of surfactants exceeded 12.7 million tons per year (Edser, 2006; Idkowiak et al., 2017). More than 2 million tons were produced in Western Europe (2013) (Idkowiak et al., 2017). After use, the remaining surfactants are discharged into sewage systems or directly into the environment (Alder and van der Voet, 2015; Arvaniti et al., 2014). Furthermore, several studies have shown that the application of sewage sludge on agricultural sites can lead to a transfer of surfactants into the environment (Ivankovic and Hrenovic, 2010; Kim et al., 2012; Madrid et al., 2020). Therefore, they can be found ubiquitous in soils, sediments, as well as ground and surface waters (Jing et al., 2013; Meesters and Schroder, 2004; Skutlarek et al., 2006).

There are four main classes of surfactants, classified by their form in aqueous solutions: anionic, cationic, zwitterionic, and nonionic (Backe et al., 2013; Zhi and Liu, 2018). The toxic effects of surfactants on humans, wildlife, and aquatic organisms are well known (Kennedy et al., 2004; Lu and Gan, 2014; Mtibaa et al., 2020). Anionic surfactants are, for example, able to bind on bioactive macromolecules and can thus change the folding of the peptide chain which can modify the biological function of the molecule (Cserháti et al., 2002). Cationic surfactants, however, bind to the cytoplasmic membrane of bacteria and disorganize them via their long alkyl chain (McDonnell and Russell, 1999). Nonionic surfactants can destroy cells through losses of ions or amino acids by binding to various proteins and phospholipid membranes, which leads to antimicrobial activity (Cserhati, 1995). Because of these toxic effects, the release of surfactants to the environment should be prevented (Brooke et al., 2004; Paria, 2008). In general, surfactants are biodegradable, but microorganisms cannot degrade all surfactants in soils (Ivankovic and Hrenovic, 2010). In that case, the distribution paths in the environment are determined by sorption and desorption processes.

Two of these hardly degradable surfactants will be investigated in more detail in the present study. One is the nonionic surfactant nonylphenol (NP) and the other is an anionic surfactant called perfluorooctanoic acid (PFOA). Both surfactants are ubiquitous in the environment (Meesters and Schroder, 2004; Niu et al., 2015). Since NP and PFOA have negative effects on human health, the knowledge about their distribution in the environment is essential to analyze possible sources of hazard (Wang et al., 2015a; Zhang et al., 2016). PFOA is suspected to have carcinogenic effects (Fair et al., 2012; Giesy et al., 2009) (see pp. 11) and NP has endocrine disrupting and carcinogenic potential (Roberts et al., 2006b) (see pp. 20).

It is important to know to what extent they can be retained or transformed in soils, because soils can form sinks for pollutants (Collins et al., 2013; Pulkrabova et al., 2019). Thus, the retention and transformation of pollutants in soils need to be analyzed (Cachada et al., 2012; Jiao et al., 2015). The distribution those is dominated by sorption and desorption properties since NP and PFOA are barely biodegradable or persistent against microbial degradation, respectively (Lu and Gan, 2014; Szakova et al., 2019).

Therefore, this study aimed to identify the most important sorbents of the surfactants in soils. Furthermore, the sorption and desorption of NP and PFOA are analyzed depending on the physicochemical properties of the soil and the surfactants. A special focus was set on influences of varying soil organic carbon contents (SOC), since the SOC is also varying in soils under natural conditions, and it is an important sorbent for PFOA and NP in soils (Higgins and Luthy, 2006; Milinovic et al., 2015a).

State of the art

Surfactants

The term surface-active agent or “surfactant” represents an amphiphilic or amphipathic heterogeneous and long-chain (C_8-C_{18}) molecule containing both hydrophilic (head) and hydrophobic (tail) moieties, which are affecting the surface tension of fluids (Centeno et al., 2017; Kalogirou and Blyth, 2020; Rosen and Kunjappu, 2012). The hydrophilic part can be ionic, nonionic or zwitterionic. The polar and ionic head group generates the surfactants interaction with water due to dipole or ion-dipole interaction (Dillarstone and Paye, 1994). Since the hydrocarbon chain of the surfactants avoids to interact with the water molecules, the chain is forced out of the water by accumulating at interfaces (Oka et al., 2020). Furthermore, if surfactant concentrations exceed a specific concentration, they tend to form aggregates, also called micelles (Tsui and Kuo, 2020). This specific concentration is called the critical micelle concentration (CMC) (Hamon et al., 2018; He et al., 2019; Zhong et al., 2018). The hydrophilic chain is directed to the water molecules, while the hydrophobic part is directed towards the interior of the aggregates (Alkawareek et al., 2018). The physical properties of surfactants (e.g. surface tension, adsorption, detergency change) change below the CMC but not above (Paria, 2008). Surfactant adsorption to an interface lead to a reduction of the initial interfacial tension, while the micelle forming minimizes the interaction between the solvent and the lyophobic part of the surfactant molecules (Deodhar et al., 2020). The equilibrium between hydrophilic and hydrophobic molecule parts (hydrophilic-lipophilic balance, HLB) gives the molecules their special properties (Yesilyurt et al., 2020; Zafeiri et al., 2017). Which are the ability to adsorb onto interfaces and the formation of self-assembly structures (Tadros, 2014).

Within the surfactants group, four main classes can be identified: anionic, cationic, zwitterionic, and nonionic surfactants (Holmberg et al., 2003; Tadros, 1984). In the past, a fifth group (polymeric surfactants) was used for emulsion and suspension preparation and their stabilization (Tadros, 2014).

The anionic surfactants are the most commonly used surfactants in industrial applications, because they are cheap in production (Linfield, 1967; Lucassen-Reynders, 1981; Porter, 1994). Most detergents contain anionic surfactants with chain length in the region of 12–16 C atoms (Trawinska et al., 2016). The polar head part is located at the end of the chain (Negm and Tawfik, 2014). Linear chains are more effective and degradable than branched chains and are, thus, used to a greater extent (Tadros, 2014). The most frequently occurring hydrophilic groups are carboxylates, sulfate, sulfonate, and phosphate (de Zubeldia et al., 2017).

Cationic surfactants mainly consist of a nitrogen cation and a monovalent anion, mostly chloride, as well as alkyl group residues (Backe et al., 2013; Zhi and Liu, 2018). They account for only 5–6% of the total surfactant production. Common classes of cationic surfactants are alkyl trimethyl ammonium chloride ($C_{12}H_{25}(CH_3)_3NCl$) and dialkyl dimethyl ammonium chloride (C_{16}–C_{18}) (Salager, 2002; Shah et al., 2012). In general, cationic surfactants are water soluble if only one alkyl group is attached (Bhat et al., 2008). With two or more alkyl chains, the surfactant becomes insoluble in water but remains soluble in organic solvents (Tadros, 2014). Under varying pH conditions, the cationic surfactants are stable in alkaline and acid environments (Benderrag et al., 2016; Hari et al., 2005). Their main property is the adsorption to negatively charged surfaces (Place and Field, 2012). This is used, e.g., to protect steel against corrosion, in flotation collectors for mineral ores, or as a conditioner in shampoos (Yahagi et al., 1991). The cationics are generally more expansive than anionics because of their high-pressure hydrogenation reaction used for their synthesis (Shah et al., 2012).

Nonionic surfactants mostly base on ethylene oxide, also called ethoxylated surfactants (Schick, 1966; Schick, 1987; Schonfeldt, 1970). There are several nonionic classes named alcohol ethoxylates, alkyl phenol ethoxylates, fatty acid ethoxylates, monoalkaolamide ethoxylates, sorbitan ester ethoxylates, fatty amine ethoxylates, and ethylene oxide copolymers (Sonia and Sharma, 2015; Tadros, 2014). The alkyl phenol ethoxylates are produced by an ethylene oxide reaction with alkyl phenol (Smith et al., 1966). These surfactants are very cheap and the most popular one is based on nonylphenol (Giger et al., 1984). Nonionics are good emulsification and dispersion agents with a high aqueous and nonaqueous solubility (Kim and Lee, 1994). The CMC of nonionics is much lower than that of anionics with the same chain length (Bhat et al., 2008).

The distinctiveness of the zwitterionic surfactants is the simultaneous appearance of both cationic and anionic groups (Buestein and Hilton, 1982). Most used zwitterionics are the N-alkyl betaines (derivates of trimethyl glycine). The main characteristics is the pH dependence. In acid solutions, the molecule is positively charged while becoming negative in alkaline conditions (Chavez et al., 1996). The isoelectric point of charge (IEP) is defined as the pH value at which the molecule shows equal ionization (Hilal et al., 1999). When the pH conditions change, the properties change as well, such as wetting, detergency and foaming (Tadros, 2014). At the IEP the properties of zwitterionics are equal to those of nonionics. Above and below this point the properties are shifted to cationics and anionics, respectively (Zimmermann et al., 2009). These surfactants are highly water soluble and compatible with other groups of surfactants, with which they can form mixed micelles (Backe et al., 2013). The surface activity, however, varies widely and is dependent on the distance between the charged groups. The maximum surface activity is reached at the IEP (Hilal et al., 1999; Zimmermann et al., 2009). Zwitterionics have very good dermatological properties as well as low eye irritation properties (Ridout, 1991). Therefore, these are often used in consumer products like shampoos or conditioners and other cosmetics (Sinclair et al., 2018).

The surfactants PFOA and NP investigated in this study belong to different groups of surfactants. PFOA and the second lead substance of the per- and polyfluoroalkylated substances (PFAS), perfluorooctane sulfonate acid (PFOS), belong to the anionic surfactants. There are also other PFAS compounds that belong to cationic (perfluoroctaneamido ammonium iodide, PFOAAmS) or zwitterionic surfactants (perfluorooctane amido betaine, PFOAB, 6:2 fluorotelomer sulfonamido betaine 6:2-FTAB) (Zhi and Liu, 2018). However, NP is one of the most predominant nonionic surfactants (Cheng et al., 2017).

PFAS and role of PFOA

The term PFAS indicates a group of anthropogenic surfactants which all have a perfluoroalkyl chain of varying length and a terminal functional group (Zaggia et al., 2016). The characteristic of those chemicals is the replacement of detached hydrogen atoms with fluorine atoms, which are responsible for the persistence in the environment (Wang and Shih, 2011). To the present state, more than 4700 individual PFAS substances are known (UBA, 2020).

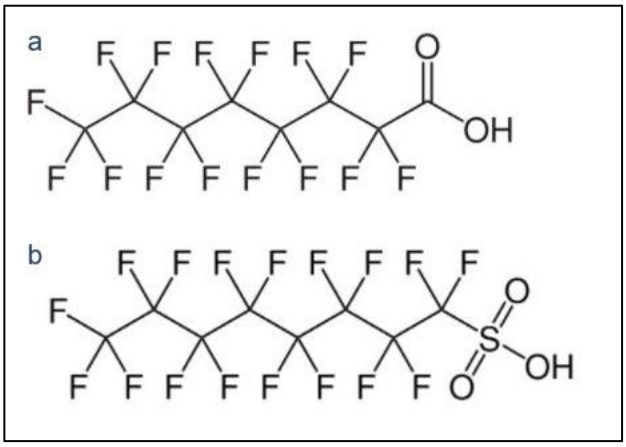

Fig. 1: Structural formula of the two lead PFAS substances (a) perfluorooctanoic acid (PFOA) and (b) perfluorooctane sulfonate acid (PFOS).

Long-chain PFAS (> C_6) are very persistent and bioaccumulative, and it is assumed, that they have toxic potentials (Campos Pereira et al., 2018; Wang et al., 2015b). Short-chain PFAS (< C_6) are also persistent, whereas toxic and bioaccumulative properties as well as soil adsorption are reduced. The lowered retention of short-chain PFAS in soils leads to rapid leaching into the groundwater (Brendel et al., 2018). Furthermore, they can hardly be removed from the water during waste water treatments and they can also be accumulated in edible parts of plants (Fujii et al., 2007; Szakova et al., 2019).

Only a high amount of energy can break the very stable fluorocarbon contained in all PFAS compounds. Under natural environmental conditions neither biotic (e.g. bacteria) nor abiotic (e.g. water, light) processes are able to decompose PFAS (Gredelj et al., 2020; UBA, 2020). If the surfactants are released, they are distributed in all environmental compartments like water, sediments, and soils (Rankin et al., 2016; Zhang et al., 2019a). Since, PFAS were found in isolated areas like the arctic, it raises the question of how the chemicals were able to reach those areas (MacInnis et al., 2019). It was found, that there are several precursors that have accumulated in the atmosphere, like fluorotelomer alcohols (FTOH) and perfluoroalkane sulfonamido (PFOSA) substances (MacInnis et al., 2017; Pickard et al., 2018). They are distributed globally through air currents on particles and metabolized into the long-lived perfluorocarboxylic acids (PFCA) and PFOS (Shoeib et al., 2006; Stock et al., 2007; Wong et al., 2018). These substances undergo atmospheric oxidation in regions with low NO_x:HO_2 ratios like the arctic. Furthermore, PFAS-containing aqueous firefighting foams (AFFF) in artic areas have increased the problem in the past (Skaar et al., 2019). The use of alternatives to PFAS is difficult, as their properties are unique. Possible alternatives are often associated with the loss of comfort or efficiency (Clarke and Smith, 2011; Coggan et al., 2019). Therefore, the prohibition of all PFAS cannot be scientifically substantiated at present. The hazard of the substances must be weighed up against the benefit to society. In general, the longer the carbon chains, the greater the probability that chemicals can be found in organisms (Awad et al., 2020; Shen et al., 2020). Thus, fluorochemical companies increasingly rely on shorter-chain fluorinated compounds with 4 to 6 carbon atoms, which are less incorporated by humans and animals (Bowman, 2015; Brendel et al., 2018; Buck et al., 2011). Even though the shorter-chain substances are less toxic, they are still persistent and even more mobile in the environment (Cousins et al., 2011; Wang et al., 2014). Hence, the shorter chain PFAS are also classified as environmentally hazardous substances (Gellrich et al., 2013; Llorca et al., 2012; Schwanz et al., 2016). So far, the use of several PFAS are restricted globally. In the United States, for example, manufactures were suspended to stop using the lead substances PFOA and PFOS as well as other related substances by the end of 2015 (OECD 15). Hence, PFOA, PFOS and four other PFAS were included in the US Environmental Protection Agency (USEPA) third Unregulated Contaminant Monitoring Rule (UCMR3) (USEPA, 2012). PFOS, its salts and perfluorooctane sulfonyl fluoride (PFOSF), have been listed in the Stockholm Convention on Persistent Organic Pollutants (POPs) under Annex B (SC, 2019). PFOA, its salts and C_9 to C_{14}-based PFCAs are listed in the Candidate List of Substances of Very High Concern in Europe under Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) (Wong et al., 2018). Among others, PFOA was listed in the Stockholm Convention in Annex A in 2019 (Choi et al., 2017; Kwak et al., 2020).

Due to the widespread use of the lead PFAS substance PFOA in the past, the surfactant can be found ubiquitous in the environment (Ahrens et al., 2011; Richardson and Kimura, 2016; Urtiaga et al., 2015). The molecular structure of PFOA ($C_8HF_{15}O_2$) shows a hydrophobic alkyl chain with a functional carboxyl group, which makes PFOA highly surface active, thermally stable, and resistant to biodegradation under both acidic and alkaline conditions (Zhu et al., 2014).

Sources of PFAS

Numerous products such as Teflon® or Silverstone® are brand names in which PFASs are contained. Their unique properties make them very popular therefore, they can be found in many commonplace products (UBA, 2020).

PFOA has been produced since the 1950s (Zhao et al., 2015) and was, due to its exceptional surface-active properties, popular in several industrial products such as firefighting foams, photolithography, pesticides, or semiconductors (Fujii et al., 2007; Schaider et al., 2014; Skaar et al., 2019). It was also popular in consumer products such as shampoos, surface coatings for carpets, stain repellents for furniture, and paper as well as textile products (Giesy and Kannan, 2001; Lin et al., 2016; Milinovic et al., 2015b). Furthermore, PFOA is released to the environment through the degradation of precursors (Boulanger et al., 2004; Lindstorm et al., 2011; Yu et al., 2009).

One of those precursors is Fluorotelomer alcohol (8:2 FTOH, C_{10}-F_{17}). Microbial activity in soils can decompose the contaminant into PFOA. FTOH and other PFAS are processed into surface-active chemicals which are used as synthetic fiber coatings (Richardson and Kimura, 2016). These can be used for textiles, paper and refine building products by making them water-, grease or dirt repellent (Ahrens et al., 2010). The textiles are mainly used for outdoors ports and industrial safety textiles, seat covers as well as carpets. PFASs are also found in polishes, waxes, all-purpose cleaners, window cleaners, and impregnation sprays (Kotthoff et al., 2015). Furthermore, they are used in the production of colors and adhesives (Ahrens et al., 2010; Dreyer and Ebinghaus, 2009; Ishibashi et al., 2008a) and it is estimated, that the annual global FTOH production exceeds 11 tons (UBA, 2020).

Another source for PFOA in the environment is fluoropolymer polytetrafluorethylene (PTFE, C_2-F_4). PFOA is needed to produce PTFE and is therefore enhanced as tracs in the final products (Gebbink and van Leeuwen, 2020; Zhang et al., 2019b). PFTE repels materials, hence it has been used since the 1950s in pans as a nonstick coating (Zhang et al., 2019a). It also coats seals because of its low roughness. In electrical engineering, PTFE is a popular material for cable sheathing. Applications can also be found in aviation, military, and medical technology (implants), in optics (lenses) and coating of laboratory equipment (Aleksandrov et al., 2019; Wang et al., 2015b). A widespread use of PTFE and other fluoropolymers is common as a breathable membrane in rain ware and functional clothing (Henry et al., 2018).

Human health risk

The widespread presence of PFAS is problematic because it poses several risks to human health. The surfactants are usually taken up by humans through food, drinks, and air (Kvalem et al., 2020). Since PFOA and PFOS have shown endocrine disruption potentials in animal studies, a similar effect for humans cannot be excluded (Villanger et al., 2020). PFASs are not metabolized in the human body and are accumulated mainly on proteins in blood, liver, and kidney (Kennedy et al., 2004; Lau et al., 2007). They can induce tumors of the testicles, liver, and pancreas, found out in studies with rodents (Biegel et al., 2001).

The transmission of PFAS from mother to child during pregnancy and lactation and the slow elimination of long-chain PFAS from the human body are particularly critical (Abraham et al., 2020; Das et al., 2008; Rylander et al., 2020). Epidemiology studies suggest, that surfactants may cause a decreased antibody response to vaccinations. Furthermore, an accumulation of PFOA and PFOS, in the human body may increase susceptibility to infection (Castano-Ortiz et al., 2019). There is also clear evidence of an association between exposure to PFOS, PFOA and PFNA and elevated serum levels of cholesterol (Schlezinger et al., 2020; Shen et al., 2020). Also, a correlation between the pollutant exposition and lower birth weight was found in an epidemiological study (Mamsen et al., 2019; Rylander et al., 2020). All those studies were based on animal studies. In contrast to animal studies, epidemiological studies show insufficient evidence for associations between exposure to PFAS and neurological development, thyroid function, or an increased risk of cancer (IARC, 2017; Schrenk et al., 2020).

The reproductive toxic effects of PFOS and PFOA are undisputed in animal experiments. But effective dosages are very high. The values measured in human blood are several orders of magnitude below the concentrations effective in animal experiments (Godduhn and Duffy, 2003b; Ishibashi et al., 2008a; UBA, 2020).

However, it has been concluded several times, that PFASs are likely to be carcinogenic for humans as well (EPA, 2006; Fair et al., 2012; Giesy et al., 2009). For example, they were found in blood and breastmilk (Jian et al., 2018) and embryonic and fetal organs (Mamsen et al., 2019). Nonetheless, further studies are needed to better estimate the specific impacts of PFAS to human health.

PFOA distribution in the environment

Due to its widespread use, PFOA is found ubiquitous in river water, oceans, sediments, dust, soil, and tissues of wildlife and humans and even in the deep oceans and in the arctic snow

(Ahrens et al., 2010; Gonzalez-Gaya et al., 2019; MacInnis et al., 2019). According to Fromme et al. (2009), PFOA can be found in food products. In contrast to other POPs however, PFOA is highly water soluble; thus, it is easily transported in aquatic environments (Prevedouros et al., 2006; Richardson and Kimura, 2016). At the same time, both the hydrophobic chain and the hydrophilic functional group of PFOA provides opportunities to adsorb onto surfaces of several environmental solid matrices (Wang et al., 2011).

Atmosphere

Current studies show that PFOA precursors are distributed globally by air currents (Wong 18), so they are able to reach even remote areas like the arctic (Joerss et al., 2020; MacInnis et al., 2019). The precursor substances are metabolized and converted into the long living PFOA. Barber et al. (2007) found a decrease in PFOA pollution in the atmosphere with increasing distance to the European coast. PFOA air concentrations varied between 1.4–6.9 pg m^{-3} while concentrations in the UK ranged between 3.1–828 pg m^{-3}, showing a drastic decrease of PFOA pollution in the Arctic regions.

Another problematic air pollution with PFOA was found in interiors of residential and office buildings. Concentrations of 0.2–152 ng m^{-3} of the precursor substance FTOH have been measured in indoor air. These are 30 to 570 times higher than in outdoor air. Possible sources are evaporation from dirt-repellent carpets or other products containing PFAS (Langer et al., 2010).

Water

The highly water-soluble PFOA reaches water bodies mainly through surface runoff in which it is transported until reaching oceans as far as the deep sea and the arctic (Ahrens et al., 2015; Choi et al., 2017; Yamashita et al., 2005). The surfactant was globally detected in most rivers and lakes (Allinson et al., 2019). In places where the chemicals are produced, processed, or used, waterbodies are more polluted (Dai and Zeng, 2019; Liu et al., 2019). This phenomenon is mostly found in industrial countries, e.g., in the bay of Tokyo. The water in the bay exhibits up to 4000 times higher PFAS concentrations in comparison to the Pacific Ocean (Masunaga and Zushi, 2016). A similar distribution was observed in Germany. The highest amount of PFAS in the North and Baltic Sea was found in the Elbe estuary close to Stade. Main sources of the surfactants were household derived sewage water (Theobald et al., 2007). However, the contamination of drinking water is most worrying. In Germany, high PFOA contaminations of the Ruhr (affluent of the Rhine, up to 177 ng l^{-1}) and Moehne (affluent of the Ruhr, up to 7.1 ng l^{-1}) rivers were found in 2006 (Skutlarek et al., 2006) besides very high contaminations of the public water. The rivers Ruhr and Moehne are important sources of drinking water in this region (Holzer et al., 2008). The highest PFOA amount in drinking water was 519 ng l^{-1} in Arnsberg compared to the maximum PFOA concentration of 647 ng l^{-1} in the Moehne River. These finding initiated an extensive environmental monitoring program in the federal state of North Rhine-Westphalia (Arenholz et al., 2011). Sources of PFOA was mainly the illegal application of contaminated sewage sludge besides industrial production (Skutlarek et al., 2006). Nevertheless, not only the avulsion of polluted soils is imperiling public water. PFOA can be transported into the groundwater by percolation through soils or bank filtration. This was proven by studies in the U.S. in near distance to fluorochemical industries (Emery et al., 2019).

However, high PFOA contaminations in natural waters are the exception. In Germany PFAS concentrations are ranging in one to two-digit ng l^{-1} regions, which are concentrations below the precautionary value of Germany (0.1 µg l^{-1}). High amounts of PFOA in waterbodies are usually temporal phenomena and a result of local pollution (Langer and Brauch, 2008).

PFOA in soils

PFOA was found in high amounts in soils in the past. Contaminations of up to 130 µg kg^{-1} were reported (Choi et al., 2017; Zhu and Kannan, 2019). Furthermore, Brusseau et al. (2020) found PFOA concentrations between 0.07 µg kg^{-1}–50 mg kg^{-1}. They investigated over 2,500 sites in more than 30,000 soil samples of all continents and found PFAS contaminations in almost every site tested. Maximum concentrations were found for PFOS (up to 373 mg kg^{-1}) and PFOA, leading to the assumption that soils are an important sink for this substance (Knight et al., 2019).

PFOA is generally deposited in soils by the application of nutrient-rich sewage sludge on arable soils (Gomez-Canela et al., 2012; Hyde, 1976). Waste water treatment plants (WWTP) have limited efficiency in removing PFOA and other PFAS from aqueous waste streams (Boulanger et al., 2005) and are accumulated in the sludge or are discharged with the partially clarified water to the surrounding rivers (Clara et al., 2008; Huset et al., 2008; Ma and Shih, 2010). Furthermore, the surfactants can be washed into the groundwater, surface water or be incorporated into plants (Clarke and Smith, 2011; Kwak et al., 2020). In the EU, PFASs are not regulated in sludge, among other organic contaminants (Gomez-Canela et al., 2012). In two german federal states, however, a summary threshold for PFAS of 100 µg kg^{-1} in sludge was established and it is recommended, that this threshold should be extended nation wide (Gomez-Canela et al., 2012; UBA, 2020).

The remediation of polluted soils is difficult and only a few methods are currently recommended, like stabilization technologies (Das et al., 2013; Hale et al., 2017; McGregor, 2018), electrodialytical remediation (Sorengard et al., 2019), and phytoremediation (Gobelius et al., 2017). However, the stabilization of polluted sites does not provide a long-term solution and phytoremediation is a slow and interminable process (Ross et al., 2018). Protecting the soil and other environmental compartments from such contamination is therefore a high priority (Sorengard et al., 2020).

Microbial decomposition of PFOA in soils

The stable physical and chemical properties of the C-F bounds of PFOA inhibits the degradation of the POP by conventinoal methods and under natutal conditions (Lee et al., 2017; Liu et al., 2017). It is possible to degrade PFOA completely in anaerobic reactors. However, this process requires high temperatures (> 1000 °C) and much time (> 25 d) (Meesters and Schroder, 2004; Parsons et al., 2008). Furthermore, there are some ways to partially degrad PFOA under specific conditions like advanced oxidation technology (Trojanowicz et al., 2018), electrochemical decomposition (Ma et al., 2015), photodecomposition (Wang and Zhang, 2016), and adsorption (Li and Zhang, 2014; Tandjaoui et al., 2019). However, these methods are not appropriate for the PFOA treatment since they need a lot of energy and can generate secondary pollutants (Yi et al., 2019).

The degradation of PFOA under mundane temperature and pressure is essential. Bioremediation is a technique to degraded pollutants environmental-friendly (Yi et al., 2019). The biodegradation of PFAS was only reported in a few studies so far (Liu and Avendano, 2013). Wang et al. (2009) investigated bacterial strains for the degradation of 8:2 fluorotelomer alcohol (8:2 FTOH), Liu et al. (2010) studied 6:2 flurotelomer alcohol (6:2 FTOH), Wang et al. (2011) 6:2 fluorotelomer sulfonate (6:2-FTS), and Rhoads et al. (2008) N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE). Only Yi et al. (2016) studied bacterial strains that were able to decompose PFOA. They found a PFOA-degradating strain in soils near a PFOA production factory. The strain was identified as *Pseudomonas parafulva,* a Gram-negative bacterium (Uchino et al., 2001). Under ideal conditions (30 °C, pH 7, 2% inoculum and initial PFOA concentration of 1000 mg l^{-1}) the degradation rate was 32.4% after 96 h. By adding 1 g l^{-1} glucose the degradation rate was increased by 15.7%. However, the PFOA-degrading strains have long degradation cycles, low efficiency, and are not able to decompose PFOA completeley (Yi et al., 2019). Thus, they are not able to decompose PFOA in the increasing demand. Therefore, further studies are needed to understand the mechanisms of these strains by a thorough analysis of the metabolic intermediates and products as well as the identification of PFOA-degradating genes. Thus, bioremidiation techniques could be improved and it would be possible to rehabilitate PFOA contaminated soils.

Sorption and desorption properties of PFOA in soils

Since PFOA is not metabolized under natural conditions, the distribution in the environment is mainly dominated by sorption and desorption properties of the surfactant (Fromme et al., 2009; Houde et al., 2006; Milinovic et al., 2015b).

The initial adsorption of PFOA in soils is a rapid process which is reversible (Bollag et al., 1992; Northcott and Jones, 2000). It is followed by slow absorption (several months) (Chen and Huang, 2011; Li et al., 2018b; Zhang et al., 2013). The sorption properties and mechanisms of selected per- and polyfluorinated surfactants on soils and sediments have been investigated in numerous studies (Li et al., 2019; Mejia-Avendano et al., 2020; Zhang et al., 2019b). Influences on the sorption of PFOA to soils result both from the physicochemical properties of the surfactant and those of the soil (Enevoldson and Juhler, 2010; Zareitalabat et al., 2013). Relevant properties are the organic carbon content (SOC), the hydrophobicity index (HI), the soil mineralogy, and the soil pH (Krafft and Riess, 2007; Oliver et al., 2019; Qian et al., 2017). The pore volume and pore diameter can also influence sorption, since PFOA is a relatively large molecule, which can also bind to soils mechanically (Arcadis, 2018).

It should be noted that the sorption behavior is strongly dependent on the respective SOC content and the soil pH. In topsoils with high SOC contents (Blume et al., 2013; Liang et al., 2019), the hydrophobicity of the pollutants determines the sorption behavior if the pH value remains under a threshold of 5.5 (Li et al., 2018b; Oliver et al., 2020). Due to the weaker protonation with increasing pH values the physio-chemical properties of PFOA change from hydrophobic interactions with the organic matter to electrostatic interactions with charged soil particles such as clay minerals or iron oxides (Oliver et al., 2019; Tang et al., 2010). In general, the sorption of anionic, organic contaminants is increasing with decreasing pH values and by an increase in solution cation concentrations (Jafvert, 1990). Several studies confirmed the described connections for PFAS (Chen et al., 2009; Zhang et al., 2013). However, the correlation between PFOA sorption and an increased cation concentration was only determined for bivalent and trivalent cations such as Ca^{2+}, Mg^{2+} and Fe^{3+}. The influence of monovalent cations like Na^{+} and K^{+} could not be confirmed (Higgins and Luthy, 2006; Wang et al., 2015b).

However, under natural pH values soil organic matter (SOM) is negatively charged because of the presence of dissociated carboxylic and phenolic acid groups (Kinniburgh et al., 1999; Wen et al., 2020). In soils where SOM is present, the sorption potential is increased (Ahrens et al., 2011; Milinovic et al., 2015b). This can be understood in terms of a reduced negative electrostatic potential of SOM caused by cation complexation (Campos Pereira et al., 2018; Higgins et al., 2005; Higgins and Luthy, 2006). Nonetheless, if the carbon content decreases, the influence of SOC on the sorption behavior also decreases (Campos Pereira et al., 2018).

The PFOA sorption potential was determined in several studies. Up to now, average PFOA distribution coefficients (K_D) of 0.12–70.8 l kg^{-1} in soil have been determined, which corresponds to log (K_D) values between –0.92–1.85 (Ahrens et al., 2011; Kwadijk et al., 2010; Milinovic et al., 2015b). Furthermore, Knight et al. (2019) investigated the sorption potential of ^{14}C-PFOA on 100 different soils and found partitioning coefficient values (log (K_D)) between –0.22–17. In 28 tropical soils, Oliver et al. (2020) found log (K_D) values between –0.9–0.69 while Li et al. (2012) analyzed 6 different river sediments with log (K_D) values between –0.9–0.62. These partitioning coefficients indicate that the sorption of PFOA is weak.

In order to estimate the distribution of PFOA in the environment, the desorption behavior is also important, in addition to the knowledge of the sorption behavior of the surfactant. So far, there is only one study that has dealt with desorption of PFOA in soils. Milinovic et al. (2015b) extracted PFOA and PFOS with a background solution consisted of 0.01 mol l^{-1} $CaCl_2$ and 0.002 mol l^{-1} NaN_3. The results showed desorption percentages for PFOA between 24–58% while PFOS was less extractable (< 13%). Due to the low sorption rates and desorption behavior of PFOA, it can be concluded that the surfactant is highly mobile in soils (Wang et al., 2013; Xiang et al., 2018).

However, there is a lack of knowledge about whether there is a threshold of the SOC content under which it does not play a role in the sorption of PFOA, even in soils with low pH values. Furthermore, the data basis for the desorption behavior of PFOA is not sufficient enough to enable generally valid statements. However, these are necessary to improve risk assessments. In addition, the desorption behavior of PFOA in aged soils remains unresearched.

Nonylphenol and nonylphenol ethoxylates

The chemical groups Nonylphenols (NPs) and nonylphenol ethoxylates (NPEOs) contain in the family of alkyl phenols (AP) and alkyl phenol ethoxylates (APEO), respectively (Shao et al., 2005). NP is the primary degradation product of the NPEOs in wastewater treatments (Xie et al., 2017), which are the most commonly used nonionic surfactants (Huang et al., 2016; Moreira et al., 2015; Wang et al., 2017).

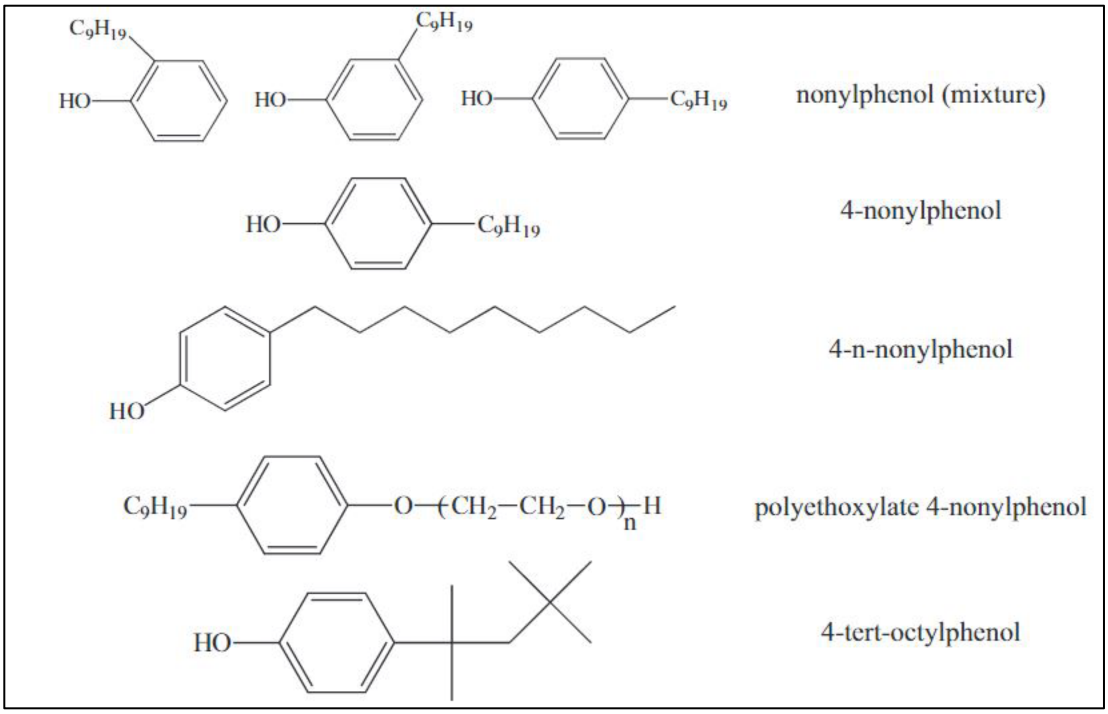

Fig. 2: Structural formula of selected alkylphenols (Priac et al., 2017).

Generally, NPs have a phenolic ring to which a nine-carbon alkyl chain is attached (Mtibaa et al., 2020; Shchegolikhina and Marschner, 2013) (Fig. 2). Differences between various NPs occur by the position of the alkyl chain in the phenolic ring and structure of the alkyl chain (linear or branched) (de Weert et al., 2008; Li et al., 2012). The alkyl chain position in the ring can be either in the para (4)- or ortho (2)- position (Mtibaa et al., 2020). In dependence on the branch pattern and position of the side chain on the ring, NPs have different estrogenic effects. The technical NP (branched, CAS number 84852-15-3) is the most common NP and consists of a mixture of the different isomers (Gabriel et al., 2012). The surfactants 4-nonylphenol (4-

NP) as well as 4-tert-octlyphenol (4-OP) are both substances of the AP group (Ademollo et al., 2008; Loos et al., 2008). Those pollutants are known to have endocrine disrupting potentials and it was found out that they disturb the hormone system of fish (Ferrara et al., 2008; Isobe et al., 2001). The estrogen receptor is responsible for the endocrine effect (Janer and Porte, 2007; Lafont and Mathieu, 2007; Porte et al., 2006). It is possible, that other APs also act estrogenic due to their similar molecular structure. Thus, the EU included 4-NP (branched and linear) the REACH list of candidates in 2012 (Gries et al., 2019). The REACH decree was established to improve the protection of human health and the environment from the risks posed by chemicals while increasing the competitiveness of the EU chemical industry (ECHA, 2013). 4-NP and 4-OP are highly hydrophobic molecules since the pK_a of 10.7–10.3 shows that ionization will only occur under alkaline condition (Düring et al., 2002). NPEOs embrace about 80% of all APEO substances, while the remaining 20% are made up by the group of ethoxylated octylphenols (OPEOs) (Ruczynska et al., 2020).

Production of NP and NPEO in the past

Nonionic surfactants are commonly used as detergents, emulsifiers, solubilizers, wetting agents, and dispersants (David et al., 2009). The most disposed nonionic is NP (Huang et al., 2016; Moreira et al., 2015; Wang et al., 2017). NPs and other APs are important chemicals for the production of phenolic resins and ethoxylates. Those are needed to produce surfactants (Wan et al., 2013). NP is produced since the 1950s and was used in industry, agriculture, and household products (Ruczynska et al., 2020). In 1997, the worldwide production of APOS was estimated at 500,000 t (Renner, 1997; Ying, 2006) and the production of NP was about 73,500 t in Europe (Ruczynska et al., 2020). Between 1997, and 2010 the production of NP decreased about 24,000 t in Europe because of the classification as a priority substance from the European Water Framework Directive (WFD) (Loos et al., 2008; Ruczynska et al., 2020). The approximately 30,000 t NP were used for the production of NPEOs (60%), for resin, plastic, and stabilizer production (37%) and for phenolic oxime production (3%) (ECHA, 2013; Lassen et al., 2013). In addition, OP was also produced in large quantities in the past. In 2011, e.g., the annual production in Europe amounted to 23,000 t. The surfactant is used as a domestic detergent, dispersing agent, and industrial as well as institutional cleaner (Berryman et al., 2004; Shao et al., 2005).

Even though NP and OP showed toxic effects to marine and freshwater species (Comber et al., 1993; McLeese et al., 1981) and endocrine disrupting effects to mammals (Moreira et al., 2015; Roberts et al., 2006b), the use of the surfactants is stilled allowed in paints and varnishes as well as for the production of polymers and adhesives (Setiyanto et al., 2018).

In the environment NPs mainly originate from the degradation of NPEOs (David et al., 2009). The sources of NPEOs are insufficiently cleaned sewage and industrial wastewaters (Ying et al., 2002). More than 60% of the produced NPEOs enter the environment via these pathways (Wang et al., 2017).

Human health risk

The surfactant NP is currently of environmental concern because of its toxicity, endocrine disruption potential and widespread contamination and persistence (Ho and Watanabe, 2018). It has adverse effects on the reproduction, immune, and central nervous system of wildlife and humans (Kim et al., 2006; Mao et al., 2011; Razia et al., 2006). Since NP has an endocrine disrupting and carcinogenic potential (Roberts et al., 2006a), it was included in the priority hazardous substance list of the European Union (Liao et al., 2014). The prohibition of the use of NP is currently not a global restriction, since it is still allowed in some countries (e.g., the United States) (Li et al., 2018b). It is possible that other APs with similar molecular structures also have endocrine disrupting potentials (Gabriel et al., 2008). The endocrine disruption potential of NP is higher than that of bisphenol A which is a well-known endocrine disruptor (Laws et al., 2000).

Shao et al. (2005) found a connection between the exposition of fish to NP and malformation of the sexual organs which in turn can affect the reproduction. The exposition to higher concentrations over a long time period can furthermore lead to an extinction of male fish. The estrogenic effect can interact in vitro and in vivo (Kwack et al., 2002) and interferes with the estrous cycle and pubertal onset in rats (Kim et al., 2002; Laws et al., 2000). Animal studies also suggest that NP interferes with morphologic and behavioral functions that are related to reproduction (Calafat et al., 2005).

There are a lot of routes of human exposure to NP, but the most important sources are food and drinking water (Li et al., 2010b). Guenther et al. (2002) and Lu et al. (2007) showed, that NP can be found ubiquitous in food products. The main source was polyvinyl chloride (PVC) films which are used for food packaging. 4-NP is able to migrate from these films into the food products (Inoue et al., 2001; Loyo-Rosales et al., 2004). Calafat et al. (2005) investigated human urine samples of 394 adults from the USA and found NP in concentrations above 0.1 $\mu g\ l^{-1}$ in 51% of the samples.

Ademollo et al. (2008) found a connection between fish consumption and NP accumulation in breast milk. High concentrations of the surfactant were found in Italian Seafood (Ferrara et al., 2008; Ferrara et al., 2005). Up to 400–1400 $ng\ g^{-1}$ fresh weight was found in crustaceans and fish respectively. In aqueous environments, even low concentrations within the scale of $\mu g\ l^{-1}$ are sufficient to have a toxic effect (Hemmer et al., 2001; Ying et al., 2002).

Zala and Penn (2004) analyzed several endocrine disruption chemicals (EDCs) and found not only harmful effects on the reproduction but also on learning, aggression, communication, motivation, and activity of humans, since these behaviors are under hormonal control. Studies with Mexican and Dutch children proved these thesis (Guillette, 2000; Vreugdenhil et al., 2002).

NP Fate in the environment

The main source of NP in the environment is the release of NPEOs with sewage treatment works. The NPEOs degraded into several by-products of which one is NP (Soares et al., 2008). NP can be found in several environmental compartments like sediments (more than 60%), soils (10%), the water phase (25%) and biota (Isobe et al., 2001; NCM, 1996; Wang et al., 2019). The widespread distribution is a result of the application of anaerobically digested sewage sludge (Ahel et al., 1994a; Giger et al., 1984; Metcalfe et al., 2001), industrial wastewater, agriculture runoffs, and landfill leachates (Ho and Watanabe, 2018; Tri et al., 2016). In addition, the application on soils is also a result of atmospheric deposition (Dachs et al., 1999; Lyons et al., 2014; Xie et al., 2006) or by leaching from the final products (Guenther et al., 2002; Maguire, 1999; Staples et al., 1998). Due to its physicochemical properties such as low water solubility (max. 4.97 mg l^{-1}) and high hydrophobicity (log (K_{OW}) 4.48) (Brix et al., 2001; Roberts et al., 2006b; Szakova et al., 2019), NP accumulates in compartments with a high organic content like sewage sludge or river sediments (Barber et al., 1988; Soares et al., 2008).

Atmosphere

NP is matured from the atmosphere by wet deposition to aqueous systems or sediments (Fries and Puttmann, 2004). Concentrations between 2.2–70 ng m^{-3} NP were found in the atmosphere which exceeded concentrations of polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) (Dachs et al., 1999). Highest concentrations of NP were found in the surroundings of WWTP (Cincinelli et al., 2003). Since NP is deposited from the atmosphere by wet deposition it can be found in rainwater (0.06–0.54 µg dm^{-3}) and snow (0.24–0.48 µg dm^{-3}) as found in a German and Belgian study (Fries and Puttmann, 2004; Soares et al., 2008)).

Water

In the hydrosphere NP is degradable through photolysis in the upper layers of rivers and lakes (Ahel et al., 1994a), but in soils and sediments the estimated half-lives are more than 60 years (Shang et al., 1999).

Ahel et al. (1994b) analyzed the release of NPEO compounds with sewage treated water and found, that more than 60% were released into the environment. NP accounted for 25% of the total release and was mainly sorbed to sludge. The contamination of NP in river waters was also analyzed in several studies (Hale et al., 2000; Sabik et al., 2003; Wu et al., 2007) and they found concentrations of NP varying between 0.7 ng l^{-1} and 15 µg l^{-1} (Bester et al., 2001; Petrovic et al., 2002) whereas contaminations in summer were significantly higher than in winter. This can be explained by higher microbial activity in the warmer months, which leads to greater decomposition of NPEOs (Kuch and Ballschmiter, 2001; Li et al., 2004). The surfactant was found globally in surface waters, but the concentrations in sediments and soils were always higher than in the aquatic environments (Azevedo et al., 2001).

NP in soils

Similar to atmospheric and water pollution with NP, contaminations in soils are closely linked to anthropogenic activities. Sewage sludge application, landfilling, and accidental spillage are mainly responsible for soil pollution (Vikelsoe et al., 2002). Another important source for NP in soils is the application of pesticides (Careghini et al., 2015; Chang et al., 2007). When soils are fertilized with sewage sludge, increased NP concentrations can be detected. In the EU the use of recycled sludge varies widely. Some member states like Denmark, Spain, France, Ireland, and the UK used more than 50% of the generated sludge for agricultural applications during the 2003-2006 period. Other states like Finland (< 5%), Greece or Netherlands (0%) used significantly less sludge as a fertilizer for agricultural purposes (Kelessidis and Stasinakis, 2012; Milinovic et al., 2015a). The directive 86/278/ECC regulates the maximum concentrations of pollutants for sludge or sludge-treated soils. There are thresholds for inorganic and organic contaminants. A sum limit for NP and NPEOs of 450 mg kg^{-1} was set in 2010 (Milieu Ltd, 2010). Compared to soils treated with conventional fertilizers, the NP concentration is raised by 1.6 mg kg^{-1} on average (Soares et al., 2008) in soils that were treated with sewage sludge. Once NP has entered the soil it is affected by numerous factors. On the one hand it can be decomposed by microorganisms. Oxygen was found to be the limiting factor for this decomposition. On the other hand, the surfactant can adsorb to the soil or undergo evaporation (Hesselsoe et al., 2001; Topp and Starratt, 2000). But the evaporation of NP from soils is not significant, since only 0.22% of 1 g NP kg^{-1} of soil was vaporized over 40 days (Trocme et al., 1988).

However, if NPEOs enter the soil solid phase, a high amount of these compounds degrades to NP. This is resulting in high contaminations of up to 1 g NP kg^{-1} soil which can reach aquifers (Choi et al., 2017; Jiang et al., 2018; Montgomery-Brown et al., 2003).

Microbial decomposition of NP in soils

In soils the microbial decomposition of NP is possible, but it is limited by oxygen supply (Hesselsoe et al., 2001; Topp and Starratt, 2000) and bioavailability (Bosma et al., 1997; Kelsey et al., 1997). The degradation of the surfactant requires a tolerance of the micro flora for the toxicity of NP (Ahmed et al., 2001; Saagua et al., 2002; Soares et al., 2003). Generally, the linear NP can be better degraded in soils than the branched isomer. The higher the temperatures in the soil and the more oxygen is available, the faster the decomposition processes (Marcomini et al., 1989; Topp and Starratt, 2000). The degradation of NP is a rapid process especially in sludge-amended soil (Corvini et al., 2004). Another decomposer in soils is the white rot fungi which can degraded up to 99% of the initial NP concentration (100 mg l^{-1}) in 25 days (Corvini et al., 2004; Soares et al., 2005). The authors found no decomposition activity of the fungi at temperatures below 4 °C even though the fungi can grow at these temperatures. Because of the high NP concentrations in soils, the toxicity can affect the microorganisms to such an extent that the surfactant becomes persistent (Kollmann et al., 2003).

Despite the environmental effects on biodegradation like temperature and oxygen supply, also the molecular structure plays an important role for degradation (Gabriel et al., 2005). Gabriel et al. (2008) investigated 18 different NP isomers on their biodegradability. More than 61% of the isomers were degraded within 9 days by 80% of the initial concentration. Other isomers were only removed by 30% in the same time. However, since they only used a selection of microorganisms and soils provide numerous microbial communities biodegradation selectivity may be less straightforward than in this experiment (Lu and Gan, 2014).

Sorption and desorption properties of NP in soils

Like PFAS, the sorption of NP in soil is divided in two phases. The initial adsorption is a rapid process which is reversible. It is followed by a process of slow absorption for several month or even years (Northcott and Jones, 2000). The sorption of NP is very strong, which reduces their biodegradability, mobility, and volatilization (Northcott and Jones, 2000; Semple et al., 2003). The longer the surfactant is sorbed to the soil, the lower the desorption ability, since the composition and structure of NP changes with time (Puglisi et al., 2007; Scow et al., 1995; Tang et al., 1998). The formation can furthermore lead to a reduced bioavailability (Senesi, 1992).

The sorption of NP in soils is mainly controlled by the organic carbon content (Höllrigl-Rosta et al., 2003; Ying and Kookana, 2005). The interactions between the surfactant and the OC are regulated by diffusion and are not completely reversible (Düring et al., 2002). If soil pH values reach the pk_a level, a stronger sorption is often observed due to a high rotation resulting in an increased interaction with the soil matrix (Höllrigl-Rosta et al., 2003).

Several studies investigated the sorption behavior of NP in soils (Jiang et al., 2018; Liao et al., 2014; Milinovic et al., 2015a). Düring et al. (2002) studied the sorption/desorption behavior of NP to 52 different soils using a batch equilibrium approach. The observed K_D values ranged between 8.52–215.65 ml g^{-1}. Also, Milinovic et al. (2015a) studied the partition behavior of NP between water and the solid matrix of five different soils with K_D values varying between 24-1059 ml g^{-1}. Similar coefficients were found in study's by Wang et al. (2019), Ying and Kookana (2005) and Liao et al. (2014) which confirms the assumption that the sorption of NP to soil is very strong. Highest correlations were found between NP and the SOC content in topsoils. Since desorption experiments showed that the sorption of NP is irreversible, the migration of the surfactant in deeper soil layers is limited (Liao et al., 2014; Milinovic et al., 2015a). This was also proven by Vogel et al. (2000) who found almost 99% of the surfactant after 730 days within the first 30 cm of the soil surface. Nonetheless, these studies investigated the sorption behavior of NP on a limited number of soils. In order to ensure a generalization of the results, the experiments would have to be carried out on as many soils with different properties as possible

Objectives and outlines of the thesis

The environmental fate of the surfactants PFOA and NP in soils are based on their sorption and desorption behavior, since they are not or not fully metabolized by microorganisms or other environmental impacts. However, as outlined above, the mechanisms of these processes are not fully understood so far, especially in soils with low SOC contents. As soils are characterized by decreasing SOC contents with depth, the adsorption processes are essential to describe the distribution of the contaminants in the entire soil and their release to groundwater basins. Recent studies examined the sorption behavior of NP and PFOA, but mainly in connection with water distribution or accumulation in sediments. Only a few studies analyzed the sorption behavior of the surfactants in soils with different physicochemical properties. Furthermore, the desorption behavior of PFOA was only described once (Milinovic et al., 2015b).

To gain a deeper understanding of the environmental fate of PFOA and NP and to improve risk assessments for areas of suspected contamination, this study was divided into three parts (Chapters 2 to 4), as described by the following:

- *In the first study*, the sorption behavior of PFOA and NP was analyzed on 96 soils from forest and agricultural sites. For this propose, batch equilibrium studies with spiked samples were performed for both surfactants on all soils. A special focus was set on the influence of decreasing SOC contents and qualities. To gain information about the SOC quality and hydrophobicity data from mid infrared spectroscopy (MIR) was used. Thus, it was possible to study the sorption behavior of the contaminants in dependence on the physicochemical properties of the soil in detail.
- *In the second study*, the desorption behavior of the same samples was investigated. Since the contamination of soils with pollutants is usually not detected immediately, it is particularly important not to determine the desorption

after some time. Therefore, the samples were stored for one year and the experiments were conducted on the aged samples. Since more than 30% NP was metabolized over the storage period, even though sodium azide was used to suppress microbial activities, the desorption results for this surfactant have not been further investigated.

- *In the third study*, the sorption and desorption behavior of PFOA was investigated on 38 agricultural soils. The previous studies showed, that not only the physicochemical properties of the soils but also the properties of the surfactant played an important role for sorption. Thus, soils with high pH values (5-7) were tested to investigate the electrostatic interactions of PFOA and the soil in more detail. Furthermore, the influence of temperature changes and variations in the leachate were tested on 11 soils in order to improve risk assessments.

The following chapters (Chapter 2 to 4) are closed papers, that have been published or will be submitted to reviewed journals. An overall discussion and conclusion with recommendations for further studies is given in the final chapter (Chapter 5).

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Chapter 2

Effects of soil organic carbon (SOC) content and accessibility in subsoils on the sorption processes of the model pollutants nonylphenol (4-n-NP) and perfluorooctanoic acid (PFOA)

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Science of the total Environment (2019), 672(1): 162-173

1. Introduction

In the past decade, stabilization mechanisms of soil organic matter (SOM) in subsoils became more important, since subsoils contribute more than half of the total soil organic carbon (SOC) stocks and are therefore highly relevant in the context of the global carbon cycle (Heitkotter et al., 2017; Rahman et al., 2018). A reduced SOC accessibility in subsoils through physical occlusion within aggregates or through association with minerals were discussed as important carbon sequestration mechanisms (Oades, 1993; Six et al., 2002; Wiesmeier et al., 2019). Most of these studies focused on the SOC accessibility within the subsoil in the context of SOC stabilization but reduced SOC inaccessibility may also affect pollutant sorption processes. Since subsoils also control the release of pollutants to groundwater systems (Isobe et al., 2001; Sepehrnia et al., 2018), the role of sorption processes of organic and hydrophobic pollutants to subsoil SOM are important in the context of risk assessment. Thus, this study aimed to understand the role of subsoil SOC on sorption processes of 4-*n*-nonylphenol (NP) and perfluorooctanoic acid (PFOA).

NP and PFOA were selected as model pollutants since they are known to be highly toxic and ubiquitously distributed in the environment (Liao et al., 2014; Yang et al., 2011; Zhu et al., 2014). NP is a metabolite of nonylphenolethoxylates (NPEO) and is characterized as an anionic surfactant with a linear and planar hydrocarbon structure. In most temperate soils, NP is a highly hydrophobic molecule, since the pK_a of 10.7 shows that ionization will only occur under alkaline condition (Düring et al., 2002). In the past, it was used as domestic detergents, dispersing agents, and industrial as well as institutional cleaners (Berryman et al., 2004; Shao et al., 2005). Thus, NP was often detected in different environmental media like water, sediments, sludge, biota, and soils (Heemken et al., 2001; Isobe et al., 2001). Since NP has an endocrine disrupting and carcinogenic potential (Roberts et al., 2006a), it is included in the priority hazardous substance list of the European Union (Liao et al., 2014).

Perfluorochemicals (PFC) are a group of chemicals, which are characterized by a fully fluorinated hydrophobic alkyl chain of varying length attached to different hydrophilic groups. Due to their strong F–C bonds they are highly resistant to degradation and thus are ubiquitously found in environmental compartments (Milinovic et al., 2015b; Zareitalabat et al., 2013). One of the main problematic substances within the PFT group is PFOA, since it shows a very high accumulation in the environment (Richardson and Kimura, 2016; Stahl et al., 2007; Urtiaga et al., 2015). PFOA is a bioaccumulative pollutant (Lin et al., 2016; Urtiaga et al., 2015; Zhu et al., 2014) and is potentially toxic to fresh water and marine mammals (Ishibashi et al., 2008b), as it is hormonally active (Godduhn and Duffy, 2003a). Furthermore, it has potential adverse effects for wildlife species (Fair et al., 2012; Giesy et al., 2010; Hoff et al., 2005). The molecular structure of PFOA shows a hydrophobic alkyl chain with a functional carboxyl group, which makes PFOA highly surface active, thermally stable, and resistant to biodegradation under both acidic and alkaline conditions (Zhu et al., 2014). Due to its exceptional surface-active properties, PFOA was popular in several industrial products such as firefighting foams, photolithography, pesticides, or semiconductors. It was also popular in consumer products such as shampoos, surface coatings for carpets, stain repellents for furniture, and paper and textile products (Giesy and Kannan, 2001; Lin et al., 2016; Milinovic et al., 2015b). Furthermore, PFOA is also released to the environment through the degradation of precursors (Boulanger et al., 2004; Lindstorm et al., 2011; Yu et al., 2009). Due to its widespread use, PFOA surfactants are found in river water, oceans, sediments, soil, and tissues of wildlife and humans (Ahrens et al., 2010; Chen et al., 2006; Dreyer and Ebinghaus, 2009). Currently, PFOA is included in the Stockholm Conventions list of persistent organic pollutants (Milinovic et al., 2015b) due to its endocrine disrupting as well as its carcinogenic potential.

In soils, maximum NP and PFOA concentration of up to 1 g kg^{-1} and 1.6 µg kg^{-1} were reported (Choi et al., 2017; Jiang et al., 2018) leading to the assumption that soils are an important sink for both substances. Thus, in terms of risk assessment, various studies focused on the sorption behavior of NP and PFOA to the solid soil phase. For example, Düring et al. (2002) studied the sorption/desorption behavior of NP to 52 different soil samples using a batch equilibrium approach. They observed K_D values ranging between 8.52–215.65 ml g^{-1}. Also, Milinovic et al. (2015a) studied the partition behavior of NP between water and the solid matrix of six different soils using batch experiments. According to Düring et al. (2002) K_D values for NP sorption varied between 24–1059 ml g^{-1}. Generally, high NP sorption potentials to the soil solid phase were related to the hydrophobic interaction between NP and SOC. So far, only few studies dealt with the interaction between PFOA and the solid soil phase (Ahrens et al., 2011; Chen et al., 2009; Higgins and Luthy, 2006). The PFOA sorption potential seemed to be lower compared to that of NP. For example, Milinovic et al. (2015b) determined the sorption of PFOA on six different soils and observed K_D values varying between 2.2–38 ml g^{-1}. They assumed that the hydrophobicity of PFOA controls the sorption in soils, since the K_D values correlated well with SOC. Furthermore, PFOA was found in leak and groundwater, which is triggered by the low sorption activity of the contaminant (Zareitalabat et al., 2013).

Although SOC was generally found to be an important factor for the sorption potential of both pollutants to soil samples, no study focused on the role of SOC in SOC depleted subsoil samples systematically. We assumed that in subsoils SOC is of minor relevance in context of pollutant sorption, since SOC will be less accessible due to its occlusion within aggregates or minerals. Consequently, SOC may not be used as a predictor variable for the retention potential of NP and PFOA in subsoil horizon.

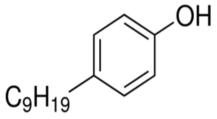
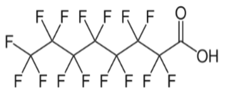
In order to better understand sorption mechanisms of NP and PFOA in soils with low SOC concentrations, we systematically evaluated and compared pollutant sorption in sub- and topsoil samples. In total 96 soil samples, were used for the batch experiments. In a first step, differences of NP and PFOA sorption between sub- and topsoil samples were identified and related to sorption mechanisms using multiple regression analyses. In a second step, we focused on the role of SOC for the NP and PFOA sorption potentials and processes in the subsoil samples. To assess the role of SOC inaccessibility in SOM mineral association, subsoil samples were differentiated in aggregated and not aggregated groups using spectral information of sieved and ground subsoil samples, respectively. In addition, SOC hydrophobicity as a function of the soil pH was analysed in its effect on NP and PFOA sorption to the subsoil samples.

2. Methods and Materials

2.1. Chemicals

For the sorption experiments, the two surfactants NP and PFOA were used as model pollutants. The two surfactants have very different structural properties but similar water solubility and K_{ow} values (Tab.1). The radioactive labeled chemicals were [ring–^{14}C(U)] 4-n-nonylphenol (specific activity of 1.85–2.22 GBq mmol^{-1} dissolved in ethanol) and [1–^{14}C] PFOA (specific activity 1.85–2.22 GBq mmol^{-1} solved in ethanol), purchased from Hartmann Analytic (Braunschweig, Germany) for analytical detection. All labeled chemicals had a purity of 99%. The unlabeled surfactants were purchased as powder from Sigma Aldrich (Munich, Germany) and dissolved in ethanol for further experimental processing.

Tab. 1: Physicochemical parameters of the selected contaminants.

Pollutant Properties	**4-n-nonylphenol (NP)**	**perfluorooctanoic acid (PFOA)**
		
Chemical formula	$C_{15}H_{2}4O$	$C_8HO_2F_{15}$
Molar mass (g mol^{-1})	220.4	414.1
Water solubility (g l^{-1})	5.43^1	9.5 (25°C)^2 / 3.4 (22°C)^3
Log K_d	$1.4\text{-}3.0^4$	$-1.9\text{-}1.2^{5,6,7}$
Log K_{ow}	4.48^1	4.59^4
pK_a	10.7^8	-0.5^2
CAS Number	104-40-5	335-67-1

[1]Ying et al. 2003, [2]Campbell et al. 2009, [3]Deng et al. 2012, [4]Milinovic et al. 2015, [5]Ferry et al. 2009, [6]Chen et al. 2013, [7]Li et al.2012 [8]Maguire 1999

2.2. Soil samples

A pool of 96 soil samples from agricultural and forest sites across North Rhine-Westphalia (NRW, Germany) was used. All samples were provided and previously analyzed by the Geological Survey NRW and the Institute for Soil Engineering, Water- and Waste-Management of the University of Wuppertal. For further processing, all samples were air-dried and sieved to less than 2 mm. For spectral analyses samples were finely ground.

Since different sorption mechanisms of PFOA and NP in topsoil and subsoil samples were expected, the soil samples were divided into a top- and subsoil data set for detailed analyses. Since we had incomplete information of the soil sampling depths, we used SOC as a variable to differentiate between a top- and subsoils, since subsoil samples are generally characterized by low SOC contents (Heinze et al., 2018b; Heitkotter et al., 2017). All samples with SOC contents of equal to or less than 0.5% were allocated to the “subsoil data set” and all samples with a SOC content of more than 0.5% were defined as “topsoil data set”. In total, the data set consisted of 54 top- and 42 subsoil samples, highly varying in chemical and physical properties (Tab. 2).

2.3. Sorption experiments

NP and PFOA sorption was determined using the batch equilibrium method (OECD, 2000). All batch experiments were performed in 15 ml centrifuge tubes. However, to avoid surfactants adsorption to tube surfaces, Pyrex® glass centrifuge tubes with phenolic screw caps and a PTFE-faced rubber liner were used for determining NP sorption (Sigma Aldrich, Germany). In contrast to that, PFOA sorption analysis were performed in 15 ml polystyrene tubes with a polystyrene screw cap (Thermo Fisher Scientific, Germany). To ensure sterile condition, all materials like spatula, centrifuge tubes, screw tops, and pipettes were rinsed with ethanol immediately prior to use.

For the batch assays, 0.5 g soil and 5 ml background solution (0.01 M $CaCl_2$ and 0.002 M NaN_3) were added to the centrifuge vials. NaN_3 was used to inhibit microbial activity throughout the batch experiments. Similar to Milinovic et al. (2015a), the solutions were then spiked with a mixture of unlabeled as well as ^{14}C-labeled NP or PFOA to achieve pollutant concentrations of 50, 150, 300, 600, and 1200 ng l^{-1} or 75, 100, 150, 200, and 300 ng l^{-1}, respectively. Controls without surfactants as well as blanks containing no soils were prepared in the same way. All samples were shaken end over end in the dark at a constant room temperature of 21 °C. According to various previous studies (Ahrens et al., 2011; Higgins and Luthy, 2006; Johnson et al., 2007), the equilibrium time was set to 24 h. After 24 h the samples were centrifuged at 3000 rpm for 30 min and the supernatant was then removed. For the determination of radioactivity in the solutions, 12 ml of scintillation cocktail (Ultima Gold, Perkin Elmer, Waltham, USA) was added to 2 ml of the supernatant and then analyzed by liquid scintillation counting with a Tri-Carb 2800TR (Perkin Elmer).

In order to describe the mechanism of pollutant sorption to the soils, the data obtained from the sorption experiments was fitted to linear isotherms (Fig. 1). Based on the linear isotherms, the K_D value as the ratio between equilibrium concentration in the soil matrix and that of its aqueous phase solution were calculated according to equation 1:

$$K_D = C_s / C_w \tag{1}$$

where C_s (µg g^{-1}) is the amount adsorbed to the soil, and C_w (µg ml^{-1}) is the equilibrium solute concentration.

2.4. Assessment of SOM occlusion in subsoil aggregates using spectral analysis

SOM occlusion in aggregates was assed using spectral data sets from the ground and the sieved subsoil samples. We assumed that sieved soil samples reveal aggregates whereas ground samples were aggregate free due to grinding. Thus, SOM inaccessibility in aggregates could be identified comparing SOM characteristics of sieved and ground soil surfaces. Since Fourier transformation infrared (FTIR) spectra are well known to reflect SOM contents and properties on soil surfaces (Ellerbrock and Gerke, 2004), spectra of the ground and sieved subsoil sample sets were scanned as described below. Differences in the spectral information between ground and sieved sample sets were analyzed using principal component analysis (PCA) and qualitative spectral interpretation of the mean spectra of both data sets.

FTIR analysis was conducted with soil samples in the mid-infrared range (MIR). Approximately 50 mg soil was filled in custom made aluminum microplates with 24 wells. The spectra were recorded with a Bruker Tensor 27 equipped with an automated microplate reader (HTS-XT, Bruker, Ettlingen, Germany). The measuring instrument was provided with an N_2-cooled mercury cadmium telluride (MCT) detector. Five replicates of each sample were measured and averaged by the OPUS software (Version 6, Bruker). The samples were scanned from 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. Gold was always used as a background spectrum. For further analysis, the spectral information from 4000–500 cm^{-1} were used to avoid random noise in the wavenumber region < 500 cm^{-1}, which occurred due to the detection method of the FTIR device.

Since ground and sieved (< 2 mm) subsoil samples were used, effects of different soil sample porosities were expected, which might produce changes in the reflectance intensities. In order to avoid these effects, the spectral data was pre-treated via standard normal variate (SNV) before further processing (Barnes et al., 1989; Rinnan et al., 2009).

2.5. Data analysis and statistical methods

Outlier tests were performed on the sorption data for NP and PFOA using the standard deviation. Whenever the standard deviation was two times higher or lower than the mean percental pollutant sorption potential, the value was excluded from the data set (Grubbs 1969). Correlations between the SOC content and the pollutant sorption to the soil solid phase were calculated to explain sorption behavior in dependence of the SOC content. Since SOC values were not normally distributed (Appendix #1), the rank correlation method of Spearman was used (Mukaka, 2012). A t-test for unpaired groups was used to compare mean characteristics of the top- and subsoil sample sets.

Multiple regression analyses were performed to identify soil properties accounting for the difference in the sorption of NP and PFOA. The analyses were done using the approach of backward elimination, to eliminate independent variables that were not statistically relevant for the regression model. To evaluate the relative influence of the independent variables on the dependent variable, standardized regression coefficients were used. Thus, the variable with highest coefficient indicated that it has the greatest influence on the dependent variable. The R^2 was used as the quality parameter of the model, which described the percentage of the variation of the dependent variable that is explained by a linear model. However, since we focus on sorption processes in subsoil samples, regression analyses were performed for top- and subsoil samples separately. To focus on sorption mechanisms in subsoils, the sample set was split into different subgroups based on, e.g., soil pH or clay contents. These subgroups were also subjected to multiple regression analysis to understand the role of subsoil SOC on pollutant sorption in more detail.

The *k*-means algorithm was used to cluster subsoil samples based on their spectral information as detailed described in Heil et al. (2019). Briefly, the algorithm works iteratively to assign partition of objects into clusters so that an object is more similar to objects in its own cluster than to objects in a different cluster (Heil et al., 2019; MacQueen, 1967). According to Heil et al. (2019) we set the optimal number of clusters by using the partition coefficient (C_P) and the partition entropy (E_P). These coefficients represent the variance within one class (E_P) and the variance between the clusters (C_P). When C_P is maximized and E_P is minimized, it is expected that the partitioning of the data set reaches its optimum.

PCA was performed to identify differences between the sieved and the ground subsoil samples using the spectral data. As described in Stumpe et al. (2012), during the course of a PCA, it is possible to calculate a score vector for each subject on a given principal component (factor vector). We used the first two scores to describe similarities between spectra. Hereby, a closer relationship of score 1 to score 2 of the spectra indicates a greater similarity between the analysed spectra.

All statistical analyses were performed with the programming language R Gui (Version 3.2.5, open-source software, R Development Core Team (2008)).

3. Results and discussion

3.1. Soil sample characteristics

Table 2 shows the soil properties that are generally considered to be relevant for sorption of pollutants. The mean, standard deviation, minimum, and maximum values for the total soil sample set and for the separated top- and subsoil sample sets are listed. The total soil sample data set covers a wide range in physicochemical properties. The SOC contents, e.g., ranged from 0.22–11.73%, with a mean of 2.15%. In addition, soil texture, soil mineralogy (iron, manganese, and aluminum contents) as well as soil structure (BET, pore volume and average pore diameter) were highly heterogeneous. Sand and clay contents covered a range between 1.3–98.3% and 0.7–50.1%, respectively.

Tab. 2: Soil sample characteristics for the total data set as well as the top- and subsoil data sets. Due to the calculation formula, it was not possible to estimate the hydrophobicity of samples with SOC contents < 0.5%.

Soil Properties		All soil samples (n = 96)				Topsoil samples (n = 54)				Subsoil samples (n = 42)			
		Mean	S_D	Min.	Max.	Mean	S_D	Min.	Max.	Mean	S_D	Min.	Max.
SOC [1]	[%]	2.15	2.91	0.03	11.73	3.65	3.16	0.55	11.73	0.22	0.11	0.03	0.48
Hydrophobicity Index [2]	[-]	-	-	-	-	0.93	0.22	0.41	1.41	-	-	-	-
pH [3]	[-]	6.05	1.34	3.75	8.6	5.85	1.22	3.75	7.9	6.3	1.6	4.1	8.6
Sand [4]	[%]	51.03	32.97	1.30	98.30	42.79	31.28	3.40	94.50	61.04	32.55	1.30	98.30
Silt [4]	[%]	31.27	24.15	0.80	92.00	36.75	22.77	0.80	92.00	24.62	24.38	0.90	81.60
Clay [4]	[%]	17.65	13.62	0.70	50.10	20.39	14.58	1.80	50.10	14.33	11.68	0.70	46.90
Fe_a [5]	[mg kg^{-1}]	0.37	0.54	< 0.01	2.52	0.59	0.65	< 0.01	2.52	0.12	0.12	< 0.01	0.5
Mn_a [5]	[mg kg^{-1}]	0.02	0.02	< 0.01	0.09	0.02	0.02	< 0.01	0.09	0.01	0.01	< 0.01	0.07
Al_a [5*]	[mg kg^{-1}]	0.09	0.06	0.01	0.32	0.12	0.07	0.02	0.32	0.07	0.05	0.01	0.16
BET [6]	[m^2 g^{-1}]	8.38	7.21	0.10	31.71	7.85	6.88	0.10	31.71	9.07	7.64	0.15	23.18
Pore Volume [6]	[cm^3 g^{-1}]	0.005	0.004	< 0.001	0.017	0.004	0.004	< 0.001	0.017	0.005	0.004	< 0.001	0.013
Pore Diameter [6]	[nm]	2.07	0.19	0.83	2.26	2.06	0.23	0.83	2.22	2.09	0.13	1.69	2.26

[1] Vario EL Elementar Analyser (Elementar Analysesysteme GmbH, Hanau, Germany, [2] after Baumann et al. 2016 ((2925cm^{-1} + 2858cm^{-1}) / 1634cm-^{1}), [3] 0.01 M $CaCl_2$. [4] Analysette (Fritsch GmbH, Idar-Oberstein, Germany), [5] Dithionith and Oxalate extracted iron, manganese and aluminum amorphous oxides, [6] nitrogen adsorption-desorption measurement, (Brunauer et al. 1938). *n = 72

The topsoil data set contained samples with SOC > 0.5% and covered a wide range of SOC contents from 0.55 up to 11.73%, with a left-skewed distribution (Appendix #1). The hydrophobicity index (HD), varied between 0.41–1.41 in the topsoil samples, which was more variable than the data reported by Baumann et al. (2016), who analyzed SOC content and SOC hydrophobicity of about 300 soils and found SOC HD indexes varying only between 0.15–0.39.

Due to the selection criteria, subsoil samples were low in SOC (0.03–0.48%) so that sorption of both pollutants to inorganic soil components was also expected. The soil texture of the subsoils is highly heterogeneous with sand and clay contents varying from 1.3–98.3% and from 0.7–46.9%, respectively. Clay content and BET surface area were closely correlated with a Spearmen r of 0.97. Amorphous oxides which can also affect organic pollutant sorption in subsoils (Li et al., 2012; Paradelo et al., 2016) varied strongly especially with iron and manganese oxides showing a left-skewed distribution.

Between sub- and the topsoil data sets no significant differences were observed for any parameter, except for SOC, which was used for separating the two data sets.

3.2. Sorption potential of NP and PFOA

Fig. 1 shows sorption isotherms of NP and PFOA exemplarily for five different soil samples with varying SOC contents. Consistent with previous studies (Ahrens et al., 2011; Düring et al., 2002; Liao et al., 2014), the sorption isotherms of both pollutants were best fitted with the linear regression model with R^2 values of up to 0.99.

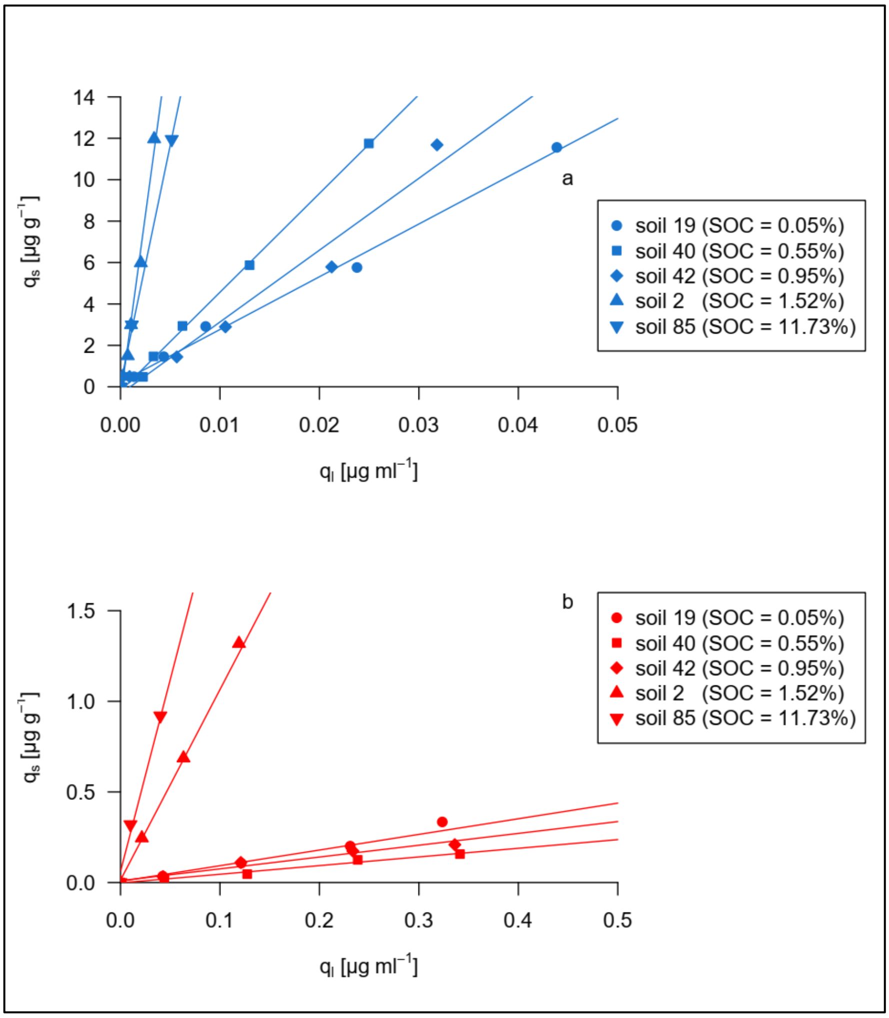


Fig. 1: Linear sorption isotherms of five representative soils with varying SOC contents representing (a) NP and (b) PFOA sorption.

For NP, log (K_D) values ranged from 1.8–3.7. Between top- and subsoil sample sets, significant differences in NP sorption were found with mean log (K_D) values of 3.2–2.4 for the top- and subsoil data sets, respectively. Although other studies did not differentiate between top- and subsoils, they observed increasing NP sorption with increasing SOC values (Chen et al., 2013; Milinovic et al., 2015a; Milinovic et al., 2015b).

For PFOA, log (K_D) values were much lower than for NP and ranged from –0.9–1.4, which is also consistent with values reported in other studies (Li et al., 2012; Milinovic et al., 2015a; Milinovic et al., 2015b). Between the top- and subsoil sample sets, no significant differences in PFOA sorption were observed, although the top- and subsoil data set showed mean log (K_D)

values of 0.22 and –0.16, respectively. The low log (K_D) values in the subsoil data set were consistent with Li et al. (2012), who reported log (K_D) values between –0.9– (–0.6) for the PFOA sorption to sediments with SOC contents less than 1%.

Interestingly, NP sorption to soil samples was not only stronger than that of PFOA (mean log (K_D) 2.8 vs. 0.05 L kg^{-1}) but also less variable (CV 17 vs. 840%). Since significant differences between sub- and top soil sorption were observed for NP only, this indicated that different mechanisms were responsible for NP and PFOA sorption.

3.2.1. Sorption mechanisms as a function of SOC content

To elucidate sorption mechanisms of NP and PFOA in the top- and subsoil sample sets, pollutant sorption was plotted as a function of SOC content within the total and for top- and subsoil data sets, separately (Fig. 2). For NP, the sorption increased exponentially with higher SOC contents, until saturation was reached with about 99% NP sorption at high SOC content (Fig. 2 I-a). The data was successfully fitted using the Langmuir isotherm model with a residual sum-of-squares (RSS) of 0.81 where NP sorption reaches saturation at SOC contents > 4%. This explains why Düring et al. (2002) observed no saturation of NP sorption as function of SOC, since they used soil samples with a maximum of 4.1% SOC content.

For PFOA, the relationship between PFOA sorption and SOC content has the best fit using a linear model with an R^2 of 0.66, thus showing a rather weak relationship between the K_D of PFOA and SOC content. This contrasts with the study of Milinovic et al. (2015b) who observed a linear relationship between the K_D of PFOA and SOC content with a r of 0.98. However, for their PFOA batch assays, they used only six soil samples, so that our results using 94 soil samples with a broad range of SOC contents may be more representative. However, as indicated by the high data scatter at low SOC content in the subsoil region, there appeared to be almost no relationship between SOC and PFOA sorption in the subsoils.

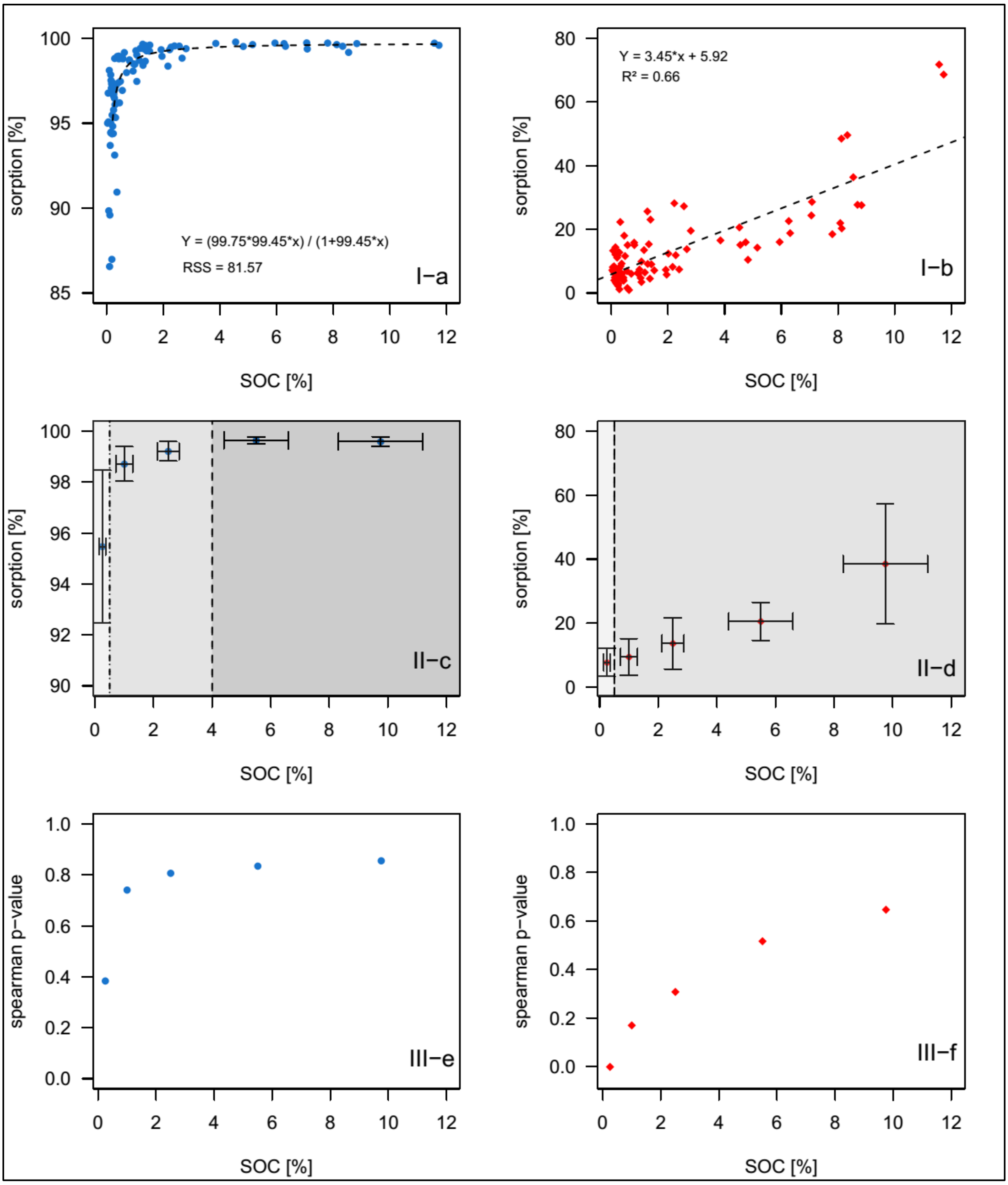


Fig. 2: (I) SOC content plotted against the mean percental sorption of NP (I-a) and PFOA (I-b), (II) standard deviation of the SOC contents and the NP (II-a) and PFOA (II-b) sorption represented at five points, (III) correlation coefficients between the SOC content and the NP (III-a) and PFOA (III-b) sorption at five points.

To describe the relationship between surfactant sorption and SOC more quantitatively, standard deviations for mean NP and PFOA sorption data as well as for SOC contents are shown at selected points within the sub- and topsoil data set (Fig. 2 I-b and 2 III-e). Fig. 2 II-c and f visualize the Spearman correlation coefficients between K_D and SOC for the same selected SOC ranges. Since sorption saturation was reached in topsoils of more than 4% SOC for NP, the topsoil data set was split into topsoils between 0.5–4% SOC as well as into topsoils with more than 4% SOC.

For NP, we found the highest sorption variability in the subsoil data set with sorption varying between 85–96% (Fig. 2 II-c). As indicated by a low variability of SOC in the subsoil, only a weak relationship between SOC and NP sorption could be observed with a correlation coefficient of 0.38 (Fig. 2 III-e). Thus, in subsoils, SOC content did not control NP sorption to a high degree. In both topsoil subsets (0.5–4% SOC and > 0.4% SOC) the variability of NP sorption drastically decreased whereas the SOC variability increased. Since the correlation coefficient between NP sorption and SOC content increased up to 0.82 in topsoils, SOC seems to be the most important driver for NP sorption in topsoils. Similarly, Milinovic et al. (2015a) identified SOC as a key controlling parameter for NP sorption in topsoils, which most likely is explained by hydrophobic interaction with SOC.

For PFOA, the variability of the sorption data is much higher than that of NP, especially within the topsoil sample set (Fig. 2 II-d). Correlation between the SOC content and PFOA sorption drastically decreased with decreasing SOC contents (Fig. 2 III-f), with coefficients of up to 0.63 in the topsoil showing an effect of SOC on PFOA sorption, while in the subsoil PFOA sorption is not related to the SOC content at all ($R^2 = 0.01$). Similarly, Milinovic et al. (2015b) also found significant correlations between SOC and PFOA sorption only in soils with SOC > 9%.

To sum up, in topsoils SOC content appeared to be the main driver for NP and PFOA sorption to the soil solid phase, whereas in the subsoil other soil constituents and mechanisms than SOC and hydrophobic interactions are relevant for sorption.

3.2.2. Sorption mechanism as function of various soil properties

To determine the relative contribution of different soil properties to the variance of the pollutant sorption potential, multiple regression analyses were conducted. For a detailed analysis of sorption processes in the subsoil, multiple regression models were run for the complete and for the top- and subsoil data sets separately. For NP, the complete and topsoil data set were reduced to soil samples with less than 4% SOC, because in soil samples with more than 4% SOC, saturation of NP sorption was reached as detailed described above.

Tab. 3: Multiple regression analyses before clustering. Standardized ß-coefficients with significant influences on the regression are shown. The R² value is the figure of merit of the regression analyses.

Surfactant	Sample sets	R^2	Standardized ß-coefficients of the independent model variables								
			SOC	Silt	Clay	pH	Fe_a	Mn_a	Al_a	BET	Pore Diameter	Hydrophobicity Index
NP	all	0.46	0.68								-0.15	
	topsoil	0.58	0.49	0.39	1.93		-0.85			-1.82		
	subsoil	0.53	0.56	0.34	0.27		-0.37		-0.39			
PFOA	all	0.60	0.91		0.14		-0.26				-0.2	
	topsoil	0.71	0.35		0.21	-0.40						0.36
	subsoil	0.42			0.84		-0.38	0.79		-0.61		

For the complete NP data set, 71% of the variability of the sorption data was explained by SOC, silt and clay content, amorphous Fe and Al oxides and the BET surface area as independent variables (Tab. 3). However, with a standardized ß-coefficient of 0.87 the SOC content was mainly controlling NP sorption. For the separate top- and subsoil data sets, the explaining variance decreased to 70–52%, respectively. Surprisingly, for the topsoil data set, clay content was dominating the NP sorption with a standardized ß-coefficient of 1.12, whereas SOC content with a standardized ß-coefficient of 0.57 was less important for NP sorption. Apart from the SOC content, SOC hydrophobicity was relevant for NP sorption, which supports the assumption that hydrophobic sorption of NP occurs in the topsoils. In the subsoil, the SOC content with a standardized ß-coefficient of 0.66 was the main factor controlling NP sorption. However, only 52% of the variance of NP sorption was explained within this sample set. Amorphous oxides showed a negative relationship to NP sorption in the top- and subsoils, which can be affected through oxides that are potentially positively charged at low pH values. That could inhibit hydrophobic interaction with the nonpolar NP molecule (Pan et al., 2009). In any case, the regression models and the low explained variance in the subsoil samples indicate that different mechanism must be responsible for the sorption of NP in the top- and subsoils.

For the complete PFOA data set, only 41% of the variability of the sorption data was explained by the content of SOC, silt, clay, Mn_a and Fe_a as well as by the pore diameter as influencing variables (Tab. 3). However, SOC with a ß-coefficient of 0.41 was the most influencing variable. When the complete data set was separated into top- and soil samples, the explained variance for the topsoil and the subsoil samples increased slightly to 52 and 57%, respectively. Whereas in the topsoil, the SOC content, clay, and Fe_a were important predictor parameters, in the subsoil SOC had no significant influence on PFOA sorption anymore. In subsoils, PFOA sorption was mainly explained by the content of clay minerals and amorphous Mn oxides. According to those predictor variables, topsoil sorption mechanisms were attributed to hydrophobic interaction between SOC and PFOA molecules, whereas in the subsoil, PFOA sorption appears to be controlled by interactions with soil mineral components.

To sum up, although subsoils are generally low in SOC, the SOC contents in the subsoils should be high enough to provide sorption sites even for the highest NP or PFOA concentration used. Nevertheless, the influence of SOC on the sorption potential of NP as well as of PFOA decreased. Thus, in subsoils sorption mechanism between SOC and the used pollutants are yet not fully understood so that we suggest the following alternative hypotheses:

1. SOM in subsoils is less available for pollutant sorption than in topsoils due to occlusion within aggregates or mineral complexes;
2. SOM quality is highly affecting pollutant sorption at low SOM concentrations in the subsoils, but SOM quality parameters were not included in the regression models;
3. In subsoils, SOC content is not controlling the sorption of NP and PFOA but the surfactant’s hydrophobicity as a function of soil pH.

These hypotheses were tested with additional analyses in the following.

3.3. Sorption processes in subsoil samples

3.3.1. Hypothesis 1: SOC inaccessibility

To verify this hypothesis, we aimed to identify aggregates in subsoil samples, which were potentially masking SOC (Fig. 3). Thus, we compared FTIR spectra of ground and sieved soil samples assuming that differences between both data sets were justified to SOM aggregation in the sieved sample set.

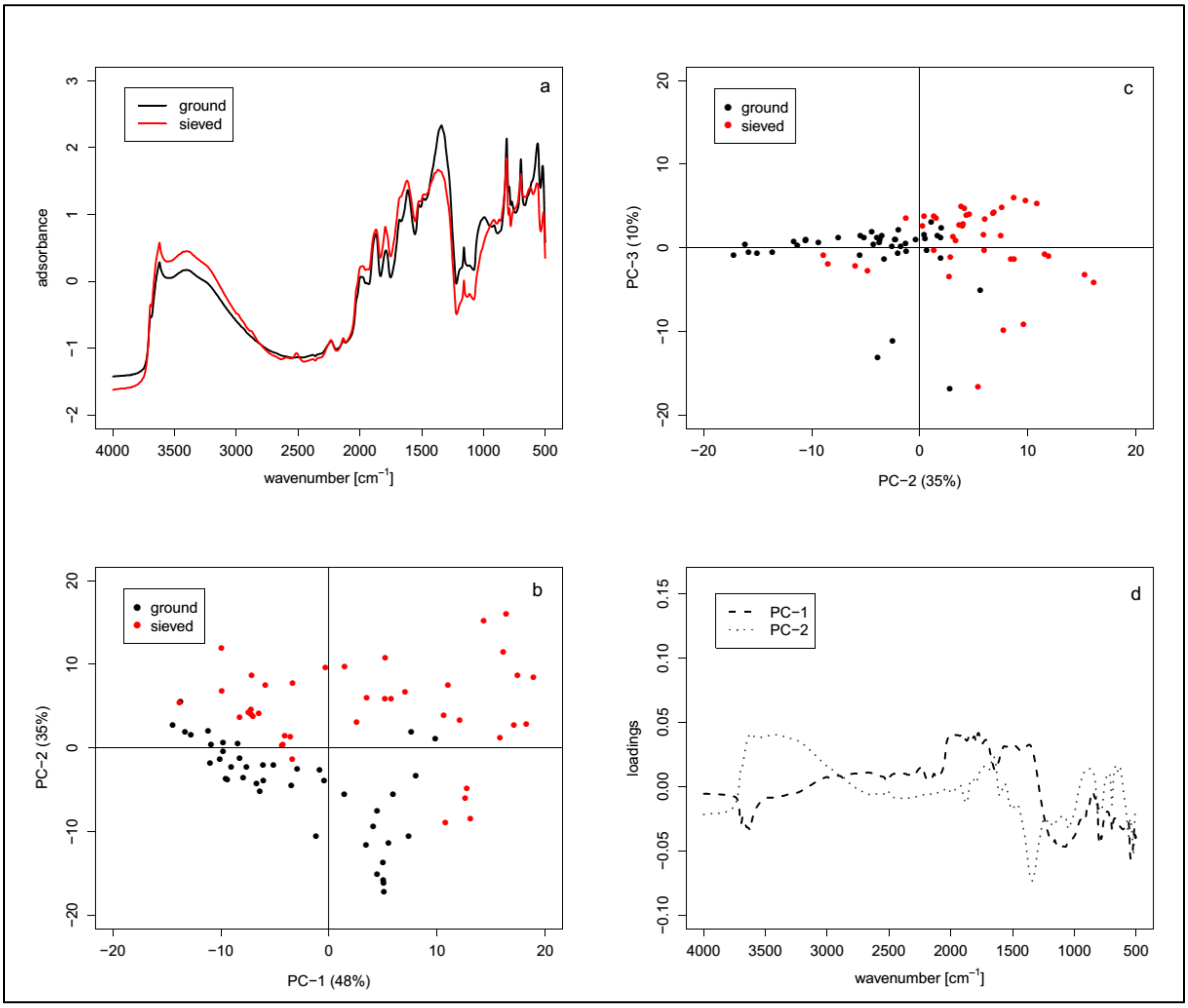


Fig. 3: (a) Mean FTIR spectra of the ground and sieved subsoil sample set, PCA of the ground and sieved data set represented by the score plot of the first and second component (b) of the second and third component(c), (d) PCA of the ground and sieved data set represented by the loadings of the first and second component.

To get a first overview we used the mean spectra of the ground and sieved sample set (Fig. 3a), since they may show differences between both data sets. We observed higher absorbance at wavenumber ~1340 cm^{-1} and a lower absorbance at wavenumber ~1620 cm^{-1} for the mean spectra of the sieved sample set. Especially, the lower absorbance at wavenumber ~1620 cm^{-1} seem to confirm that hydrophilic parts of the SOM interact with the minerals and are thus less available on the aggregate surfaces of the sieved soil samples. Although aggregation seem to affect SOM composition on aggregates surfaces, we could not find SOM to be an inaccessible bound within soil aggregates since the hydroxylic C–O–H groups showed a higher absorbance within the sieved sample set. However, peaks of O-H groups (1410 cm^{-1}, 2850–2920 cm^{-1}) were absent in the mean spectra because of the generally low SOC contents in subsoils.

To focus on spectral differences between ground and sieved subsoil data sets, a PCA was conducted. The scores of the first (PC1) and the second (PC2) components as well as of the second and the third components are visualized in Fig. 3b and Fig. 3c. The best separation of the ground and sieved spectra was observed in the PC1/PC2 score plot. Nevertheless, the separation was also visible in the PC2/PC3 score plot of the ground and sieved spectra.

Although PC1 explained 48% of the variance in the spectral data, PC1 was not relevant for the separation of the ground and sieved soil data. PC2 visually separated the ground and sieved spectral data set with an explained variance of 29%. Thus, the PC2 loadings were used to identify wavenumbers being important for the separation between the ground and sieved sample sets (Fig. 3d). PC2 was characterized by a strong negative loading at wavenumber ~1340 cm^{-1} and a positive loading at wavenumber ~1620 cm^{-1}, corresponding to hydroxylic C–O–H and hydrophilic C=O groups, respectively (Bornemann et al., 2010; Bornemann et al., 2008; Ellerbrock et al., 2016b). Additionally, various positive and negative loadings occurred at wavenumbers of less than 1100 cm^{-1}, indicating that other soil properties than SOM quality were relevant for the separation between the ground and sieved soil sample sets. (Nguyen et al., 1991), e.g., attributed the wavenumber region between 800–500 cm^{-1} to SiO bulk modes of quartz overtones and iron, aluminum, or other metal oxides. Since Aquino et al. (2007) found the carbonyl groups (C=O) in SOM to be preferentially involved in SOM mineral interactions, the observed spectral differences might indicated that oxides are masked through their association with hydrophilic SOM groups in the sieved samples and that this is no longer visible after grinding. However, hydrophobic O–H groups (1410 cm^{-1}, 2850–2920 cm^{-1}) (Bornemann et al., 2010), which are relevant in the context of NP and PFOA sorption, were not identified to be relevant for the separation between the ground and sieved sample set.

We concluded that the spectral differences between the ground and sieved spectral data sets was potentially attributed to SOM mineral aggregation within the sieved soil sample set. A formerly assumed SOM inaccessibility could not be verified but SOM mineral interaction might influence the SOM quality on the surfaces of the unground soil samples. Thus, to understand the role of subsoil SOM for NP and PFOA sorption processes, effects of SOM quality on aggregate surfaces were further investigated as described in the following. Nevertheless, we assumed soil aggregation to be responsible for the low explained variance of the pollutant sorption in the subsoil data set. Sorption potentials were measured on sieved soil samples, whereas several basic soil parameters, which were used as predictors for the regression analyses, were analyzed using ground soil samples. Due to aggregation processes, the soil surface of sieved samples may not be reflected in the properties of the ground soil samples, so that it is not possible to relate pollutant sorption to basic soil properties to a full extent.

3.3.2 Hypotheses 2: Effects of SOM quality

To test this hypothesis, only FTIR spectra of sieved subsoil samples were analyzed with focus on SOM quality measures. To reduce the effort of a qualitative characterization of each single spectrum, the subsoil spectra were clustered and the mean spectrum of each cluster was used for qualitative spectral interpretation. The cluster analyses separated the subsoil data set into cluster A and B (Tab. 2 and Fig. 4).

Tab. 4: Physicochemical parameters of the subsoil cluster A and B with results of the multiple regression analyses after clustering. Standardized ß-coefficients with significant influences on the regression are shown.

Subsoil Properties		Cluster A				Cluster B			
		Mean	S_D	standardized ß-coefficients		Mean	S_D	standardized ß-coefficients	
				NP ($R^2 = 0.76$)	PFOA ($R^2 = 0.46$)			NP ($R^2 = 0.62$)	PFOA ($R^2 = 0.71$)
SOC	[%]	0.20	0.11	0.56		0.27	0.10	0.58	
pH	[-]	5.08	0.89			6.70	1.13	0.63	
Sand	[%]	91.96	4.24			43.17	25.49		
Silt	[%]	4.41	2.99		-0.57	36.51	24.03		
Clay	[%]	3.65	2.38		0.48	20.31	6.67		0.68
Fe_a	[mg kg^{-1}]	0.05	0.05	-0.64	-0.88	0.19	0.13		
Mn_a	[mg kg^{-1}]	0.001	< 0.001			0.02	0.02	-0.81	0.80
Al_a	[mg kg^{-1}]	0.05	0.04			0.08	0.04		
BET	[m^2 g^{-1}]	1.97	2.00			13.99	5.77		-0.55
Pore Volume	[cm^3 g^{-1}]	0.001	0.001			0.008	0.003		
Pore Diameter	[nm]	2.00	0.18			2.15	0.05		-0.26
log(K_D) NP	[-]	2.30	0.38			2.44	0.17		
log(K_D) PFOA	[-]	-0.26	0.24			-0.12	0.29		

No significant differences were observed between SOM contents of cluster A and B. However, differences in SOC quality were identified between cluster A and B using spectral information. Cluster A was characterized by higher spectral absorbance between bands 2200–2000 cm^{-1} due to carbohydrate overtones (Janik et al., 2007b). Furthermore, higher absorbance was determined at the peak around 1660 cm^{-1} caused by vibrations of carbonyl C and at around 1410 cm^{-1} based on aliphatic C–H group vibrations (Ellerbrock et al., 2016a). The band between 1620–1600 cm^{-1} was also more distinct in cluster A due to vibrations of phenolic compounds. The peak at around 1660 cm^{-1} caused by vibrations of hydrophilic C–O–H groups (Bornemann et al., 2010). Peaks attributed to aromatic structures, e.g., at 1410 cm^{-1}, 2850 cm^{-1}, and 2920 cm^{-1} were absent in both clusters, likely because the subsoil samples were depleted in SOC. However, the subsoil clusters A and B were qualitatively separated by differences in SOC.

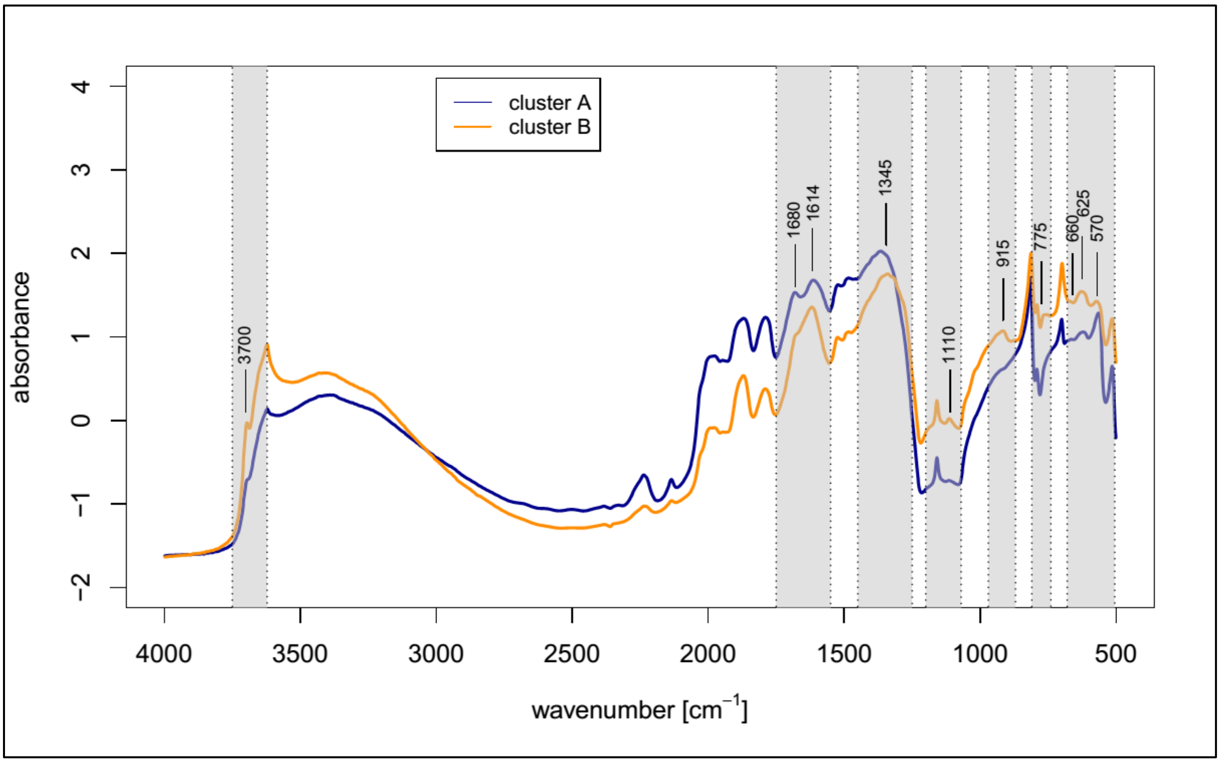


Fig. 4: (a) Mean soil spectra of the subsoils of cluster A and B, (b) spectral differences between the mean of cluster A and B are marked.

Apart from differences in these SOC quality measures, the two clusters could also be differentiated by soil texture. Cluster A covered sand rich soils with an average sand content of 92 ± 4%., whereas the soil texture of cluster B is much more heterogeneous with 43 ± 25% sand, 37 ± 24% silt, and 20 ± 7% clay content. Furthermore, kaolinite was identified to dominate the clay mineralogy of cluster B, since Al–OH stretching vibrations at 3692–3620 cm^{-1}, Al–OH deformation vibrations at 1016 cm^{-1} and at 920 cm^{-1}, and also a sharp peak at 1112 cm^{-1} were identified (Janik et al., 2007a; Nguyen et al., 1991; Yitagesu et al., 2011). Significant differences in the BET surface were found in the two clusters, which is significant lower in cluster A (1.97 m² g^{-1}) than in cluster B (14 m² g^{-1}). A reason could be the higher sand content in cluster A, compared to cluster B. With focus on the oxides, cluster A revealed lower amorphous iron and manganese oxide contents with 0.05 and 0.001 mg kg^{-1}, respectively, than cluster B with 0.19 mg kg^{-1} iron and 0.02 mg kg^{-1} manganese oxide, but differences were not statistically significant. Albeit cluster A and B were characterized by significantly different soil properties, the sorption potential for NP and PFOA was not different between the two clusters. Thus, we could not directly relate significant differences between cluster A and B to pollutant sorption potentials. Thus, in a next step, multiple regression analyses were performed separately for the different clusters.

For cluster A, the variance of NP and PFOA sorption to subsoil samples could explain up to 80 and 75% (Tab. 4), respectively. Thus, the explained variance was significantly increased compared to the variance of the total subsample set with 52% for NP and 57% for PFOA. For cluster B, the variance of NP and PFOA sorption to the cluster subsoil samples explained up to 62 and 71%, respectively. Although less variance was explained for the pollutant sorption in cluster B compared to cluster A, an increase of explained variance was observed compared to the total sub set. Thus, multiple regression indicated that specific cluster characteristics were relevant for pollutant sorption to the subsoil samples.

For cluster A, the NP sorption was largely explained by SOM content with a standardized ß-coefficient of 0.73. Therefore, the SOM content was more important as predictor for NP sorption than for the total subsoil sample set with standardized ß-coefficients of 0.56. The clay content did not have any effect on NP sorption, which was not surprising since cluster A was dominated by mineral soil constituents. However, amorphous Mn and Al oxides, as well as the pH value were identified to be also relevant for NP sorption. In cluster B, for the NP sorption the SOM content and soil pH were identified as dominating predictor variables with standardized ß-coefficients of 0.58 and 0.63, respectively. However, the standardized ß-coefficient of SOC was lower than for cluster A. This is possibly explained by aggregation processes in the clay richer subsoil samples of cluster B, thus reducing SOC availability for NP sorption.

In the regression analysis for PFOA sorption of cluster A, only negative standardized ß-coefficients for the independent variables were determined, so that no important soil sorbate for PFOA was identified. Apparently, SOC content did not explain differences in PFOA sorption in those samples, although SOC sorption sites should be fully accessible due to the low clay and oxide content of the samples. In cluster B, the content of clay and amorphous manganese oxides are the dominating predictor variables for PFOA sorption with standardized ß-coefficients of 0.68 and 0.80, respectively. This showed that in subsoils containing clay, those minerals appeared to provide sorption sites for PFOA. This appeared to be also true for amorphous manganese oxides, which were also found in much higher concentrations in cluster B than in cluster A.

In summary, the subsoil clustering allowed more detailed insights into pollutant sorption processes and helped to reduce the high unexplained variance of the total subsoil sample set. Nevertheless, an unexplained variance of up to 38% remained.

3.3.3. Hypotheses 3: Effects of surfactant properties

As shown above, attempts to improve the explained variance of PFOA sorption in subsoils by classifying soil samples according to their physicochemical properties were not successful. We therefore assumed that not only soil properties, but also PFOA characteristics might control its sorption in the subsoil. With a pK_a value of about –0.5 (Tab. 1), PFOA is a strong acid, which is only protonated and thus hydrophobic at low pH. This pH dependent change between a polar and a hydrophobic state should affect its sorption behavior (Deng et al., 2012). In contrast, the surfactant NP is only a weak acid with a pK_a value of 10.7, resulting that it is protonated under pH conditions of temperate soils (Maguire, 1999). This behavior is clearly reflected in the pH dependent differences in correlation coefficients of the two surfactants with SOC (Fig. 5). For PFOA, the spearman correlation coefficients between PFOA and SOC drastically increased at soil pH less than 5.5, whereas no significant pH effect on the NP correlation to SOC was observed. Since being no linear but rather an abrupt increase of correlation coefficients from 0.48 up to about 0.80 between PFOA and SOC, this effect may not be identified by including pH as an independent variable in a linear regression model. We therefore attributed this distinct pH dependent behavior of PFOA to its protonation and subsequent hydrophobic properties only at low pH, while at higher pH, dissociation and the subsequent polar and anionic properties prevent hydrophobic interactions with SOC.

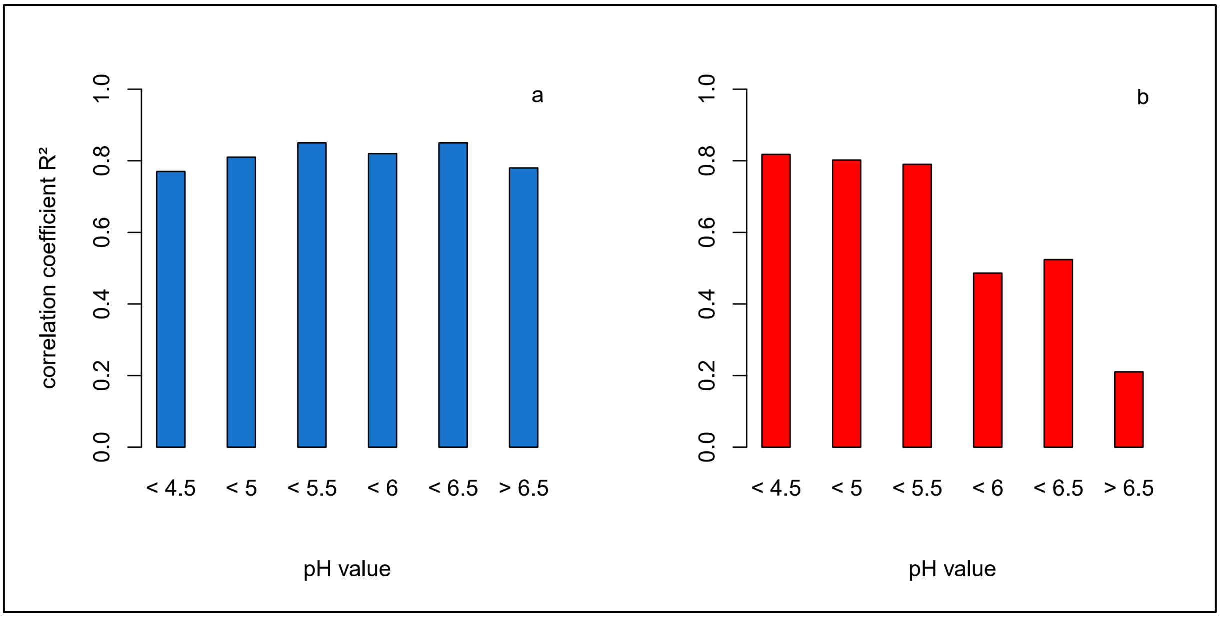


Fig. 5: Spearman correlation coefficients between SOC contents and sorption of NP (a) and PFOA (b) within the different pH groups.

In a next step, multiple regression analyses were performed for the complete, as well as the separated top- and subsoil data sets, grouping soil samples according to their pH of > 5.5 or < 5.5. Table 3 clearly shows that a pH of 5.5 was an important threshold for PFOA sorption. For the complete as well as for the topsoil data set the regression models explained up to 96 and 98% of the PFOA variability when soils with pH < 5.5 were used for analysis. For those data sets, SOC was an important variable with respect to the standardized ß-coefficients, indicating that at low pH, hydrophobic interactions between the protonated PFOA molecule and the hydrophobic SOC was one of the dominating sorption mechanisms. However, much less explained variance was found when the complete data set or the topsoil data set with pH values higher than 5.5 were used for multiple regression analyses. This indicated that when PFOA is present in its dissociated polar state sorption mechanisms are less understood.

However, for the subsoil data set, PFOA sorption was poorly explained in the acidic subgroup, as reflected in an R^2 of 0.28 (Tab. 4), whereas 82% of the variability of the sorption in subsoils with a pH > 5.5 could be explained. For both subsoil data sets, SOM was no important predictor for the PFOA sorption. At pH > 5.5, clay as well as amorphous manganese contents seem to control PFOA sorption, indicating electrostatic interactions between the clay associated oxides and PFOA.

Summing up, although the pH dependent properties of the PFOA molecule control its interaction with the soil solid phase, PFOA sorption mechanism to the subsoil are still not fully understood. Small differences in room temperature during the batch assays possibly affected sorption since micelle formation as reflected in the water solubility of PFOA is known be highly sensitive to temperature changes, doubling with a temperature increase by 3 °C (Campbell et al., 2009; Fujii et al., 2007). The micelle formation of surfactants is known to induce abrupt changes in the surfactant properties (Santos and Panagiotopoulos, 2016). Since we did not monitor the temperature of the batch solution systems, temperature effects on the surfactants properties were not quantified and thus may have an unsystematic effect on the pollutant sorption processes. However, further studies should focus on temperature effects especially of PFOA sorption in batch assays.

4. Conclusion

The sorption of NP to top- and subsoil samples was significantly higher and less variable than that of PFOA, indicating that soils are a sink for NP but less for PFOA. In topsoils, SOC content mainly contributed to the sorption of NP and PFOA. For NP, hydrophobic interactions between NP and SOC were identified as the most important sorption mechanism. For PFOA, different sorption mechanisms were identified in dependence to soil pH conditions. At low pH values (< 5.5) PFOA has hydrophobic characteristics whereas at high pH values (> 5.5) it is negatively charged leading to hydrophobic interaction with SOC or electrostatic interaction with soil mineral constituents. Thus, not only SOC content, but also soil pH is an important information in terms of risk assessments to assess PFOA sorption to the soil solid phase.

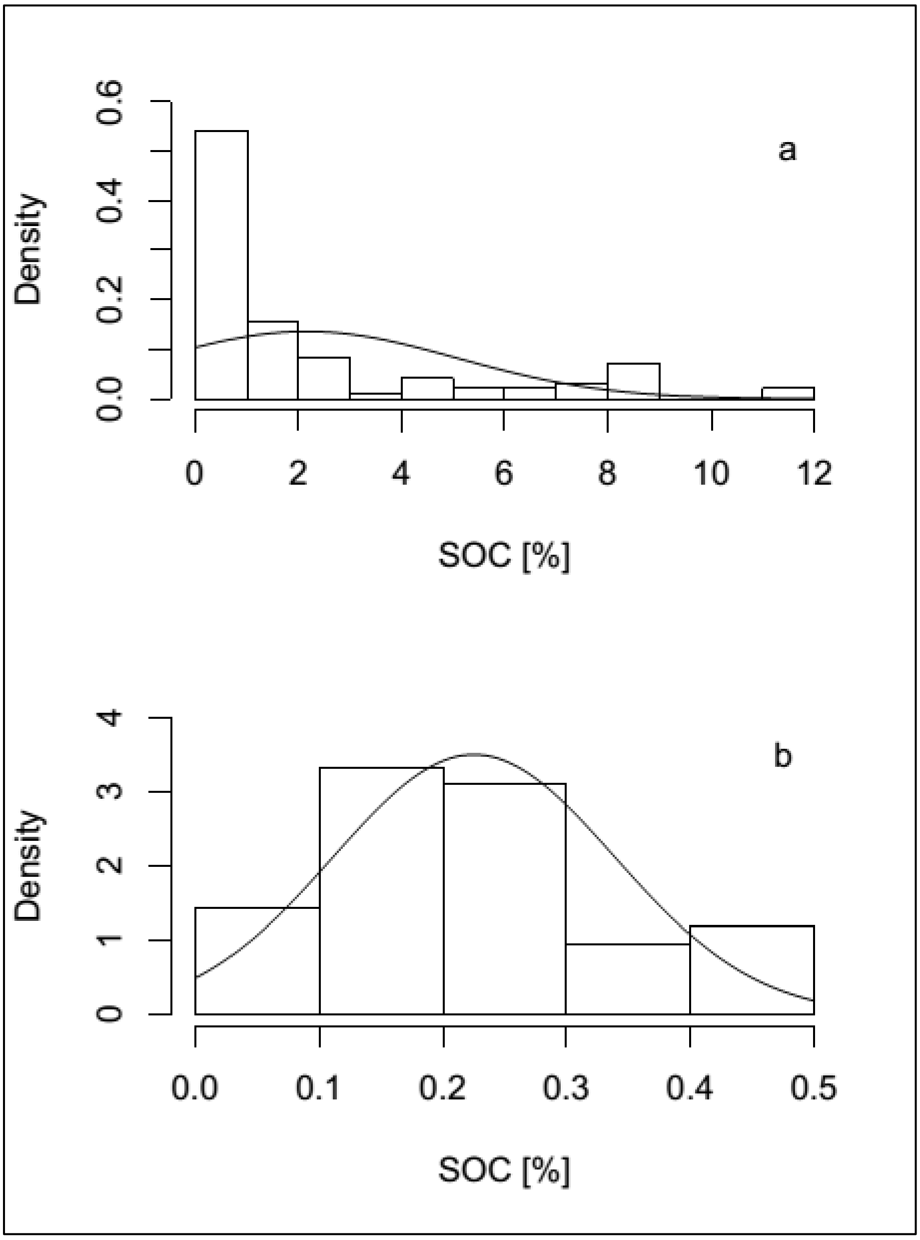
In subsoils, the relevance of the SOC content for pollutant sorption drastically decreased but was not found to be due to SOC inaccessibility through SOC occlusion in aggregates. For NP, an increasing importance of SOC quality was observed in SOC poor subsoils. Thus, SOC aggregation with the mineral fraction is important in this context, since aggregation will affect SOC quality characteristics on aggregate surfaces. For PFOA, the sorption potential in clay mineral and SOC depleted subsoils remained unpredictable, since SOC did not act as a sorbent for PFOA in those samples. However, if clay minerals are present in subsoil samples, they will control the sorption of PFOA to the soil solid phase, especially at higher pH conditions when PFOA is negatively charged. Nevertheless, the role of subsoil SOC for PFOA sorption processes remained unclear.

Acknowledgement

We would like to thank the Geographical Survey NRW and the Institute of Foundation Engineering, Water- and Waste-Management, Soil- and Groundwater-Management from the University of Wuppertal for providing the soil samples. We would also like to thank the RUBION at the Ruhr-Universität Bochum for providing us laboratories and equipment for working with radioactive chemicals and Heidrun Kerkhoff for laboratory assistance.

Appendix:

#1



Appendix 1. Histogram of SOC contents for (a) all and (b) for subsoil samples

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Chapter 3

Effects of soil organic carbon (SOC) content and accessibility in subsoils on the desorption processes of the model pollutants nonylphenol (4-n-NP) and perfluorooctanoic acid (PFOA).

1. Introduction

The occurrence of the persistent organic pollutants (POP) perfluorooctanoic acid (PFOA) and nonylphenol (NP) is ubiquitous in the environment, which leads to a high risk of human uptake (Schick and Oellig, 2019; Zhu and Kannan, 2019). Because of that, those two surfactants are currently of high research interest (Gebbink and van Leeuwen, 2020; Madrid et al., 2020).

PFOA is a per fluorinated chemical (PFC). The characteristic of those chemicals is the replacement of detached hydrogen atoms with fluorine atoms, which are responsible for the persistence in the environment (Wang and Shih, 2011). PFOA has been produced since the 1950s (Zhao et al., 2015). Because of its surface activity, thermal stability, and resistance to acidic and alkaline conditions, PFOA was popular in several industrial products such as firefighting foams (AFFF), photolithography, pesticides, or semiconductors. It was also popular in costumer products like shampoos, surface coatings for carpets, stain repellents for furniture, and paper and textile products (Lin et al., 2016; Zhu and Kannan, 2019).

NP, however, has endocrine disrupting and a carcinogenic potential (Ishibashi et al., 2020; Roberts et al., 2006) and is therefore listed on the priority hazardous substance list of the European Union (Liao et al., 2014). The prohibition of the use of NP is currently not a global restriction, since it is still allowed in some countries (e.g., the United States) (Li et al., 2018b). It is a metabolite of nonylphenolethoxylates (NPEO) (Mtibaa et al., 2020). Those are non-ionic surfactants, which are contained in domestic detergents, dispersing agents, and industrial as well as institutional cleaners (Choi et al., 2016; Sun et al., 2019). Thus, NP can be found in several environmental compartments, such as water, sediment, and soil (Jiang et al., 2018; Wang et al., 2019).

The contamination of soils with PFOA and NP has reached concentrations of up to 130 µg kg^{-1} and 1 g kg^{-1} (Jiang et al., 2018; Zhu and Kannan, 2019), which is an indicator for the importance of soil as a sink for these organic pollutants. Since, PFOA and NP are persistent pollutants, sorption-desorption processes are primarily responsible for the distribution in the environment. Subsoils are especially important in this context, as they are controlling the release of pollutants to the groundwater system (Isobe et al., 2001; Sepehrnia et al., 2018). Therefore, it is important to understand the distribution pathways in order to produce efficient risk assessments (Düring et al. 2002).

The sorption processes of PFOA and NP are already described in chapter 2. It was found that the sorption of NP was contingent on the soil organic carbon (SOC) content, especially in topsoils with high SOC contents over 2%. With decreasing SOC, the quality of the organic matter (OM) became more important for hydrophobic interactions between NP and SOC. Depending on the soil pH, SOC ($pH < 5.5$) or soil minerals ($pH > 5.5$) were the most important sorbent for PFOA in topsoils. In subsoils, however, the sorption of PFOA in clay mineral and SOC depleted soils were unpredictable. If clay and iron minerals were present, they controlled the sorption. The role of SOC in subsoils for PFOA sorption remained unclear. Nonetheless, with 86–99.9% (K_D-values 60–4,840 l kg^{-1}) of the initial concentration, the adsorption of NP to the soil solid phase was significant higher, than the adsorption of PFOA with 1–69% (K_D-values 0.12–27.6 l kg^{-1}). These were also the results of previous studies were K_D-values between 24–2461 l kg^{-1} were found for NP (Wang et al., 2019; Ying and Kookana, 2005) and for PFOA K_D-values between 0.12–1485 l kg^{-1} (Li et al., 2018b) were found, respectively. All sorption processes could be fitted with linear models.

The initial adsorption of surfactants in soils is a rapid process which is reversible (Bollag et al., 1992; Northcott and Jones, 2000). It is followed by a process of slow absorption for several month or even years. Generally, soil aging leads to a stepwise formation of fraction resistance to biodegradation, desorption, and mineralization (Puglisi et al., 2007; Tang et al., 1998). In this case, the bioavailable and extractable fraction declines, whereas the irreversibly sorbed fraction of the contaminant increases (Senesi, 1992; Shchegolikhina et al., 2012). This leads to an increasing irreversible bound of contaminants while the biodegradable and extractable fraction decreases. Therefore, the desorption potential of contaminants is expected to be lower than that of younger soils. Additionally, previous studies on soils contaminated with organic pollutants showed, that aging has an effect on the contaminants desorption ability (Xu et al., 2008).

Thus, the aim of this study was to detect the desorption potential of contaminated soils over time. Mostly desorption experiments are conducted immediately after the sorption experiments (Milinovic et al., 2015a; Milinovic et al., 2015b; Wang et al., 2019), but the process is continuous and reversible, if environmental conditions are changing. Therefore, it is important to know if desorption processes are changing with time (Brusseau et al., 2019). To detect desorption potentials over time, the samples of the sorption experiments were stored for one year.

2. Methods and Materials

2.1. Chemicals

For all desorption experiments, PFOA and 4-*n*-NP were used as model pollutants. The radioactive labeled chemicals were [$1–^{14}C$] PFOA (specific activity 1.85–2.22 GBq $mmol^{–1}$ solved in ethanol), and [ring–$^{14}C(U)$] NP (specific activity of 1.85–2.22 GBq $mmol^{–1}$ dissolved in ethanol) purchased from Hartmann Analytic (Braunschweig, Germany) for analytical detection. They had a purity of over 99%. The unlabeled surfactants were purchased as powder from Sigma Aldrich (Munich, Germany) and dissolved in ethanol for further experiments. For further pollutant properties see Chapter 2, Tab. 1.

2.2. Soil samples

A soil set of 72 samples with various characteristics from agricultural and forest sites across North Rhine-Westphalia (Germany) was used. All samples were provided by the Geological Survey NRW and the Institute for Soil Engineering, Water- and Waste-Management of the University of Wuppertal. For further processing, all samples were air-dried and sieved to less than 2 mm. The soil sample characteristics were analyzed according to DIN Standards. Based on outlier tests, the PFOA and NP datasets were reduced to 61 and 71 samples in further calculations as shown in Tab. 1.

Tab. 1. Physicochemical soil sample characteristics for the PFOA and NP data set.

Properties		Samples PFOA (n = 61)				Samples NP (n = 71)			
		Mean	S_D	Min.	Max.	Mean	S_D	Min.	Max.
SOC[1]	[%]	2.17	3.01	0.03	11.73	2.00	2.87	0.03	11.73
DOC[2]	[mg kg^{-1}]	320	511	57	3373	310	507	18	3373
DOC[2]	[mg l^{-1}]	64	102	11	675	62	101	4	675
DOC/SOC	[-]	0.04	0.06	0.00	0.42	0.04	0.05	0.00	0.34
pH[3]	[-]	6.1	1.4	3.8	8.6	6.0	1.4	3.8	8.6
CeC_{eff}[4]	[mmol$_c$ kg^{-1}]	63.7	56.3	7.8	260.9	59.6	55.0	6.5	260.9
Sand [5]	[%]	50.2	33.5	1.3	98.3	53.1	33.7	1.3	98.3
Silt [5]	[%]	31.3	24.1	0.8	82.4	29.9	24.1	0.8	82.4
Clay [5]	[%]	18.4	13.6	0.9	50.1	17.0	13.5	0.7	50.1
Fe_a [6]	[%]	0.34	0.45	0.00	2.00	0.31	0.43	0.00	2.00
Mn_a [6]	[%]	0.02	0.02	0.00	0.07	0.02	0.02	0.00	0.08
Al_a [6*]	[%]	0.08	0.05	0.01	0.21	0.08	0.06	0.01	0.23
BET [7]	[m² g^{-1}]	8.37	7.03	0.14	31.71	7.72	6.94	0.10	31.71
Pore Volume [7]	[cm^3 g^{-1}]	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.02
Pore Diameter[7]	[nm]	2.07	0.21	0.83	2.26	2.06	0.22	0.83	2.26
Fluoride[2]	[mg kg^{-1}]	4.3	5.0	0.0	26.5	3.9	4.8	0.0	26.5
Chloride[2]	[mg kg^{-1}]	10.3	19.6	0.0	126.9	10.1	18.6	0.0	126.9
Nitrite[2]	[mg kg^{-1}]	0.2	0.3	0.0	1.1	0.2	0.3	0.0	1.5
Bromide[2]	[mg kg^{-1}]	0.2	0.3	0.0	1.3	0.2	0.3	0.0	1.3
Nitrate[2]	[mg kg^{-1}]	44.3	116.0	0.0	809.6	51.9	134.7	0.0	809.6
Phosphate[2]	[mg kg^{-1}]	1.6	6.5	0.0	41.7	1.3	6.0	0.0	41.7
Sulfate[2]	[mg kg^{-1}]	236.8	810.9	0.0	4775.6	177.1	706.2	0.0	4775.6
Calcium[2]	[mg kg^{-1}]	121.5	268.8	0.0	1475.9	105.0	240.5	0.0	1475.9
Potassium[2]	[mg kg^{-1}]	27.5	27.1	0.0	187.0	26.4	25.8	0.0	187.0
Magnesium[2]	[mg kg^{-1}]	18.3	33.2	0.0	155.6	16.1	30.1	0.0	155.6
Sodium[2]	[mg kg^{-1}]	14.0	20.8	0.0	135.6	12.6	19.2	0.0	135.6
Phosphor[2]	[mg kg-1]	3.7	4.2	0.0	19.7	3.6	4.2	0.0	19.7

[1]Vario EL Elementar Analyser (Elementar Analysesysteme GmbH, Hanau, Germany, [2]Warm water extraction: 10g soil, shaken 30min and vaccum filterd (0.45 µm) measured with Dimatoc 2000 (DIMATEC Analysetechnik GmbH, Essen, Germany) [3]0.01 M $CaCl_2$. [4]After ISO 11260 (2018). [5]Analysette (Fritsch GmbH, Idar-Oberstein, Germany), [6]Dithionith and Oxalate extracted iron, manganese and aluminum amorphous oxides, [7]nitrogen adsorption-desorption measurement, (Brunauer et al. 1938). *n=46 for PFOA and n=55 for NP.

Regarding to the SOC content, the focus on this study was set on the dissolved organic carbon (DOC) content. DOC was measured by shaking 10 g soil with 50 ml sterile water for 30 min. Subsequently, the suspension was centrifuged for 10 minutes at 3000 rpm and afterwards vacuum filtered (0.45 µm). The OC content was then measured using a Dimatoc 2000 (DIMATEC Analysetechnik GmbH, Essen, Germany).

During the evaluation of the data, an underestimation of the PFOA content during the sorption tests was assumed. Therefore, it was checked whether the DOC content could cause the surfactant to be pressed down in the tube during centrifugation. This would lead to an underestimation of the PFOA concentration during pipetting.

Thus, the DOC content of the supernatant of sample 96 with the highest DOC content (3373 mg kg-1 or rather 674.6 mg l-1) was diluted with sterile water in ten different concentration steps (100–10%).

Several studies found average DOC concentration in European soils from 1 to 80 mg l-1 (Camino-Serrano et al., 2014; van den Berg et al., 2012). For example, Borken et al. (2011) found DOC contents between 20 and 89 mg l-1 in the topsoil and 1-23 mg l-1 in the subsoil in 22 forest soils in Germany. Camino-Serrano et al. (2016) found concentrations of 2-50 mg l^{-1} in the entire soil profile in 97 forests sites. Kalbitz et al. (2003) investigated DOC concentrations in three agricultural soils in a long-term trial. The soil without fertilization had a DOC concentration of 7.2 mg l^{-1}, while higher concentrations were found in the soils with mineral (12.6 mg l^{-1}) and organic (13.9 mg l^{-1}) fertilization.

Since the selected soil 96 is an alluvial soil with an exceptionally high SOC content (11.57%), the DOC content is accordingly significantly higher than the average DOC content in European forest soils. This high concentration was deliberately chosen to peak the impact of DOC in this context.

2.3. Desorption experiments

PFOA and NP desorption was determined using the batch equilibrium method (OECD, 2000). All batch experiments were performed in 15 ml centrifuge tubes. To avoid surfactants adsorption to tube surfaces, PFOA sorption analysis was performed in 15 ml polystyrene tubes with polystyrene screw caps (Thermo Fisher Scientific, Germany). NP experiments were conducted in Pyrex® glass centrifuge tubes with phenolic screw caps and a PTFE-faced rubber liner (Sigma Aldrich, Germany). To ensure sterile condition, all materials, i.e., spatulas, centrifuge tubes, screw tops, and pipettes were rinsed with ethanol immediately prior to use.

The desorption experiments were performed with spiked samples, which were aged over one year (chapter 2). The initial concentrations were 75, 100, 150, 200, and 300 µg l^{-1} for PFOA and 50, 150, 300, 600, and 1200 µg l^{-1} for NP. Sorption experiments were conducted with 0.5 g soil and 5 ml background solution (0.01 M $CaCl_2$ and 0.002 M NaN_3). Sodium azide (NaN_3) was used to inhibit microbial activity throughout the batch experiments. Controls without surfactants, as well as blanks containing no soil, were prepared in the same way. After determining the surfactant concentrations, the supernatant was removed and the remained soil was slackened with a vortex. The samples were then stored in the closed tubes. Every three month, the tubes were opened to avoid anaerobic conditions. At the end of the one-year storage period, the remaining soil was tested for desorption potentials in two extraction steps. For the first extraction step, 5 ml of the background solution was added to the aged samples. All samples were then shaken end over end in the dark at a constant room temperature of 21 °C. According to the sorption experiments it was assumed, that the equilibrium time was reached after 24 h. Afterward, the samples were centrifuged at 3000 rpm for 30 min and the supernatant was decanted. For the radioactive determination of the solutions, 12 ml of scintillation cocktail (Ultima Gold, Perkin Elmer, Waltham, USA) was added to 2 ml of the supernatant. The solution was analyzed through liquid scintillation counting with a Tri-Carb 2800TR (Perkin Elmer). The second extraction step was performed with 5 ml pure ethanol (99.9%) in the same way, after the removal of the supernatant from the first desorption step.

In order to describe the mechanism of pollutant desorption to the soil, the data obtained from the desorption experiments was fitted to linear isotherms. Based on the linear isotherms, the K_D (ml g^{-1}) value defined as the ratio between equilibrium concentration in the soil matrix and that of its aqueous phase solution were calculated according to equation 1:

$$K_{D-des} = \frac{C_s}{C_w} \qquad (1)$$

In equation (1), Cs (µg g–1) is the amount of surfactant adsorbed to the soil and Cw (µg ml–1) the equilibrium solute concentration.

Furthermore, the hysteresis coefficient modified after Xiangke et al. (2000) was determined as the ratio between sorption and desorption partitioning coefficients:

$$H = \frac{K_{D-des} - K_{D-sor}}{K_{D-des}} \tag{2}$$

where $K_{D\text{-sor}}$ is the partitioning coefficient of the previous sorption experiments (ml g^{-1}).

Finally, the percentage of desorption was determined for both surfactants. The starting concentration of the respective soil sample (Appendix) served as a reference value. For a better understanding an example is given. With an initial concentration of 5 µg NP in the soil, a desorption of 25 % in the first extraction step would mean, that 1.5 µg of the surfactant has been dissolved out of the soil. A desorption of 10% in the second extraction step would mean a dissolution of a further 0.25 µg NP, since the percentage is again based on the initial value.

2.4. Metabolic activity

Because of the chosen experimental design, it was not possible to quantify the molecules of NP and PFOA in the soil dilution, but the amount of radioactive ^{14}C atoms. Despite the fact that sodium azide was used, metabolites of NP and PFOA could have formed over the storage period (Chefetz et al., 2006; Hendrix et al., 2019).

To quantify the accumulative mineralization over the storage period, 4 soil samples with varying SOC contents (Tab. 2) were incubated in an instrument that is able to measure soil respiration (CarbObot, PWR Electronics 2011). Since, organic material gets decomposed over several steps, until the OM is mineralized in its inorganic main components (Hamer and Marschner, 2002; Yoshitake et al., 2007), microbial respiration is an approximation for microbial activity. Through the respiration, OC is released as carbon dioxide (CO_2) and absorbed by a caustic potash solution (KOH).

Since the C atoms of the used surfactants were ^{14}C labeled, the surfactant concentration could be determined by sampling the KOH solution. Thus, NP and PFOA derived CO_2 was determined by mixing 2 ml of the KOH solution with 12 ml scintillation cocktail and measured with a Tri-Carb 2800TR. After each KOH sampling, the KOH solution was renewed.

To recreate the conditions of the restored samples, 20 g soil were put in a sample container and spiked with 8 ml of the contaminant solution. The ^{14}C labeled concentrations were 1200 and 300 µg l^{-1} for NP and PFOA, respectively. The varying initial concentrations were a result of the different adsorption potentials of the two surfactants. The KOH solution had a molarity of 0.25 M with a volume of 10 ml. The solution was changed every week during the first month. After one month, the solution was sampled and renewed once a month. The total trial period was 6 months.

2.5. Data analysis and statistical methods

The desorption and physicochemical results were tested for statistical outliers before further analyses were conducted. Results were excluded from the data set, if double the amount of the average standard deviation was exceeded (Grubbs, 1969). Due to these results, the sample stock for PFOA decreased from 72 to 61 and for NP from 72 to 71 soils.

The adjusted data set was than tested for Spearman correlations between the soil properties and the desorption behavior, since the data set was not normally distributed. Separate correlations were conducted for soils with high and low SOC contents as well as for the whole data set. Furthermore, the data was tested for multiple regression with the elimination method in all data set variations. The elimination method was used, to exclude all data that was not statically relevant for the model. To compare the relative influence of the independent variables in the different data sets, standardized regression coefficients were used. The R^2 represents the quality of the model.

All statistical analyses were performed with the programming language R Gui (Version 3.2.5, open-source software, R Development Core Team (2008)) and SPSS.

3. Results and discussion

3.1. Soil sample characteristics

The soil sample characteristics are shown in Tab. 1. To get a good overview of the desorption behavior of the two surfactants under several soil conditions, the data covers a wide variation of different soil properties.

The physicochemical soil properties were heterogenous in the PFOA and NP data sets. Especially the SOC contents differed widely with a minimum of 0.03% and a maximum of 11.71%, respectively. Due to the fact, that the desorption is a process of releasing contaminants from the soil matrix, DOC content is another important characteristic in this context. It represents the amount of OC that is extractable by water. DOC content in this data set ranged between 57–3373 mg kg^{-1} (11–675 mg l^{-1}) for the PFOA and 18–3373 mg kg^{-1} (4–675 mg l^{-1}) for the NP data set. Mean values were 320 mg kg^{-1} (64 mg l^{-1}) for PFOA and 310 mg kg^{-1} (62 mg l^{-1}) for NP. The soils with very high DOC contents of more than 1900 mg kg^{-1} (380 mg l^{-1}) were alluvial soils with high SOC contents overall. As already mentioned, DOC values in European forest and agricultural soils range from 1 to 80 mg l^{-1} (Camino-Serrano et al., 2014; Kalbitz et al., 2003; van den Berg et al., 2012). Thus, the data used not only represent average values, but desorption can also be described on soils with above-average DOC.

Another indicator for exchangeable molecules is the effective cation exchange capacity (CEC$_{eff}$). The average sum of the exchangeable cations was 60 mmol$_c$ kg^{-1} with a range of 253 mmol$_c$ kg^{-1}. This range reflects natural variance well. Tomašić et al. (2013) for example, found CEC ranges of 20–400 mmol$_c$ kg^{-1} in over 50 soil samples in Croatia.

In addition to the CEC, the single cation and anion concentrations in the soil suspension were detected. The results also differed considerably. Whereas calcium and sulfate concentrations were highest with maximum values of 1475 and 4775 mg kg^{-1}.

Soil texture, mineralogy (iron, manganese, and aluminum contents), and structure (BET, pore volume, and average pore diameter) were very heterogenous as well. Since PFOA and NP are very long molecules, we suspected that the surfactant will be held back by mechanical interactions with soil pores and surface structures. In the analyzed samples, BET surfaces ranged from 0.1–32 $m^2 g^{-1}$. Both sandy and clayey soils were considered in the data sets with maximum values of 98% sand and 50% clay.

Soil pH values varied between 3.8–8.6 with a mean of 6, because samples were taken from farmland (higher pH values) as well as from forest soils (lower pH values).

3.2. Desorption potential of PFOA and NP

The desorption potential of PFOA and NP is shown in Fig. 1. Consistent to previous studies (Düring et al., 2002; Milinovic et al., 2015a; Milinovic et al., 2015b; Zhi and Liu, 2018) both pollutants were best fitted with liner isotherms in both extraction steps. Isotherms are shown for five soils differing in SOC contents, which are representative for the SOC range of the data set.

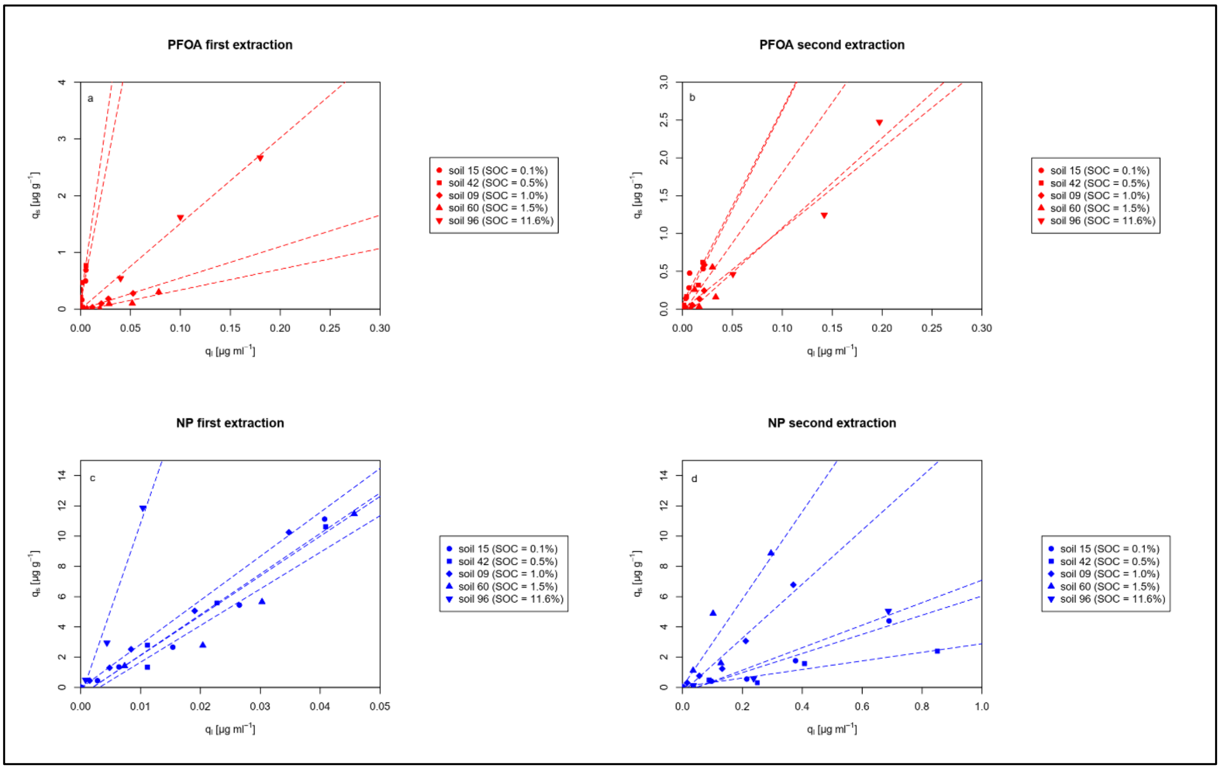


Fig. 1. Linear sorption isotherms for five representative soils with varying SOC contents, representing the first (a) and second (b) extraction of PFOA and the first (c) and second (d) extraction of NP.

The desorption behavior of PFOA and NP were tested on one-year incubated samples. Since samples from a previous study were used, the start concentrations of NP and PFOA differed for all soils. The various start concentrations are shown in Appendix #1. It is notable, that with an average of 97%, the initial NP concentrations in the restored samples were much higher, than that of PFOA (14%), because the sorption potential of NP is much higher than that of PFOA (Chapter 2). However, the PFOA sorption varied widely between 1.7–71.8% while NP sorption ranged between 86.6–99.8%, respectively (Tab. 2).

Tab. 2. Sorption-Desorption behaviors of the PFOA and NP data sets.

Soil Properties		PFOA (n=61)				NP (n=71)			
		Mean	S_D	Min.	Max.	Mean	S_D	Min.	Max.
Sorption	[%]	14.3	14.0	2.3	71.8	97.2	3.0	86.6	99.8
$K_{D\text{-sor}}$	[ml g^{-1}]	2	4	0	26	1114	1145	65	4768
1st Desorption	[%]	46.0	29.0	1.4	97.5	4.3	1.8	1.0	9.5
$K_{D\text{-des}}^{1}$	[ml g^{-1}]	132	608	0	4652	320	225	98	1092
2nd Desorption	[%]	42.9	23.0	8.2	113.7	38.6	24.4	2.9	89.5
$K_{D\text{-des}}^{2}$	[ml g^{-1}]	23	19	2	113	57	93	2	371
Hysteresis	[-]	0.7	0.4	-0.8	1.0	0.6	0.2	0.0	0.9

For PFOA, the extraction agent water was able to desorb nearly half of the contaminant with an average of 46%. In some soils, the desorption exceeded 95% of primally sorbed contaminant. In 7 soils the desorption was below 5%. Those soils had very low SOC (< 0.5%) and iron oxide (< 0.4%) contents. Furthermore, those soils were sandy with more than 75% sand and, therefore, the primarily sorption was low and did not exceed 10%. The second extraction agent ethanol was able to desorb an average of additionally 43% of the surfactant. The desorption portioning coefficients ($K_{D\text{-des}}^{1}$ and $K_{D\text{-des}}^{2}$) were almost always higher than the sorption ($K_{D\text{-sor}}$) values, indicating hysteresis. The desorption hysteresis coefficient proofs this fact, since the average value is 0.7 indicating higher desorption potentials.

In soils with high SOC contents, PFOA desorption rates of the first and second extraction exceeded 100% (Fig. 2).

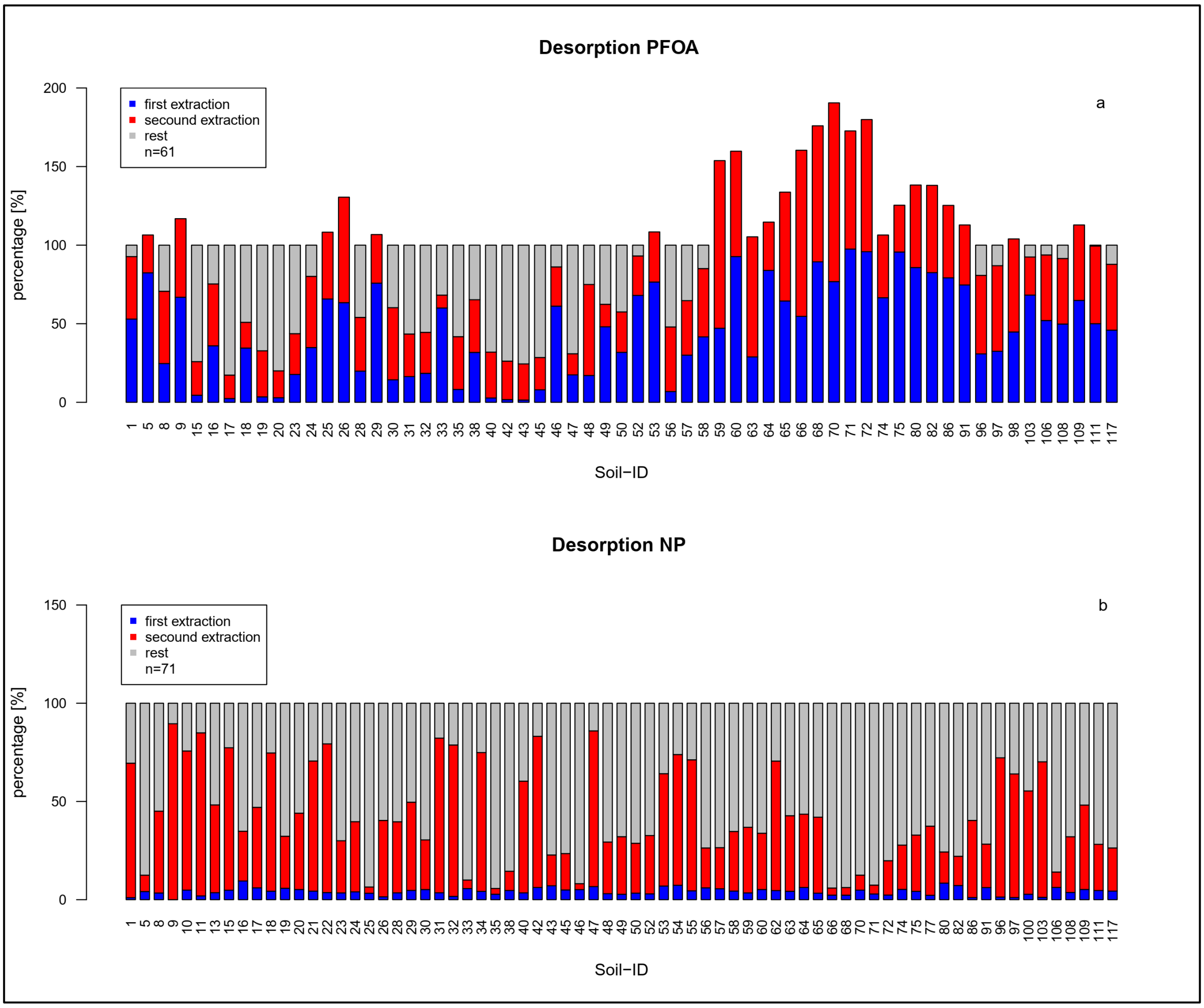


Fig. 2: Desorption of a) PFOA and b) NP in the first and second desorption step.

Since, PFOA has a high surface activity, the standard deviations of sorption and desorption experiments were much higher than that of NP (Tab. 2, Appendix #2). Therefore, measurement errors can lead to the high recovery rates in the PFOA data set. In addition, the experimental design differs from the international standard, since we did not use the HPLC-MS method to quantify PFOA concentration. The used method of radioactive PFOA concentration detection, however, has some advantages over the HPLC-MS method. The surfactant tends to sorb to all surfaces and laboratory-ware, which leads potential error sources (Shoemaker et al., 2009). This effect is specifically high in case of filtration. The recovery of PFOA from filter membranes can lead to detection error of up to 79% (Lath et al., 2019). With the use of radiolabeled PFOA, the exposure to laboratory materials such as spatula and tubes is reduced in comparison to the German DIN standard (38414-14, 2011) and international standard (Li et al., 2018a; Zhang et al., 2019), where Liquid-liquid extraction or solid phase extraction with subsequent filtration must be performed prior to the detection with a HPLC-MS. Furthermore, the detection with a ß-counter only takes up one pipette step after the shaking and centrifugation of the contaminant. Furthermore, the centrifugation makes the filtration unnecessary in this specific method. Hence, the disturbance variables in this method are very low and can be quantified by analyzation of blank samples.

Nonetheless, the chosen method for PFOA detection also revealed some sources of error. As shown in Fig. 3, the centrifugation of the contaminants had an influence on the recovery rate of the supernatant. Due to the centrifugal forces, the contaminant, which is sorbed to DOC, is pushed to the bottom of the tubes. This led to a decline of the recovery rates with a mean amount of 11%.

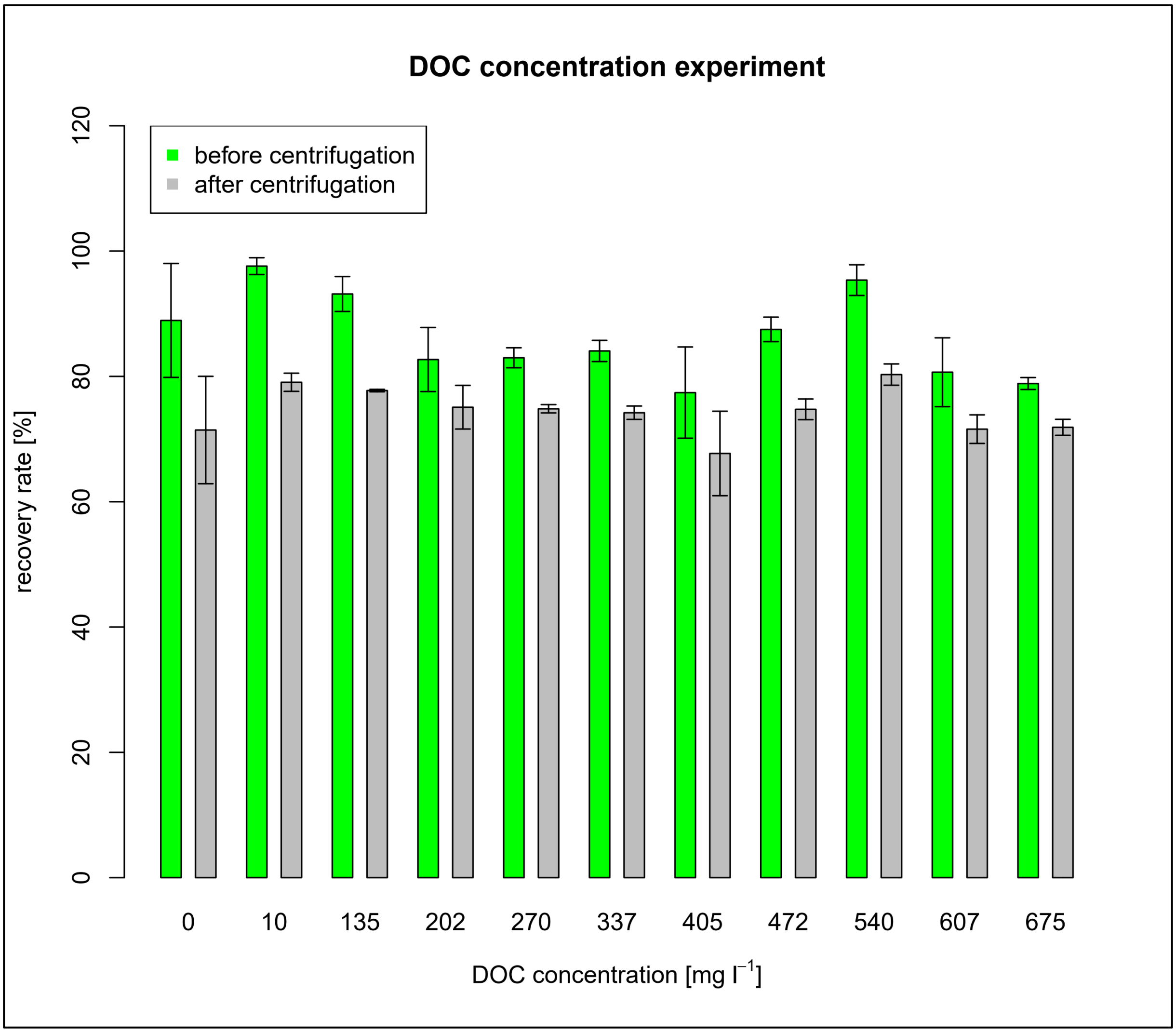


Fig. 3. Influence of centrifugation and DOC content on the recovery rate of PFOA. The DOC concentration of 0 mg l^{-1} is representing the blank.

We wanted to find out, if this effect was increased by the DOC content. Thus, ten different DOC concentrations were tested. Since the fluctuation before and after centrifugation were higher in samples with less DOC content and in the blanks, it can be assumed, that DOC inhibits the centrifugation effect. Nonetheless, the effect could also be the result of measurement errors.

Therefore, the underestimated PFOA concentrations in the sorption experiments led to recovery rates over 100% in the desorption experiments in the second desorption step. The centrifugation processes subsided the ^{14}C-concentration in this test, but the DOC content had no statistical effect in this context. Since the recovery rate of PFOA decreases with increasing DOC content both before and after centrifugation, an influence of the turbidity of the sample cannot be excluded. The higher the DOC content, the browner the soil solution becomes. Since the measurement method is based on counting light flashes, turbidity can lead to an underestimation of the surfactant content.

Since the underestimation of the surfactant contents in the second desorption step could not be conclusively clarified, the second desorption was not further analyzed for both PFOA and NP.

For NP however, water extraction was not able to dissolve more than 10 % of previously sorbed NP. The irreversible desorption is consistent to previous studies (Cheng et al., 2017; Milinovic et al., 2015a). In the second extraction step however, ethanol was able to desorb about 39 % of the contaminant with a maximum of 90 %. Nevertheless, in some soils, not more than 3% of the initial NP contamination was extractable. Due to the fact that ethanol destroys the soil structure and dissolves organic bonds (Rokunuzzaman et al., 2019), the release of NP in the environment can be considered negligible.

3.3 Mineralization of the restored samples

Since soil samples were stored over one year, we wanted to find out, if the surfactants were mineralized during the incubation period. Since it has been shown, that sodium azide reduces bacterial populations in soils (Chen et al., 2004; Torang et al., 2003; Wolf et al., 1989) it is often used as a sterilizing agent in laboratorial sorption and desorption experiments (Lesan and Bhandari, 2003; Sharer et al., 2003). Nevertheless, NP is known to be easily decomposed in soil environments (Topp and Starratt, 2000). For example, Dettenmaier and Doucette (2007) found a NP mineralization of 90 % (initial concentration 47 mg kg^{-1} NP) in 150 days. PFOA, however, is difficult to degraded in soils (Pan and Zhang, 2015) and is therefore classified as persistent (Lin et al., 2016; Wang and Zhang, 2016).

To quantify the accumulative mineralization in our experiment within the storage period of 12 month, an incubation experiment was conducted and mineralization of the contaminants was monitored for half a year. Four soils were selected with varying soil properties as well as diverse desorption behaviors (Tab. 3). Soil 1 was chosen, because it is a very sandy soil (86.7 %) with low pH (4.2) and moderate SOC (1.4 %). Furthermore, it is a soil with one of the highest PFOA sorption potentials (23.1 %) and it had a low NP desorption. Soil 47 was chosen, because of its low SOC content (0.4 %) in combination with a very high sand portion (98 %). Because of the low sorption of PFOA (1 %) the desorption potential was minimal. Simultaneously, was the NP sorption with 90.9 % comparatively low. The soils 54 and 72 were chosen, because of their high SOC (2.3 and 2.4 %), CEC$_{eff}$ (89 and 137 mmol$_c$ kg^{-1}) and Fe$_a$ (0.2 and 0.6 %) contents. On this data basis, it was possible to quantify surfactant mineralization under different soil conditions.

Tab 3. Soil sample characteristics and desorption results of the four samples in the mineralization experiment. For physiochemical analyzation methods see Tab. 1.

		PFOA				NP			
Soil-ID		1	47	54	72	1	47	54	72
Sorption	[%]	23.1	1.0	-	0.8	99.6	90.9	99.5	99.6
1st extraction	[%]	53.0	17.5	-	95.8	1.0	6.7	7.3	2.4
2nd extraction	[%]	39.7	13.4	-	84.1	68.4	79.2	66.5	17.5
Hysteresis	[-]	0.7	1.0	-	-0.8	0.9	0.4	0.2	0.8
SOC	[%]	1.4	0.4	2.3	2.4	1.4	0.4	2.3	2.4
DOC	[mg kg^{-1}]	110.1	66.3	182.68	216.2	110.1	66.3	182.7	216.2
DOC/SOC$_{ratio}$	[-]	0.7	1.0	0.2	-0.8	0.7	1.0	0.2	-0.8
Sand	[%]	86.7	98.3	49.3	-	86.7	98.3	49.3	-
Silt	[%]	7.0	0.9	45.4	-	7.0	0.9	45.4	-
Clay	[%]	6.3	0.9	5.2	-	6.3	0.9	5.2	-
pH	[%]	4.2	4.7	7.3	5.8	4.2	4.7	7.3	5.8
Fe$_a$	[%]	0.0	0.0	0.2	0.6	0.0	0.0	0.2	0.6
Al$_a$	[%]	0.0	0.1	0.2	0.2	0.0	0.1	0.2	0.2
BET	[m^2 g^{-1}]	0.3	1.1	1.1	7.8	0.3	1.1	1.1	7.8
Pore diameter	[nm]	1.7	1.8	2.2	2.2	1.7	1.8	2.2	2.2
CEC$_{eff}$	[mmol$_c$ kg^{-1}]	30.0	19.5	88.9	137.1	30.0	19.5	88.9	137.1
Chloride	[mg kg^{-1}]	1.9	0.7	21.3	10.7	1.9	0.7	21.3	10.7
Sulfate	[mg kg^{-1}]	8.0	0.0	14.4	15.4	8.0	0.0	14.4	15.4
Calcium	[mg kg^{-1}]	0.3	0.4	59.1	50.1	0.3	0.4	59.1	50.1
Magnesium	[mg kg^{-1}]	0.3	0.0	4.2	7.2	0.3	0.0	4.2	7.2

The accumulative mineralization for PFOA and NP in the four soils is presented in Fig. 4. In the experimental setup, each soil was represented by three replicates. The replicates were sampled five times each over the measurement period. Thus, a sample size of 15 results for each soil and pollutant combination.

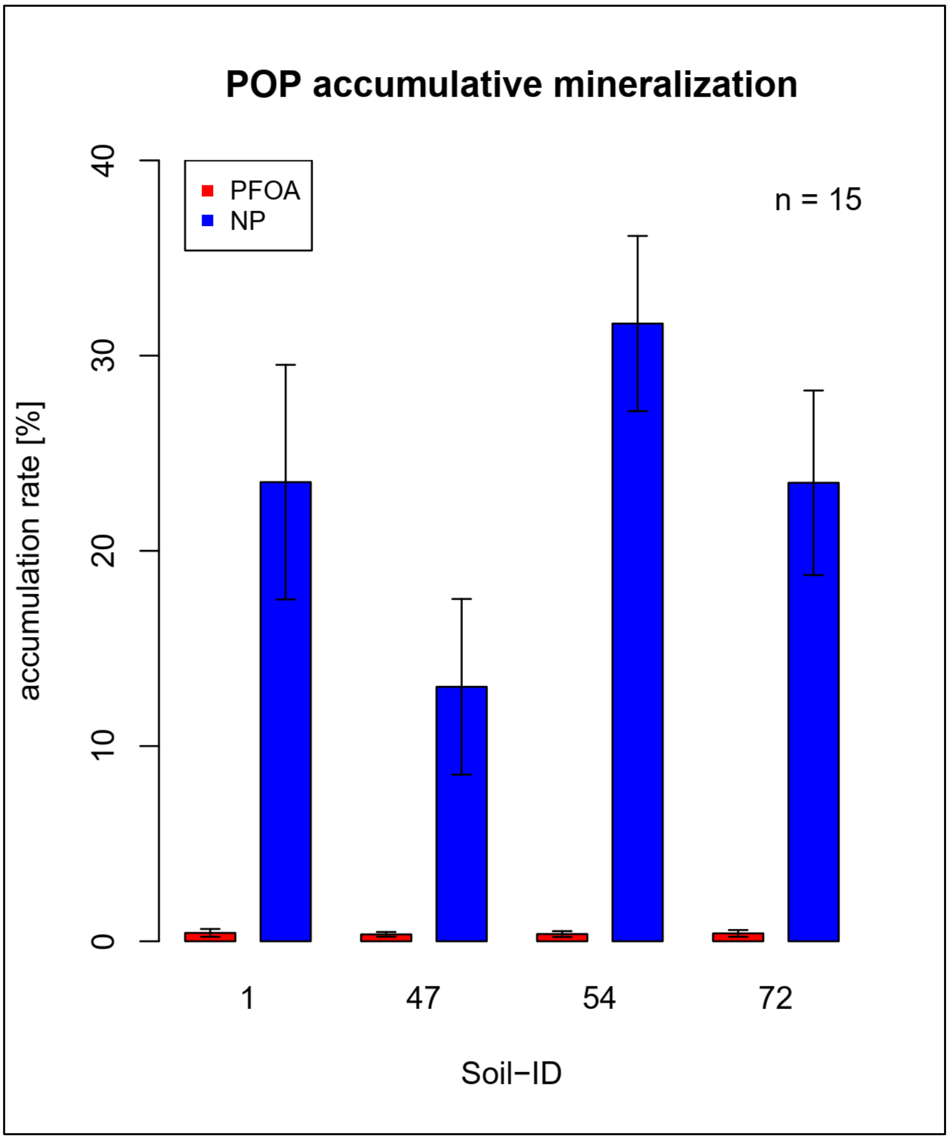


Fig. 4. Accumulative mineralization of PFOA and NP within a storage period of six month.

The cumulative mineralization rate of PFOA in this experiment was neglectable, since a one percent mineralization rate was not exceeded over the observation time. Hence, it was verified that PFOA is persistent within this test series. This result is, as already mentioned, consistent with several studies (Bolan et al., 2021; Cheng et al., 2008; Choi et al., 2019). The quantified PFOA concentrations in the potassium hydride solution were potentially measuring errors.

The NP concentrations, however, were much higher and the mineralization rate was varying between 10–32%. The lowest mineralization was found in the soil with the lowest SOC and DOC content. The results are showing, that NP was mineralized over the time period at an average of 23%, although sodium azide was used to inhibit microbial activity. Nevertheless, sodium azide is a bacteriostatic agent and not a sterilant. That is why the microbial community remained present and only the microbial activity was inhibited for a short time. After that, the inhibition of the microbial activity losses its effect. Therefore, microbial activity was possible after a short time period (Chefetz et al., 2006; Rozycki and Bartha, 1981).

In this experiment, NP decomposition was detected after 27 days, which is consistent to Hendrix et al. (2019), who found microbial activity after several days in soils mixed with NaN_3. Therefore, the chosen ^{14}C-method was not able to describe the desorption behavior of NP but that of NP and its metabolites. Since, NP concentrations were not detected, statistical analyses to describe NP desorption in dependence on soil characteristics were excludes from further analysis. However, since it was proven that PFOA was not mineralized, PFOA desorption is further analyzed.

3.4 Desorption potentials as a function of the SOC and DOC content

To explain the desorption mechanisms of PFOA, linear regressions of the pollutant desorption was plotted in dependence on SOC and DOC content (Fig. 5).

In the following, data that is marked with ** is indicating a significance level of 0.01 while data with * show a significance level of 0.05. Within the first extraction step, the regression between SOC and the desorption was not significant. Consistent to the sorption experiments (Chapter 2) the desorption results in the SOC range 0 to 0.5 % ranges widely (2–77 %). Nonetheless, low but significant correlations between SOC and the desorption were found (0.4**). Similar results were found in dependence of the DOC content. While the regression shows a wide spread of PFOA desorption (1–82 %) in soils with low DOC (< 200 mg kg^{-1}) contents, a low but significant correlation was detected (0.3*).

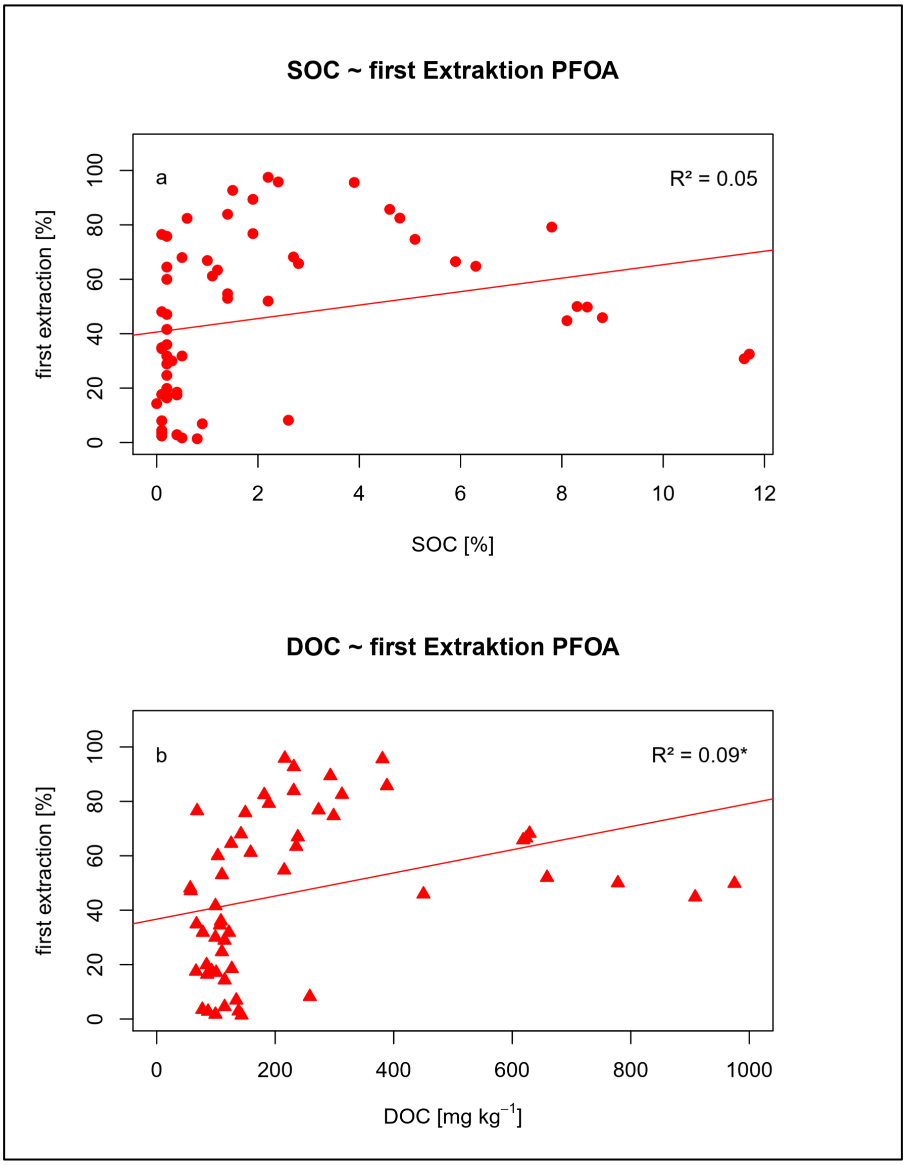


Fig. 5. Dependences of the desorption of PFOA on the SOC (a) and DOC content (b).

Based on the varying desorption behavior in dependence of the SOC and DOC content, the data set was split up into three SOC groups as shown in Fig. 6.

In contrast to the sorption experiments, the first subgroup was defined by SOC contents smaller than 0.7% and not 0.5%, since the multiple regression analyzes for soil with SOC contents lower 0.5% was overfitted. Hence, the low SOC subgroup needed more data. Since, similar regressions were found in dependence on the three different DOC content groups the results are not presented.

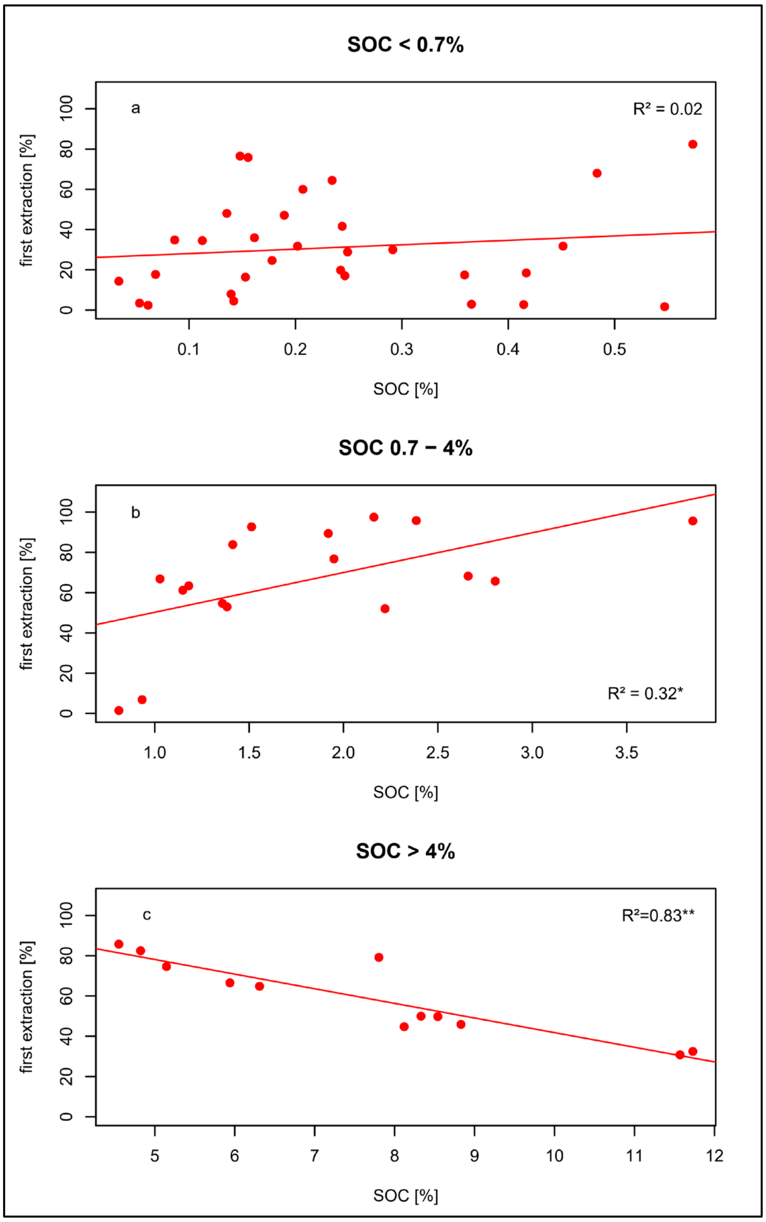


Fig. 6. PFOA desorption results in dependence of the SOC content in three different groups- (a) SOC below 0.7%, (b) 0.7-4% and (c) over 4% SOC content.

In soils with low SOC (< 0.7%) and DOC (< 200 mg kg^{-1}) contents, the desorption varied between 2–82%. The regression was slightly positive, but not statistically significant (Fig. 5a).

In this data set, the desorption was independent from SOC and DOC contents. This connection was also found during the sorption experiments.

In soils with SOC contents between 0.7–4%, the regression was positive and significant at a significance level of 0.05. The linear model ($y = 19.76 * x + 30.49$) was able to explain 32% of the data variations. In terms of linear regression, the SOC content appears to have a small but positive effect on desorption, but it is oppositional to the expected influence. However, no significant correlation could be determined in this context. In order to adequately describe desorption in this group, additional soil data must be used as explanatory variables.

Above the threshold of 4%, however, the dependences were significantly negative correlated. With the linear regression model $y = –7.27 * x + 114.5$ the variations within the data were explained by up to 83% (p-value < 0.05). In addition, a significant correlation (-0.91**) was found for soils with SOC contents above 4 %. The negative dependence of PFOA desorption on the SOC enriched soils was expectable, since SOC is the main sorbent of the surfactant in topsoil samples (Chapter 2).

Another important variable in the sorption experiments was soil pH. Soils with low pH-values under 5.5 showed significant correlations between SOC and the sorption behavior, as a result of the hydrophobic characteristics of PFOA. In soils with pH-values above 5.5, however, the contaminant is negatively charged which leads to electrostatic interactions with the soil mineral components (Groffen et al., 2019; Li et al., 2018b) and the polar properties prevent hydrophobic interactions with SOC. Thus, weaker correlations were found in this pH subgroup in the sorption test series. Same analyzes were conducted with the desorption data (Tab. 4).

Tab. 4. Correlations between SOC contents and desorption behavior [%] in different pH subgroups.

pH group	n	R^2 SOC	mean SOC [%]
< 4.5	10	-	2.73
< 5	18	0.015	2.41
< 5.5	22	0.06	2.46
> 5.5	39	0.46**	2
> 6	33	0.53**	1.58
> 6.5	26	0.54**	1.6
> 7	18	0.66**	0.69

As expected, the threshold of 5.5 pH also plays an important role for the desorption processes. The relationship between pH and SOC for the desorption experiment was inverse to the sorption behavior. The pH groups with values beneath 5.5 showed no correlation between the SOC content and the desorption behavior, although SOC values were with over 2 % very high. Whereas above the threshold of 5.5 the correlations were significant and increased with increasing pH values. The average SOC contents decrease with increasing soil pH. It can therefore be assumed that, in addition to the changing surfactant properties, the decreasing SOC content also has an influence on the increasing correlation coefficients.

3.3.2 Desorption potentials as function of various soil properties

The physicochemical properties SOC and DOC were able to explain about 40% of the variance of PFOA desorption in the first extraction step. The correlation between these properties and the desorption behavior was negative. This means, that SOC and DOC can inhibit desorption, especially in topsoils, where SOC contents are much higher than in subsoils (Angst et al., 2016; Heitkotter and Marschner, 2018). This relation would be expected, since PFOA absorbs to SOC in topsoils.

However, 60% of the variability remains unexplained. Therefore, a multiple regression analysis was conducted under consideration of all physicochemical soil properties. The backward elimination model was used, in order to obtain statistically significant soil properties.

Multiple regression analyses were executed separately, both for the complete data set, as well as for the previously described SOC subgroups. Therefore, the processes in subsoils, which are depleted in SOC and DOC contents, could be better understood (Heinze et al., 2018; Heitkotter et al., 2017). The results are shown in Tab. 5.

Tab. 5. Multiple regression analyses. Standardized ß-coefficients with significant influences on the regression are shown. The R² value is the figure of merit of the regression analyses.

Sample set	n	R²	Standardized ß-coefficients of the independent model variables							
			SOC	Clay	pH	Fe_A	Al_A	BET	Ca^{2+}	Na^+
all	61	0.44		1.04**			0.23*	-0.66*		
SOC<0.7	31	0.69	-0.36*	0.43*	-0.96**		0.37*		0.6*	0.36**
SOC 0.7-4	18	0.68	-0.64*	2.15*		0.76*		-2.3*		
SOC > 4	12	-								

For the complete data set, 44% of the variability of the first desorption data was explained by clay and aluminum contents and the BET surface. It was noticeable, that SOC was not an explanatory variable in the complete data set model, although the correlation between SOC and desorption was significant. However, with a standardized ß-coefficient of 1.04 clay was mainly controlling PFOA desorption, as well as the BET surface with a coefficient of –0.66. The high surface activity of the contaminant explained this relationship. The larger the soil surface and the more clay minerals are available, the stronger are the interactions with the surfactant. This leads to a lower release of PFOA in soils with large surface structures and high clay mineral contents.

For the SOC subgroups, the explained variance increased to 69 and 68%, respectively. In the subgroup with SOC below 0.7%, SOC, pH, calcium, and natrium were added as explanatory variables, while the BET surface was not significant anymore. With a standardized ß-coefficient of –0.96, soil pH was dominating the desorption of PFOA in this model. This connection matched with the results of Tab. 4. Soils with high pH values tend to desorb more PFOA, than soils with lower pH values. Because, the adsorption potential of the electrostatic surfactant properties and the soil mineralogy in soils with high pH values (> 5.5) are weaker, than the adsorption between the hydrophobic interactions of PFOA with the SOM in soils with high pH values (< 5.5).

With an R^2 of 0.68, the goodness of the third model was similar to the second model, albeit the explanatory variables differed. Besides SOC and clay content, also iron and BET had an influence in this model. The ß-coefficients in this model were higher, than in the first two models. But similar to the complete data set, clay content and the soil surface area were dominating the desorption behavior of the contaminant in this SOC range.

Multiple regressions could not be performed for SOC enriched soils, as too few samples were available in this model. If the independent variables were reduced, the model quality was lower than that of the whole data set ($R^2 = 0.4$). However, the SOC content was already able to explain 83% of the data. Thus, the fit of the linear model for soils with SOC contents above 4 % was already higher than the fit of the other multiple regression models.

4. Conclusion

The desorption potential of PFOA in SOC depleted as well as in SOC enriched soils was much higher than that of NP. In soils with SOC contents above 4%, SOC was dominating the dissolubility of PFOA negatively. This means, that with increasing SOC content desorption decreased. In SOC depleted soils the relevance of SOC for the PFOA desorption decreased drastically. The desorption potential of soils with low SOC contents and high pH-values was very high, which lead to a high risk of PFOA loss within those soils. For the intermediate group, clay and BET surface were the controlling variables. SOC content played only a minor role.

Nevertheless, the collected data suggest that PFOA can be desorbed by up to 45% on average, regardless of soil properties. Thus, the risk of PFOA losses under natural conditions can be high, not only in fresh samples as tested before, but also in aged samples. When the SOC contents are high and the pH-values are under the threshold of 5.5 the release of PFOA is lower than in soils with low SOC and clay mineral contents.

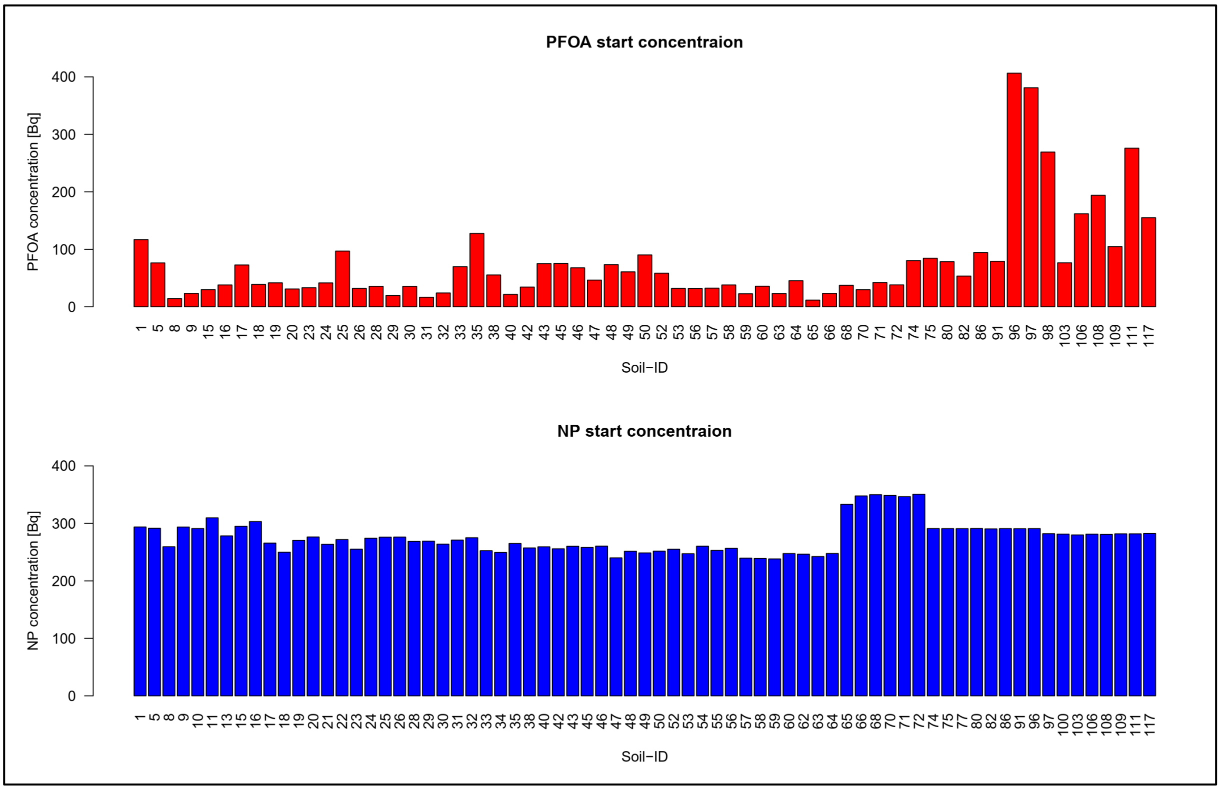
The desorption of NP could not be predicted and explained with this method, since the surfactant was mineralized within the storage period and the radiocarbon results were not representative for this molecule. Nonetheless, the results indicated that NP is not extractable under natural conditions, even if it is metabolized. Therefore, soils are potential sinks for NP. For further experiments, another method should be used to quantify NP concentration or soils must be sterilized instead of spiked of sodium azide to avoid microbial activity over the storage period.

Acknowledgement

We would like to thank the Geographical Survey NRW and the Institute of Soil- and Groundwater-Management from the University of Wuppertal for providing the soil samples. We would also like to thank the RUBION at the Ruhr-Universität Bochum for providing us laboratories and equipment for working with radioactive chemicals and Heidrun Kerkhoff and Katja Gonschorek for laboratory assistance.

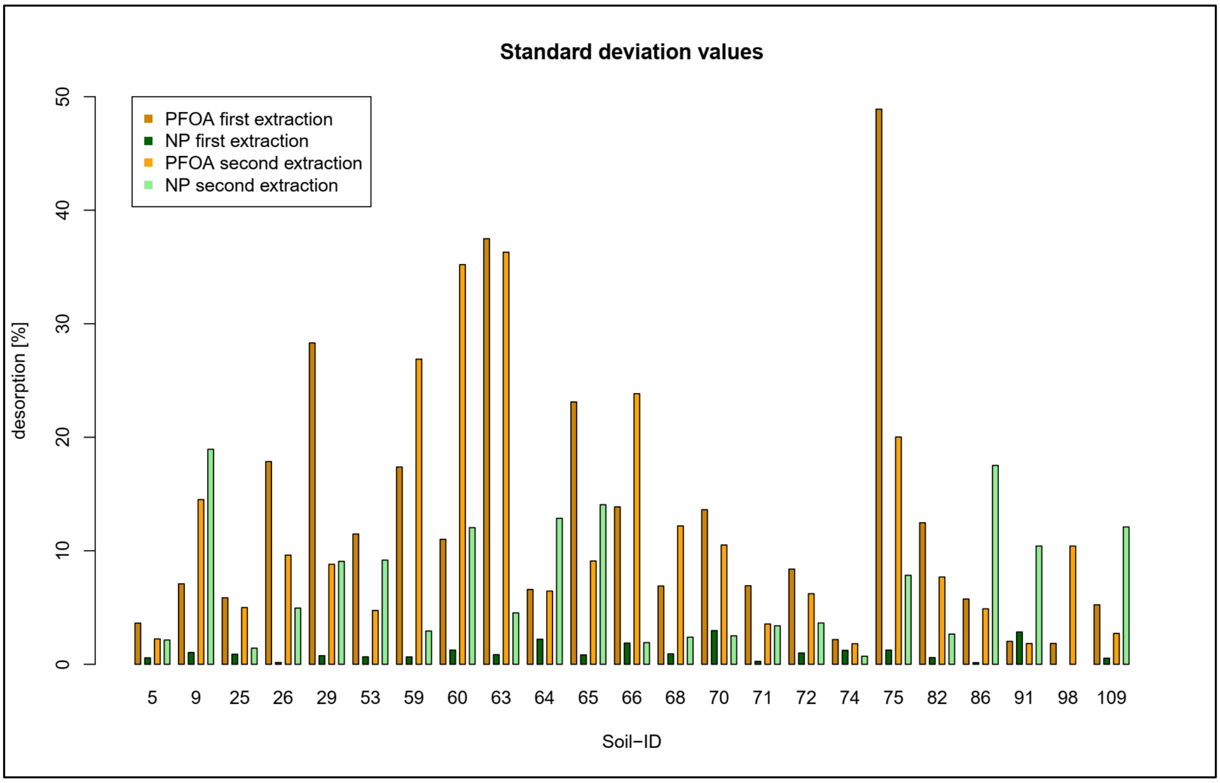
Appendix

#1



Appendix 1. Initial concentrations of all soil samples in Becquerel.

#2



Appendix 2. Desorption standard deviations for PFOA and NP in the first and second extraction step for all samples with overall desorption above 100 % in the PFOA data set.

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Chapter 4

The sorption and desorption behavior of PFOA in arable top- and subsoils in dependence on varying soil matrix characteristics.

Based on the final report of the project “investigations on the sorption mechanisms of PFAS in Soils” from the Ministry for Environment, Agriculture, Conservation and Consumer Protection of the state of North Rhine-Westphalia.

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Introduction

Surfactants are a group of chemicals, which are known for their cleaning and solubilization properties (Cormier et al., 2022; Tang et al., 2006). They consist of a polar hydrophilic head group (charged or uncharged) and a nonpolar hydrophobic hydrocarbon tail. Synthetic, or anthropogenic surfactants are economically important, since they are widely used, for example, in household cleaning products (Schick and Oellig, 2019), textiles (Di Corcia, 1998), paints (Deodhar et al., 2020), medical applications (Krafft and Riess, 2007), firefighting foams (Magrabi et al., 2002), or surface protecting agents (Kostov et al., 2009).

Per- and polyfluoroalkylated substances (PFAS) are one group of these anthropogenic surfactants. All have a perfluoroalkyl chain of varying C-length (hydrophobic) and a terminal functional head with a carboxylic or sulfonate group (hydrophilic) (Oliver et al., 2019; Zaggia et al., 2016). The surfactants have unique physicochemical properties, such as chemical, radiation and biological stability, extreme low surface tension, and a high surface activity (Yesilyurt et al., 2020; Zaggia et al., 2016; Zhang et al., 2019b). PFAS are of global concern, because of their ubiquitous distribution (Ahrens et al., 2011; Campos Pereira et al., 2018), persistence (Houtz et al., 2013), bioaccumulative potential (Conder et al., 2008), and toxicity (Apelberg et al., 2007). As soon as PFAS are introduced into the environment, for example through the application of sewage sludge, decontamination is only possible through soil washing or heat treatment, due to their high persistence (Ross et al., 2018). Since these methods are effective for PFAS, but are associated with high cost and time, it is important to obtain accurate knowledge of sorption and desorption processes to ensure retention of the pollutant. Remediation has been performed for decades for metals, pesticides, and organic pollutants (Brown et al., 2005; Cornelissen et al., 2011; Ghosh et al., 2011). So far, numerous experiments have been carried out in which the retention of PFASs was tested on biochar (Kupryianchyk et al., 2016), modified clays (Das et al., 2013), mixed mineral-organic materials (Lath et al., 2018), as well as several other materials, with varying degrees of success.

In contrast to other persistent organic pollutants (POP), the environmental distribution of PFAS differ due to their extreme surface-active properties (Goss and Bronner, 2006). The lead compound perfluorooctanoic acid (PFOA) more closely investigated in this study, has a high-water solubility (Campbell et al., 2009; Deng et al., 2012). Thus, it is easily transported in an aquatic environment (Prevedouros et al., 2006; Richardson and Kimura, 2016). Furthermore, PFAS have a high leaching capacity which is expressed by the low k_{OC} values in soils and sediments ($10^{3.0}$ for PFOS and $10^{2.1}$ for PFOA) (Zareitalabat et al., 2013). This additionally promotes their transport in the environment. At the same time, both the carbon-fluorine chain, and the carboxylic head group (-COOH) of, for example, PFOA, provides opportunities to adsorb onto surfaces of several environmental solid matrices (Mei et al., 2021; Wang et al., 2011). The simultaneous hydrophobicity and hydrophilicity result in the fact that, unlike other POPs, PFAS spreads in the environment through both hydrophobic and electrostatic interactions (Lyu et al., 2020b; Xing et al., 2021). Therefore, predictions of environmental behavior are not solely determined by a single sorbent bulk property, such as the SOC content (Barzen-Hanson et al., 2017; Li et al., 2018b). Several studies have investigated the transport behavior of PFAS in the environment (Brusseau et al., 2019; Gassmann et al., 2021; Zhou et al., 2021). The results suggest, that the transport of the surfactants is significantly influenced by the physiochemical properties of the soil (i.e. OM, minerals, and surface roughness) (Li et al., 2018b; Lyu et al., 2020a; Lyu et al., 2019), the chemical composition of the background solution (i.e. pH, ionic strength, cation type) (Lv et al., 2018), co-existing organic compounds (e.g. non-aqueous phase liquids) (Brusseau, 2018; McKenzie et al., 2016; Van Glubt and Brusseau, 2021), and water saturation (Brusseau and Van Glubt, 2019; Li et al., 2021; Lyu et al., 2018).

In addition to studies on the transport of PFASs in classical column experiments, numerous studies on the sorption and desorption of the pollutants were also undertaken(Li et al., 2019; Mejia-Avendano et al., 2020; Zhang et al., 2019b). Influences on the sorption of PFAS on soils result both from the physicochemical properties of the PFAS and from those of the soil

(Enevoldson and Juhler, 2010; Zareitalabat et al., 2013). It should be noted that the sorption behavior is strongly dependent on the respective SOC values and the soil pH. In topsoils with high SOC contents (Heinze et al., 2018), the hydrophobicity of the pollutants determines the sorption behavior if the pH remains under a threshold of 5.5. Due to the weaker protonation with increasing pH, the physicochemical properties of PFOA changes from hydrophobic interactions with the organic matter to electrostatic interactions with charged soil particles like clay minerals or iron oxides (Oliver et al., 2019; Tang et al., 2010). However, soils in middle Europe acidify on the surface under natural conditions (Wan et al., 2013), which is why several studies have identified the SOC content as the main sorbent for PFOA in topsoils (Ahrens et al., 2011; Campos Pereira et al., 2018; Milinovic et al., 2015).

There are still several uncertainties about how soil matrix conditions, e.g., pH, surface-bound cations or temperature, can influence PFAS sorption in soils (Li et al., 2018a). Campos Pereira et al. (2018), studied the influence of cation composition and pH to the sorption of PFAS on an organic soil horizon. They found, that the cation effect on long-chain PFAS (C_8–C_{13}) is much smaller than on short-chain PFAS (C_4–C_7). In their experiments, the long-chain PFAS, like PFOA were preferentially sorbed to the condensed domains of the humin fraction. Thus, pH variations predominated the sorption processes instead of cation effects, while the short-chain PFAS were bound to humic and fulvic acid, where cation effects are more significant. In contrast to that, Higgins and Luthy (2006) found a significant cation effect on PFAS sorption with increasing Ca^{2+} concentrations, indicating that electrostatic interactions played an important role in the sorption process. Unlike pH and cation variation effects on the sorption of PFAS, temperature influences have been insufficiently studied so far. Jia et al. (2010) investigated the temperature effect on PFOS sorption in soils. They found an increased sorption with increasing temperatures, since the sorption process was predominated by diffusion of PFOS on humic acid. They were able to measure a doubling of sorption with a temperature increase of 30 °C, indicating a spontaneous, endothermic, and entropy driven process. Nonetheless, there is no data for the temperature influence of PFOA sorption in soils.

However, since the water solubility of PFOA decreases significantly with decreasing temperatures (9.5 g l^{-1} at 25 °C and 3.4 g l^{-1} at 22 °C), a temperature effect on the sorption of the surfactant is suspected (Campbell et al., 2009; Deng et al., 2012).

The so far insufficient investigations on the temperature influence and the contradictory statements on the influence of cations and pH changes on PFOA sorption in soils, require a more detailed investigation. Thus, the aim of this study was to better understand sorption and desorption processes of PFAS in soils, with a special focus on the lead substance PFOA, based on their special physiochemical properties. In addition to the general description of the sorption and desorption processes of PFAS in soils, it should also be clarified to what extent changing environmental properties (i.e., pH, cation concentration, and temperature) influence the retention of the contaminants in soils. As a result, a better overview under which PFAS can be remobilized in soils is provided, to improve the risk assessment for this group of contaminants.

2. Methods and Materials

2.1 Chemicals

The sorption experiments were conducted with the persistent organic pollutant PFOA. The surfactant has a water solubility of 9.5 g l^{-1} at 25 °C and 3.4 g l^{-1} at 22 °C, respectively (Campbell et al., 2009; Deng et al., 2012). PFOA is a strong acid with a pk_a value of –0.5 (Campbell et al., 2009). Radiolabeled [1-^{14}C] PFOA molecules were used for the sorption experiments, with a specific activity of 1.85–2.22 GBq mmol^{-1}. The radiolabeled chemicals were solved in ethanol, for analytical detection (purchased from Hartmann Analytics, Braunschweig, Germany). To get the desired concentrations for the sorption experiments the labeled PFOA molecules were mixed with unlabeled molecules. The labeled chemicals had a purity of 99% (American Radiolabeled Chemicals, U.S.A.) and the unlabeled chemicals had a purity of 95% (Sigma Aldrich, Germany). The unlabeled surfactants were purchased as powder from Sigma Aldrich (Munich, Germany) and were also dissolved in ethanol for further experimental processing.

2.2 Soil samples

A pool of 39 soil samples from 20 different agricultural sites across North Rhine-Westphalia (NRW, Germany) was used. All samples were provided by the Geological Survey NRW and the Ministry for Environment, Agriculture, Conservation and Consumer Protection of the state of North Rhine-Westphalia (LANUV NRW). The data set was built up of 21 topsoil (0–30 cm) and 18 subsoil (30–60 cm) samples, highly varying in chemical and physical properties (Tab. 1). For further processing, all samples were air-dried and sieved to less than 2 mm.

2.3 Sorption and desorption experiments

PFOA sorption was determined using the batch equilibrium method (OECD, 2000). All experiments were performed in 15 ml polystyrene centrifuge tubes with a polystyrene screw cap (Thermo Fisher Scientific, Germany), to avoid surfactants adsorption to tube surfaces (Milinovic et al, 2015a). To ensure sterile condition, all materials like spatula, centrifuge tubes, screw tops, and pipettes were purged with ethanol. Furthermore, water used for the background solutions was autoclaved prior to use.

The background solution (0.01 M $CaCl_2$ and 0.002 M NaN_3) was spiked with a mixture of labeled and unlabeled PFOA in concentrations of 21.5, 75, 150, and 300 µg l^{-1}. For the batch assays, 0.5 g soil and 5 ml background solution were added to the centrifuge vials. NaN_3 was used to inhibit microbial activity throughout the batch experiments (Hendrix et al, 2019).

Controls without surfactants and blanks containing no soils were prepared in the same way. All samples were shaken end over end in the dark at a constant room temperature of 21 °C. According to previous studies (Eberle et al., 2019; Schaefer et al., 2019), the equilibrium time was set to 24 h. After this time the samples were centrifuged at 3000 rpm for 30 min and the supernatant was then removed. For the determination of radioactivity in the solutions, 12 ml of scintillation cocktail (Ultima Gold, Perkin Elmer, Waltham, USA) was added to 2 ml of the supernatant that was subsequently analyzed by liquid counting with a Tri-Carb 2800TR (Perkin Elmer).

In order to describe the mechanisms of pollutant sorption to the soils, the data obtained from the sorption experiments was fitted to linear isotherms. Based on the linear isotherms, the K_D value as the ratio between equilibrium concentration in the soil matrix and that of its aqueous phase solution were calculated according to equation 1:

$$K_{D-sor} = \frac{C_s}{C_w} \qquad (1)$$

where C_s (µg g^{-1}) is the amount adsorbed to the soil, and C_w (µg ml^{-1}) is the equilibrium solute concentration.

To determine the desorption potential of PFOA, the samples used in the sorption experiments were used again after the supernatant was removed and 5 ml fresh background solution was added to the samples. The desorption experiments were conducted in the same way as the sorption experiments. Similar to the sorption experiments, K_D values were calculated for the desorption data, according to equation 1 ($K_{D\text{-}des}$). Furthermore, the hysteresis coefficient was determined to describe the relation between the sorption and desorption strength. Equation 2 was modified according to Xiangke et al. (2000):

$$H = \frac{K_{D-des} - K_{D-sor}}{K_{D-des}} \qquad (2)$$

The hysteresis coefficient can adopt values between –1 to +1, where negative values refer to stronger sorption than desorption and positive values stronger desorption vice versa.

2.4 Environmental effects

In order to better describe the environmental behavior of PFOA, additional sorption tests were performed on 11 soil samples that were subjected to three different treatments.

These samples were selected based on their sorption and desorption behavior as well as their physicochemical soil properties. Samples from all over NRW were considered. The selected samples represented a wide range of different soil characteristics (Tab. 3). To simulate the environmental influences, three different manipulations were conducted as described in the following.

Firstly, influences of changing pH values were investigated on the 11 soil samples with a background solution used in the sorption and desorption experiments (0.01 M $CaCl_2$ and 0.002 M NaN_3). In order to lower given pH values, 0.1 M hydrochloride acid (HCl) was used and 0.1 M sodium hydroxide solution (NaOH) was used to increase the pH. With the application of acid and base, pH values of 3, 5, and 7 should be adjusted. Since, PFOA has a very high surface activity, a measurement of the pH with the surfactant in solution at the onset of the experiment was not possible. The results would be manipulated, due to adsorption of the surfactant to the pH meter (Lath et al, 2019). Therefore, the pH values were adjusted in the background solutions containing no soils, since only a small amount of soil samples were available. After the sorption experiments were finished and 2 ml supernatant was pipetted in the counting vials, the pH of each sample was measured in the remaining 3 ml in the tube.

Secondly, six different background solutions were selected and tested for the PFOA sorption behavior. These different background solutions are intended to reflect changes in the salt concentration and composition of rain and surface waters. In addition to $CaCl_2$, which was used in the screening test, the salt sodium chloride (NaCl) was also investigated. Both salts were tested in three different molarities (0.01 M, 0.005 M, and 0.001 M), resulting in a total of six different background solutions.

Lastly, the temperature influence was tested to find changes in the sorption behavior depending on the season. Therefore, the temperatures 0 °C for winter simulations, 20 °C for the spring and fall season, and 30 °C as an approximation of maximum summer temperatures were selected. Since the thermostatic shaker was not able to decrease the temperature under 10 °C the experiments were conducted in a cold chamber at 4 °C. Here too, the background solution of the sorption and desorption test series was used (0.01 M $CaCl_2$ and 0.002 M NaN3).

2.5 Data analysis and statistical methods

Outlier tests were performed on the sorption and desorption data of PFOA using the standard deviation. Whenever the standard deviation was two times higher or lower than the mean, the value was excluded from the data set (Grubbs, 1969).

Correlations between the SOC content and the pollutant sorption to the soil solid phase were calculated to explain sorption behavior in dependence of the SOC content. Furthermore, a multivariable ANOVA (MANOVA) was used, to identify differences between the results of the different treatments.

Multiple regression analyses were performed to identify soil properties accounting for the difference in the sorption and desorption of PFOA. The analyses were conducted using the approach of backward elimination, to eliminate independent variables that were not statistically relevant for the regression model. To evaluate the relative influence of the independent variables on the dependent variable, standardized regression coefficients were used. Thus, the variable with the highest coefficient indicated that it has the greatest influence on the dependent variable. The R^2 was used as the quality parameter of the model, which described the percentage of the variation of the dependent variable that is explained by a linear model.

All statistical analyses were performed with the programming language R Gui (Version 3.2.5, open source software, R Development Core Team (2008)).

3 Results and discussion

3.1 The influence of physiochemical properties of anionic PFAS on soil sorption

Once surfactants are introduced into the soil, they are subjected to different processes, such as sorption or degradation. Detailed knowledge of these processes is necessary to understand their behavior in the environment. The sorption of surfactants depends on several factors, which are the physiochemical properties of both the soil and the surfactant, as well as the environmental influences affecting them (Ying, 2006). Once the sorption processes of a surfactant are explored, it is possible to estimate their distribution in different environmental compartments (e.g., sediments, soils, or water). In addition, insights into bioavailability and microbial degradation can be gained from the data. In this study, the sorption and desorption properties of the anionic surfactants from the PFAS group will be investigated in more detail. Since this group of surfactants is belonging to the persistent organic pollutants, they are not exposed to biological degradation (Tan et al., 2022; Zhang et al., 2022a), which is why this process is not considered any further.

At environmental pH values (approximately 4-9), PFAS usually exist as anions due to their low pk_a values (Burns et al., 2008; Deng et al., 2012; Vierke et al., 2013), which are for example -3.27 for PFOS, -0.2 for PFOA and 0.14 for PFHxS (Krafft and Riess, 2015). Simultaneously, soils consist of both positive and negative charges and they contain permanent- and variable-charged surfaces (Bolan et al., 2021; Uehara and Gillman, 1980). Variable charges are developing through dissociation of functional groups in OC and through chemical reactions (e.g. protonation & deprotonation) on mineral surfaces (Blume et al., 2013), while permanent-charges are fixed (Qafoku et al., 2004). Thus, soil surface charges vary under different solution pH, ionic strength, and reactions with anions and cations (Oliver et al., 2019). The surface charge of soils is an important determinant in terms of PFAS sorption, as it significantly effects the sorption process through electrostatic interactions.

However, the exact influence of soil surface charge on the sorption of PFASs in soils and sediments is poorly understood until today (Campos Pereira et al., 2018; Oliver et al., 2019; Ullberg, 2015). Nevertheless, it is known, that the sorption of anionic, ionizable, organic pollutants in soils increases with pH decrease and an increase in cation concentration (Campos Pereira et al., 2018; Jafvert, 1990). An increasing PFAS sorption due to decreasing pH values and increasing contents of polyvalent cations has already been documented several times in the literature, e.g. for Ca^{2+} (Chen et al., 2009; Higgins and Luthy, 2006; Zhang et al., 2013), Mg^{2+}, Fe^{n+}, and Al^{3+} (Wang et al., 2015c). A connection to monovalent cations has not been found so far (Campos Pereira et al., 2018). In addition to the physiochemical properties of the soil, the surfactant and the chemical composition of the solution, indications are that the presence of other anionic surfactants may influence the sorption and transport of PFASs additionally. Guelfo and Higgins (2013) for example, tested the effect of sodium decyl sulfate (SDS) on the sorption properties of several PFAS and found an increased sorption of perfluoroheptanoate (PFHpA) (up to 91%), but no impact on PFOA sorption. They concluded, that SDS may impact the transport of PFOA in soils, which was further investigated by Zhang et al. (2022b). The authors stated, that a background solution containing 10 mg l^{-1} SDS had a significant effect on PFOA transport in the tested soils, resulting in an increased mobility of the surfactant. The effect was determined by soil properties and cation types. Higher mobilization was reached in soils with higher net negative surface charge and larger soil particles and the presence of Ca^{2+} instead of Na^{+} cations.

From the results obtained so far, it can be concluded, that the sorption and desorption of PFAS in soils is determined by the special physiochemical properties of the surfactants. The ambient pH value determines, whether the surfactants are protonated or deprotonated. If the surfactants are uncharged, sorption is dominated by hydrophobic interactions between the surfactant and the soil organic matter. In the protonated state, electrostatic interactions with the charged soil surface determine the sorption process.

Therefore, it is necessary to deal with the respective physiochemical conditions of the soil before considering the sorption and desorption processes.

Physiochemical soil properties

The physicochemical soil properties of the 20 farmland soils are shown in Tab. 1. Since top- and subsoil samples were taken on each site, the SOC contents vary between 0.06–3.58%. Because of the frequent liming, the pH was, with a mean of 6.1, high for Middle European soils (Blume et al., 2013). These high pH values lead to a high effective cation exchange capacity (CEC_{eff}) with a mean of 62.4 $mmol_c$ kg^{-1}. The CEC is an important indicator in the context of PFAS sorption, since the surfactants are present as anions under natural conditions. The value indicates the quantity of cations that the soil is able to adsorb at present pH values. Therefore, it can be assumed that the electrostatic interactions between the anionic surfactants and the soil decrease as the CEC increases (Li et al., 2018b).

Tab. 1: Physicochemical soil properties of all soil samples.

Soil Properties		Samples (n = 39)			
		Mean	S_D	Min.	Max.
SOC[1]	[%]	1.04	0.76	0.06	3.58
pH[2]	[-]	6.13	0.52	5.06	6.89
CeC_{eff}[3]	[$mmol_c$ kg^{-1}]	62.44	31.56	9.86	169.50
Conductivity[4]	[µS cm^{-1}]	61.29	32.71	13.20	153.10
Sand[5]	[%]	21.17	29.19	0.01	92.01
Silt[5]	[%]	68.08	28.16	6.25	90.21
Clay[5]	[%]	6.50	3.08	1.64	16.53
Fe_a[6]	[%]	2.97	1.60	0.32	7.48
Mn_a[6]	[%]	0.51	0.35	0.00	1.73
Al_a[6]	[%]	1.03	0.62	0.13	3.40
Fluoride[7]	[mg kg^{-1}]	3.95	2.12	0.55	8.65
Chloride[7]	[mg kg^{-1}]	6.27	7.06	0.00	27.01
Nitrite[7]	[mg kg^{-1}]	0.20	0.22	0.00	0.95
Bromide[7]	[mg kg^{-1}]	0.08	0.10	0.00	0.25
Nitrate[7]	[mg kg^{-1}]	33.96	40.56	0.00	153.73
Phosphate[7]	[mg kg^{-1}]	10.43	10.37	0.00	39.16
Sulfate[7]	[mg kg^{-1}]	13.80	17.27	1.12	103.43
Calcium[7]	[mg kg^{-1}]	40.79	28.09	6.37	128.60
Potassium[7]	[mg kg^{-1}]	12.81	14.04	0.90	67.46
Magnesium[7]	[mg kg^{-1}]	3.80	1.99	1.09	11.23
Sodium[7]	[mg kg^{-1}]	9.92	6.81	1.90	29.79
Phosphor[7]	[mg kg^{-1}]	5.23	3.96	0.32	13.98

[1]Vario El Elementar Analyser (Elementar Analysesysteme GmbH, Hanau, Germany, [2]0.01 M $CaCl_2$, [3]After ISO 11260 (2018), [4]After DIN ISO 11265 (1997), [5]Analysette (Fritsch GmbH, Idar-Oberstein, Germany), [6]Dithionith and Oxalate extracted iron, manganese and aluminum amorphourous oxides, [7]Warm water extraction: 10 g soil, shaken 30 min and caccum filterd (0.45 µm) measured with Dimatoc 2000 (DIMATEC Analysetechnik GmbH, Essen, Germany).

The data set contained with a maximum of 92% sandy and with a maximum of 90% also silty soils. The clay content also showed heterogeneous conditions with a range of 1.6–16.5%. It is an indicator, like SOC, for potential binding sites of electrostatic interactions. Nonetheless, it is possible, that the clay content was underestimated because of the chosen detection method. Sinkovicova et al. (2017) found, that the laser diffractometry method, which was used in this study, provides a deviation of 8% between this method and the classical pipette method in top- and 7% in subsoils only for the clay content. However, since the underestimation has systematically led to the same error in all samples, this effect is no longer considered in further evaluations.

The amorphous iron content had a range of about 7% with a mean of 3%. In addition to the previous two studies, soil conductivity and water-soluble anions and cations were analyzed, to describe the sorption and desorption behavior of PFOA more precisely. The electrical conductivity of a soil provides information about the salt content, since the conductivity in water increases with rising salt concentrations (Blume et al., 2013). The conductivity of the analyzed samples varies widely from 13.2–153.1 µS cm^{-1}. Thus, the variation in electrical conductivity covers the normal range of variations in undisturbed soil samples (Malicki and Walczak, 1999; Shrestha and Lal, 2011). Anion and cation concentrations also vary greatly. Calcium, e.g. varied between 6.4–128.6 mg kg^{-1}. Those ions approximate the soil salt concentration. If, e.g., calcium and chloride concentrations are high, it is assumed that the $CaCl_2$ concentration in the sample is also high. Based on the wide variation of fixed and variable surface charge, the sorption of PFOA is tested at different surface charges.

3.2 PFAS sorption and desorption in soils

The sorption of PFAS is firstly dependent on the chain length. The longer the surfactant, the more strongly it can be bound to the soil solid phase (Campos-Pereira et al., 2022). Furthermore, PFASs sorption is determined simultaneously by hydrophobic interactions with the organic matter and by electrostatic interactions with the soil surface (Du et al., 2014).

Electrostatic interactions in soils can form between the negatively charged functional head of PFAS and charged surfaces of the adsorbent. Charged surfaces are derived from both organic and mineral phases. Clay minerals, for example, can acquire negative charges through isomorphic substitution. In this process, a structural cation is substituted for a cation of lower valence. The replacement creates a charge imbalance and the surface charge is fixed by the extent of substitution (Blume et al., 2013). SOM also carries negative surface charges, through the dissociation of carboxylic and phenolic groups under natural pH conditions (Kinniburgh et al., 1999). This leads to an increased PFAS sorption with increasing cation concentrations due to the reduction of the electrostatic SOM potential caused by complexation (Higgins et al., 2005; Higgins and Luthy, 2007). Positively charged surfaces are determined, for example, by the concentrations of iron or aluminium oxides (Armanious et al., 2016). The mixture of positive and negative soil surface charge is called the ionic strength and it is largely determined by the variable charge and the current pH value (Blume et al., 2013; Qafoku et al., 2004).

In addition to the net surface charge, ions in the soil can influence PFAS sorption through electrostatic double-layer compression (Du et al., 2014), surface charge neutralization (Zhang et al., 2019a), divalent cation bridging effects (Wu et al., 2022), salting out processes (Cai et al., 2022) and competitive adsorption (Kabiri and McLaughlin, 2021). Furthermore, several studies demonstrate, that dissolved organic matter (DOM) can reduce PFAS sorption on carbonaceous sorbents (Deng et al., 2015; Hansen et al., 2010; Zhao et al., 2011). The DOM binds to the soil surface and thus competes with the surfactants. Moreover, the DOM can occupy micropores, which are then no longer available for the surfactant sorption.

Unlike other non-ionic organic pollutants, PFAS sorption is not determined by a single soil property (like OC). This context was described, for example, by Li et al. (2018b) who summarized international research results of PFASs sorption in sediments and soils. It became clear, that individual soil parameters (e.g., pH, clay content, CEC) only show weak correlations to PFAS sorption.

Nevertheless, strong correlations between SOM and PFAS sorption have been found consistently (Fabregat-Palau et al., 2021; Higgins and Luthy, 2006; Li et al., 2019). In addition to the SOC quantity, which was described in detail in chapters 2 and 3, an influence of the SOM quality is possible. The quality of SOM is expressed by chemical properties, such as net charge, and structural composition (Campos-Pereira et al., 2022; Zhao et al., 2014; Zhi and Liu, 2019). The SOM quality depends on its origin and can be altered, for example due to decomposition (Campos-Pereira et al., 2022). In this context, Zhang et al. (2015) found, that PFOS mainly binds to the humic fraction, while humic (HA) and fulvic acids (FA) have no influence. The authors explain this by the higher hydrophobicity and polarity of the HA/FA fraction. In contrast, Zhao et al. (2014) found correlations in the PFOS and PFHxS sorption between both the humic and HA/FA fractions. The influence of the HA/FA fraction was also observed for the sorption of other hydrophobic substances. Based on the results, Campos Pereira et al. (2018) investigated the issue and found, that the short-chain PFASs mainly bind to the HA/FA fraction while long-chain PFASs bind to the humic acids. In a recent study, the authors found a correlation of PFAS sorption and SOM quality (Campos-Pereira et al., 2022). The carbohydrate content (O-alkyl C) was related to the overall binding of the five investigated PFAS (PFOS, EtFOSA, PFBS, PFUnDA, and PFOA). However, since only three different soils were investigated, further research is required in order to be able to make generally valid conclusions. SOM analyses using ^{13}C nuclear magnetic resonance (NMR) technology indicate, that the binding strength of PFAS is positively correlated to the quantity of aliphatic hydrocarbons and carbohydrates, and negatively correlated to the amount of aromatic C and phenolic as well as carboxylic residues (Zhao et al., 2014). However, these analyses have large inaccuracies because it cannot be accurately determined whether the increased sorption strength is caused by the improved SOM quality or quantity (Oliver et al., 2020b). Thus, it was concluded, that the SOM quality is, like the quantity, not able to describe the sorption of PFASs comprehensively.

The transport of PFAS in soil is further determined by the soil surface charge and ionic strength of the soil solution (Cai et al., 2022; Campos Pereira et al., 2018; Wang et al., 2015a). Lyu et al. (2019) described the relationship between surface charge and PFOA sorption in three different soil types. They found a positive correlation between increased ionic strength in negatively charged soils and PFOA sorption. In positively charged soils, however, an increase in ionic strength led to a reduced overall sorption. In addition, the sorption of PFAS is attenuated by the presence of inorganic anions, such as chloride (Cl^-), sulfate anions ($[SO_4]^{2-}$), and dichromate ($Cr_2O_7^{2-}$) (Deng et al., 2010; Wang et al., 2012; Zhang et al., 2011).

In general, an increased cation concentration in the soil solution also leads to a higher PFAS sorption (Campos Pereira et al., 2018; Higgins and Luthy, 2006; Oliver et al., 2019). However, this relationship must be considered in more detail. The valence of the cations plays a special role. Wang et al. (2015b), for example, observed that higher valence led to increased sorption of PFHxS in sludge in the order $Na^+ < Mg^{2+} < Ca^{2+}$ and Campos Pereira et al. (2018) found the same relationship for C_5-C_8 PFAS in an organic soil horizon with the order Na^+ (10 mM) = Ca^{2+} (3 mM) < Ca^{2+} (5 mM) < Al^{3+} (2 mM). Matching these results, Cai et al. (2022) were also able to find increased PFAS sorption with increased cation concentrations in two different soils ($Na^+ < Mg^{2+} \leq Ca^{2+}$). The relation increased with increasing chain length and it was greater for the sulfonates than for the carboxylates. Increased sorption in this context can be explained by ligand bridging with divalent cations. In other words, the cations are able to form a bridge between the negatively charged surfactants and the negatively charged soil surface (Du et al., 2014). The bridging effect is the reason why, among others, Higgins and Luthy (2006), were not able to find a connection between increased Na^+ concentrations and PFAS Sorption for eight PFAS in five sediments (Mejia-Avendano et al., 2020; Oliver et al., 2019; Xiao et al., 2011). The monovalent cation is not able to build these bridges and has thus no influence on PFAS sorption. The same effect was observed for the monovalent cation potassium (Mejia-Avendano et al., 2020; Wu et al., 2022). Based on the results of Cai et al. (2022) and Campos Pereira et al. (2018), increased PFAS sorption with rising monovalent cation concentration can be attributed to an increased ionic strength, which in turn weakens the negative repulsion between the surfactants and the soil surface.

As already mentioned, the availability of anions and cations in the soil solution is largely dependent on the current pH value (Cai et al., 2022; Tang et al., 2010). Therefore, indications of a pH-dependent sorption of PFAS in soils can also be found in the literature (Alonso-de-Linaje et al., 2021; Kabiri et al., 2021; Oliver et al., 2019). Studies on both isolated fractions of OM and soils rich in OM showed pronounced pH-dependent PFAS sorption, with increasing affinity as the pH decreases (Campos Pereira et al., 2018; Zhao et al., 2014). This dependence results from protonation of the functional groups with decreasing pH, which again results in a decrease of the negative surface charge of the OM. This in turn causes a reduction in the repulsion between the negatively charged PFAS and the OM (Higgins and Luthy, 2006).

Charge neutralization through metal binding also appears to enhance PFAS binding (Campos Pereira et al., 2018; Higgins and Luthy, 2006). In the study of Campos Pereira et al. (2018), a PFAS sorption increase with decreasing pH was observed for 10 of the 14 investigated PFAS. The cation concentration had a smaller influence on PFAS sorption, than the soil surface charge, which was determined by the pH, respectively. The authors found in a subsequent study, that the pH effect increased with the chain length and highest sorption was found for C10 and C11 PFAS (Campos-Pereira et al., 2022). The enhanced sorption with increasing surfactant chain length is probably caused by increasing charge interactions between the perfluorocarbon backbone and the substrate (Johnson et al., 2007; Xiao et al., 2011), which results from the excess negative charge (δ-) on the electronegative fluorine atoms (Campos-Pereira et al., 2022). The authors finally concluded, that the pH-dependent sorption to the three investigated organic soil materials was a result of changing surface charge due to protonation of acidic functional groups.

Desorption of PFAS in soils is dependent on the initial sorption, the surfactant charge and the SOC content (Xiao et al., 2019). Studies show, that a fraction of PFOS (up to 97%) is irreversible sorbed in soils (Pan et al., 2009; You et al., 2010), while desorption of PFOA and PFHxS in soils and sediments is reversible (Milinovic et al., 2015; Zhao et al., 2014). In the study of Navarro et al. (2022), the authors investigated desorption of PFOA, PFOS, and PFHxS in estuarine sediments, and found high correlations between desorption and SOC ($R^2 = 0.87$). A reduced salt content of the extraction solution resulted in a decreasing desorption. Finally, the authors pointed out that aging of the samples may lead to an entrapment of the surfactants in soil micropores, which could further prevent desorption.

From the results presented, it can be summarized that the sorption of PFAS in soils depends on both the physiochemical properties of the surfactants and the soils. Increasing PFAS chain length, result in an increased sorption potential. Under natural pH conditions, the surfactants occur as anions due to their low pk_a values, and electrostatic interactions between the negatively charged pollutants and soil surface dominate their sorption. It is further observed, that sorption increases with increasing cation concentrations in the soil solution, especially with increasing polyvalent cations, and with decreasing pH values. The pH dependence has a greater effect on PFASs sorption, than changing cation concentrations.

Different studies have investigated the sorption of PFAS in soils and sediments until now. Among others, Fabregat-Palau et al. (2021)) detected K_D values for eight PFASs in six soils. Values for PFOA ranged between 2.6–37 l kg^{-1} while those for PFOS varied from 32 to 207 l kg^{-}1. Lowest sorption was observed by the short-chain perfluorobutanoic acid (PFBA) with 0.55–1.2 l kg^{-1} and perfluorobutane sulfonic acid (PFBS) with 0.6–3 l kg^{-1}. Highest sorption was measured for the surfactant perfluorododecanoic acid (PFDoA) with eleven CF_2 components (422–3082 l kg^{-1}). Maximum sorption was observed in soils with high SOC values (39–41%) and high contents of iron oxides (up to 19,670 mg kg^{-1}). Wei et al. (2017) determined the sorption of PFOS on six different soils and found K_D values ranging from 14–66 l kg. The soils in this study had significantly lower levels of SOC, 0.87-2.71%, than the soils in the analysis of Fabregat-Palau et al. (2021), which has led to weaker sorption. Milinovic et al. (2015) also studied the sorption behavior of three PFASs in six soils, with SOC ranging between 0.2–39%). Unlike other studies (Cai et al., 2022; Li et al., 2022; Xiao et al., 2019), the authors were able to explain variation in sorption data solely by SOC. The sorption of PFOS (19–295 l kg^{-1}) was highest followed by PFOA (2.2–38 l kg^{-1}) and PFBS (0.4–6.8 l kg^{-1}).

3.3 Sorption and Desorption of PFOA

The results in the following refer to PFOA, which has a chain length of eight, and thus lies in the middle range of PFAS sorption. As already described, the sorption of the homologous PFOS is higher, since the sorption of the sulfonic PFAS is stronger than that of the carboxylic PFAS.

Both, sorption and desorption behavior of PFOA, were tested in this study. The adsorption was linear and independent of the SOC content of the sample (Appendix #1). This corresponded with the results from previous studies (Mejia-Avendano et al., 2020; Zareitalabat et al., 2013;

Zhu and Kannan, 2019). Overall, the data showed a heterogenous picture. Highest sorption (25.6%) was found in soil 1b, which was a silty soil with an average clay content (7.9%). Low sorption potentials were found in sandy soils, with low SOC and cation contents (Fig. 1).

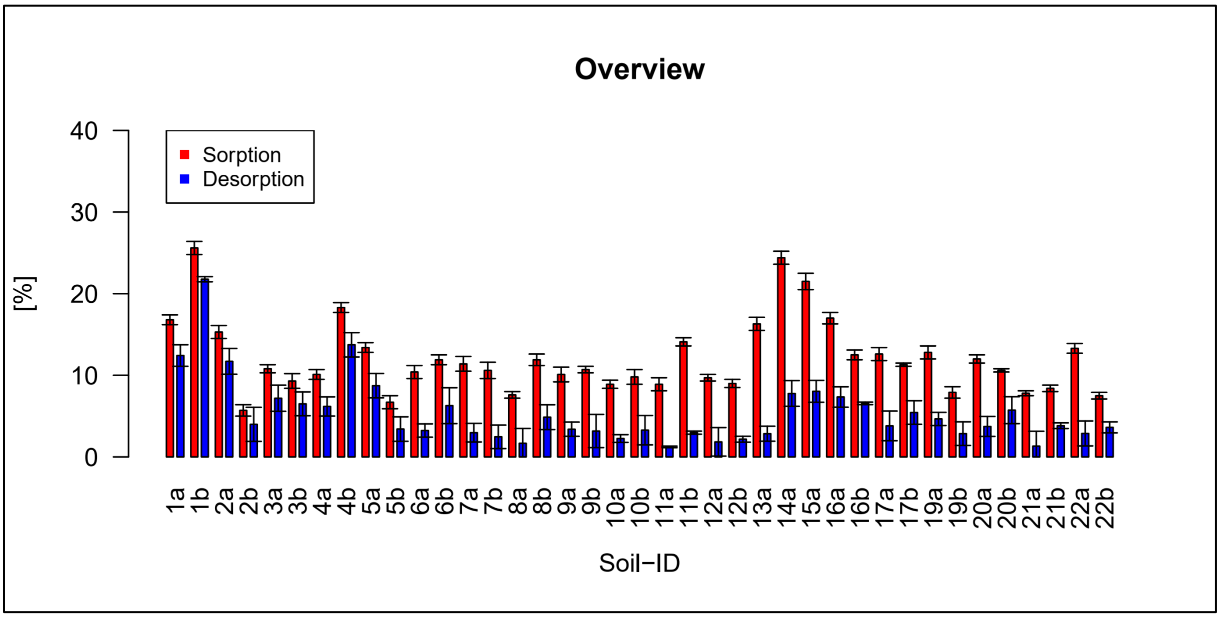


Fig. 3: Overview of the sorption and desorption results for all soil samples. The desorption is shown in dependence on the measured sorption results.

In figure one, the desorption of PFOA is displayed as a function of the sorption rate. This means, that the previous sorption of a sample determines the reference magnitude of desorption. Thus, with a sorption of 25% and a desorption of 85%, the desorption shown in the figure is 21.25%, respectively. As shown in Appendix #2, the standard deviations (S_D) for sorption (0.6%) and desorption (1.2%) where very low, after the data has been corrected for outliers. However, desorption S_D was twice as high as sorption S_D values.

The sorption of PFOA varied from 5.6–25.6%. Maximum sorption was reached in the subsoil 1b (25.6%). It was a silty soil (86.5% silt) with comparatively low SOC (0.3%) and moderate CEC_{eff} (47 $mmol_c\ kg^{-1}$) and amorphous iron (2.6%) contents. The sorption K_D values of PFOA ranged between 0.6–3.5 ml g^{-1} which rather covers the lower sorption range of other studies (Ahrens et al., 2011; Aly et al., 2019; Milinovic et al., 2015). Knight et al. (2019) for example tested the sorption behavior of ^{14}C-labled PFOA on 100 different soils and found K_D values in the range between 0.56–14.84 ml g^{-1}. However, the analyzed soils had higher clay contents (up to 88%) and pH values below the threshold of 5.5 (min = 4.9), resulting in higher PFOA adsorption. Considering the given SOC values in this study (0.06–3.6%), the K_D range matches well with those found in literature (Chen et al., 2013; Li et al., 2018b; Oliver et al., 2020a). For example, Milinovic et al. (2015) found K_D ranges of 0.8–4.3 ml g^{-1} with SOC values varying from 0.2–3.9%.

When water was added to detach the sorbed PFOA, an average of 42% was desorbed from the soil. The extraction agent was able to desorb a maximum of 85% in sample 1b, which previously showed the highest sorption. Since there is currently a deficiency of studies on the desorption behavior of PFOA in soils, it is difficult to put the results into a scientific context. However, Schaefer et al. (2021) have recently published two studies describing the desorption of PFOA, along with 8 other PFAS, in two different soils (Schaefer et al., 2022). These were sandy soils with low SOC contents (< 0.5%), very low clay contents (<0.1%) and pH values higher than 5.5. The soils were collected from an Aqueous Film-Forming Foam (AFFF) impacted site from the US Department of Defense in the United States (US). The desorption K_D values in all experiments ranged between 1.1–4.8 ml g^{-1}. In our study, in subsoils containing less than 0.5% SOC the K_D values ranged between 2–24 ml g^{-1}. Since 13 instead of two different soils were investigated in the present study, a higher variance of the data is not unusual in this case. It is noticeable, that Schaefer et al. (2021) found higher desorption of PFOA in some soils despite lower clay contents. A higher initial sorption could have provided higher desorption potentials, as PFOA was applied into the soil over several years. Additionally, Milinovic et al. (2015) tested the desorption of PFOA. The authors found desorption rates in the soils with SOC contents below 3.9% between 24–58%. The initial sorption of the contaminant was 0.8–4.3 ml g^{-1}. Since the soils had higher clay contents (10–17%), desorption was reduced due to the clay mineral bounding and bridging action (Wang et al., 2012; Xiang et al., 2018).

The hysteresis coefficient was, with one exception, always positive ($\bar{x}$ = 0.7). This indicates a higher desorption of PFOA compared to the sorption (Düring et al., 2002) and that the sorption was partially irreversible (Chen et al., 2016; Pan et al., 2009; Zhi and Liu, 2018). Thus, hysteresis was an effect related to the sorption of PFOA in soils.

3.3.1 Influence of soil properties

The average sorption of PFOA in this experiment was 12% (Appendix #2). Similar to other studies (Ahrens et al., 2011; Chen et al., 2013; You et al., 2010), a significant correlation ($p < 0.01$) to the SOC content was found (Appendix #3). However, the correlation was with an R^2 of 0.4 considerably lower than partly described in the literature (Chefetz et al., 2008; Luers and tenHulscher, 1996; Spark and Swift, 2002).

The reduced correlation can be explained by the comparably high pH values ($\bar{x}$ = 6.1). Thus, hydrophobic interactions between PFOA and the SOC were covered by electrostatic interactions between the surfactant and the mineral components of the soil.

Since the clay content of a soil is an indicator of potential binding sites for electrical interactions (Groffen et al., 2019; Li et al., 2018b), a significant correlation between clay content and PFOA sorption was expected at the given pH values. However, a R^2 of 0.4 was distinctly lower than initially expected. As the pH values in this test series are fluctuating close to the critical threshold of 5.5, the processes of hydrophobic binding to the organic matter and electrostatic interactions with the mineral surfaces are highly likely to overlap. Thus, both effects occur side by side, which reduces stronger correlations in both cases (Aly et al., 2019; Hellsing et al., 2016; Oliver et al., 2019). This effect is additionally enhanced by the fact that we found significant correlations of PFOA with the positively charged minerals iron (R^2 = 0.34), manganese (R^2 = 0.43), aluminum (R^2 = 0.42) and calcium (R^2 = 0.36), as well as the sum parameter CEC_{eff} (R^2 = 0.33). The described correlations were on a similar level as that of the clay content. Thus, the electrostatic interactions of PFOA sorption are not exclusively determined by the clay content but by all binding sites of the soil. In addition, negative correlations between the surfactant and cations are found in case of desorption. This once again demonstrates that the content of cations in the soil significantly influences both the sorption and desorption of PFOA, as desorption increases with decreasing cation contents.

As in other studies (Kabiri et al., 2022; Oliver et al., 2020a; Yin et al., 2022), the variation of PFOA sorption could not be satisfactorily described with individual soil properties, since they are often dependent on each other. This means, for example, that soils with high clay contents will be richer in SOC. The same applies to CEC. It varies with clay and SOC content as well as the pH value. Therefore, it is reasonable to include multiple soil properties simultaneously, when sorption and desorption of PFAS in soils are discussed. Hence, multiple regressions were calculated in the following to be able to describe this relationship more accurately.

In order to describe the sorption and desorption behavior of PFOA more precisely, backward multiple regression analyzes with the sorption and desorption data [%] as the dependent variables and the physiochemical soil properties as independent variables were conducted. All variables were z transformed to be able to determine the respective influence on the model. The physiochemical properties of the samples were divided into soil sorbents, soil solution characteristics, soil properties, and consecutively included in the model (Tab. 2). As already described in Chapters 2 and 3, the sorption behavior of PFOA changes depending on the given pH, due to the physiochemical properties of the surfactant. Under natural relevant pH values, they mainly consist as anions (pk_a = -0.5), due to the loss of a cation from the functional head (Campbell et al., 2009; Deng et al., 2012). Thus, they can interact with charged soil surface through electrostatic interactions (Campos Pereira et al., 2018; Mejia-Avendano et al., 2020). The high electronegativity of fluorine and the presence of electron pairs in its environment creates a negatively charged shell around the positively charged nuclear carbon chain, which was hypothesized to contribute to these interactions (Xiao et al., 2011). Being deprotonated at neutral to basic pH values, the surfactant has two possibilities to bind electrostatically to the soil solid phase. On the one hand, the negatively charged surfactant can bind to the positively charged soil surfaces. On the other hand, it can also bind to the negative soil components by bridging bonds, e.g. through Ca^{2+} or Na^{+}. In this case, bridging is stronger with multiply charged cations than with singly charged ones (Nguyen et al., 2020; Oliver et al., 2019; Ullberg, 2015). In addition, the perfluorinated carbon chain of PFAS promotes their interactions with hydrophobic molecules, through hydrophobic interactions and electrostatic repulsion (Chen et al., 2019; Jia et al., 2010; Teymourian et al., 2021).

A pH value of 5.5 was determined as the critical threshold, under which hydrophobic interactions (pH < 5.5.) or electrostatic interactions (p > 5.5) are predominant (Chen et al., 2013; Li et al., 2018b; Oliver et al., 2019). Therefore, multiple regressions were performed with all soil samples as well as with samples pH > 5.5. An analysis of the soil samples with pH values < 5.5 could not be performed, due to the small sample number (n = 6).

Tab. 2: Multiple regression. Standardized ß-coefficients with significant influences on the regression are shown. The R^2 value is the figure of merit of the regression analyses. *indicating 5% confidence interval, ** indicating 1% confidence interval.

			Sorption				**Desorption**			
Data basis			all independent variables		soil sorbens		all independent variables		soil sorbens	
Sample sets			all	pH > 5.5	all	pH > 5.5	all	pH > 5.5	all	pH > 5.5
		n	39	32	39	32	39	32	39	32
		R^2	**0.77**	**0.91**	**0.24**	**0.24**	**0.78**	**0.89**	**0.44**	**0.27**
standardized ß-coefficients	soil sorbents	SOC		-0.53	0.32*	0.37	-0.53	-0.96*	-0.29*	-0.3
		Sand		0.65**			1.68**	1.86*	0.17**	1.33
		Silt	-0.83**				0.8	1.19	0.13*	1.36
		Clay			0.26		-0.43	-0.4		
		Fe_a	-0.45	-0.70*		-0.6	-0.33			
		Al_a				0.65		-0.76		
		Mn_a	1.69**	2.49**			1.23*	2.36**		
	soil characteristics	pH								
		CEC_{eff}	1.73**	1.88**			1.24	2.29**		
	soluble soil characteristics	Conduct.	0.38	0.53			0.72	0.96*		
		Fl^-	0.86**	1.16**			0.76*	1.28**		
		Cl^-	-0.72**	-0.87**			-0.86**	-1.36**		
		Br^-	-0.52*	-0.65			-0.32	-0.4		
		SO_4^{2-}	1.08	1.07			1.09			
		NO_2^-	0.56*	0.7**			0.28	1.68*		
		PO_4^{3-}	0.67	0.47*				0.69*		
		Ca^{2+}	-0.86	-0.69			-0.79	-1.23*		
		Mg^{2+}	-1.45**	-1.92**			-1.08	-2.06**		
		K^+	0.38	0.46*			0.023	0.67*		
		Na^+	-0.39	-0.61*			-0.4	-0.91**		
		P	-0.45							

Using multiple linear regression, 77% of the sorption variance was explained by all physiochemical soil parameters. As expected, mainly the charged particles in the soil determine the sorption of PFOA. The greatest influence is exerted by the amorphous manganese (1.69) and magnesium contents (-1.45) as well as the sum parameter of the exchangeable cations CEC_{eff} (1.73). In contrast to other studies, the SOC content has no influence in this model (Enevoldson and Juhler, 2010; Miao et al., 2017; Milinovic et al., 2015). Since the used soil samples are arable soils, the pH values are higher than in the mentioned studies. Due to the continuous fertilization, the natural acidification of the soil is counteracted (Goulding, 2016; Xu et al., 2020). This reduces the influence of hydrophobic interactions with SOC. As the cations in the soil can both cause precipitation of the surfactant by coagulation and at the same time led to sorption by bridging, a further detailed interpretation of the individual ß-coefficients of the ions is deliberately refrained from at this point, as these processes have the opposite effect. When only the samples with pH higher than 5.5 are considered, the quality of the model increases to 91%. The explanatory variables are similar to those in the entire data set. However, it can be assumed that the hydrophobic interactions with the organic matter no longer have an influence on sorption in this model due to the selected samples, which results in an improvement of the model validity.

In order to determine the soil sorbents of PFOA sorption, regressions were performed in the two data sets using only the independent variables of the soil sorbents in a further step. As expected, the quality of the model decreased drastically ($R^2 = 24\%$). Nevertheless, it was thus possible to determine that the SOC content in the total data set had a significant influence when considering all soils. This supports the assumption that the hydrophobic properties of the surfactant are influencing the PFOA sorption in pH ranges below 5.5. This hypothesis is strengthened by the fact that there is no longer a significant influence of the SOC content when considering soil samples with pH values greater 5.5. Furthermore, a correlation analyzes with the six soil samples with pH values smaller than 5.5 has shown, that SOC correlates significantly ($p < 0.05$) with the PFOA sorption ($R^2 = 0.75$) in this model.

The results suggest that the soils studied had a net negative surface charge, as PFOA sorption increased with increasing ionic strength. This can be explained by the reduction of the repulsion of the negatively charged surfactant on the one and the formation of cation bridges on the other hand (Belhaj et al., 2019; Navarro et al., 2022; Nguyen et al., 2020).

On the basis of the analyses carried out, it can thus be concluded that the sorption of PFOA in arable soils, with pH values greater than 5.5 and an overall net negative surface charge, was largely determined by electrostatic interactions between the soil solution and the surfactant.

If the pH value falls below the threshold of 5.5, protonation of the surfactant increases and it can be assumed that the hydrophobic interactions with the organic substance dominate the sorption process. PH values lower than 5.5 can be found mainly under forest and grassland sites due to the natural acidification of soils (Goulding, 2016; Xu et al., 2020). Therefore, in many studies the organic matter content was determined as the primary influencing factor of PFOA sorption, since they used forest soils (Campos Pereira et al., 2018; Li et al., 2019; Li et al., 2010).

In addition to the sorption data, the desorption results were also analyzed using multiple regression. Desorption was also described in this case by soil solubility characteristics. Considering all data, 78% of the variance could be explained. In contrast to the sorption model, the sand content has the greatest influence. The positive ß-coefficient indicates that the desorption increases with increasing sand contents. As texture is a sum parameter of sand, silt and clay, the variables co-correlate with each other. Hence, the strong influence of the sand content suggests that the decrease in clay minerals leads to increased desorption of the surfactant, as this reduces the formation of cation bridges. When considering soil samples with pH values greater than 5.5, the explanatory variance increases to 89%. In this model, the amorphous manganese content and CEC_{eff} have the greatest influence, resulting from the electrostatic binding of the surfactant. If only the soil sorbents are considered, the quality of the model drops significantly to 44% for all samples and 27% for pH > 5.5, respectively. As in the case of sorption, the SOC content has the strongest influence on the data set of all samples. The negative correlation between desorption and SOC is caused by stronger PFOA adsorption in soils with high SOC contents than in SOC depleted soils, resulting in a reduced desorption potential. However, since the influence of SOC is very small with a ß-coefficient of -0.29 and the explanatory variance of the model amounts to 44%, this process plays a rather minor role. Exactly as in the case of the sorption model, no significant influencing variables of the multiple regression can be found in the data set pH > 5.5. This again shows that it is not the soil sorbents but the ion concentration in the solution phase, which dominates the desorption of PFOA in this pH range.

3.3 Environmental influences on PFAS and PFOA sorption

With the investigations and analyses described, it was possible to explain the processes of PFOA sorption in the studied soils. However, the experiments were conducted under the same ambient conditions, but pollutants in the environment are not always exposed to the same surrounding conditions. Therefore, the influence of changing environmental conditions was additionally analyzed. For this purpose, pH values, the ambient temperature, the cation concentration, and composition in the soil solution, which are decisive for sorption, were diversified.

For this purpose, 6 sites with both top- and subsoil samples were selected, considering physicochemical soil properties and the spatially distribution of the sample location all over NRW. Hence, the sample pool comprised 11 soils, since one soil was too shallow to take a subsoil sample (Tab. 3).

Tab. 3: Soil sample characteristics for the treatment data set. For detection methods see Tab. 1.

Soil Properties		Soil-ID										
		1a	1b	4a	4b	5a	5b	14a	16a	16b	21a	21b
SOC	[%]	0.9	0.3	0.9	0.3	1.4	0.1	3.0	1.8	0.7	1.8	0.3
Sand	[%]	24.3	5.7	3.3	2.1	75.6	92.0	17.6	1.5	1.3	1.8	0.0
Silt	[%]	70.8	86.4	90.1	88.9	22.7	6.2	67.7	89.8	89.5	90.2	89.4
Clay	[%]	4.9	7.9	6.6	7.1	1.8	1.7	11.1	6.1	7.8	5.7	7.8
CeC_{eff}	[$mmol_c$ kg^{-1}]	60.3	46.7	68.0	63.2	32.1	9.9	79.6	85.4	67.9	56.8	54.2
pH	[-]	6.1	6.7	6.6	6.7	5.1	5.4	6.3	6.3	6.3	5.9	6.1
Conductivity	[µS cm^{-1}]	63.6	49.5	61.7	53.8	40.7	24.5	92.1	70.9	53.2	46.6	34.7
Fe_A	[%]	3.3	2.6	3.1	2.5	6.1	0.3	7.3	3.6	2.8	5.7	3.6
Mn_A	[%]	0.6	0.4	0.6	0.5	0.2	0.0	1.7	0.9	1.0	0.8	0.3
Al_A	[%]	0.8	0.9	0.6	0.7	0.7	0.1	3.4	1.3	1.4	1.3	1.1
Fluoride	[mg kg^{-1}]	4.8	3.3	6.1	6.5	3.0	1.4	0.9	3.0	1.8	5.8	3.6
Chloride	[mg kg^{-1}]	1.0	0.0	2.2	8.7	2.6	0.1	14.3	4.5	0.0	12.1	0.0
Nitrite	[mg kg^{-1}]	0.1	0.0	0.2	0.0	0.2	0.0	0.3	0.7	0.2	0.3	0.0
Bromide	[mg kg^{-1}]	0.0	0.0	0.2	0.0	0.0	0.0	0.2	0.0	0.2	0.0	0.0
Nitrate	[mg kg^{-1}]	33.0	4.8	19.4	8.5	16.3	1.8	136.7	31.9	28.3	14.7	3.4
Phosphate	[mg kg^{-1}]	17.2	0.0	19.6	0.0	12.0	0.0	3.1	15.6	0.0	8.3	0.0
Sulfate	[mg kg^{-1}]	6.0	19.3	5.1	20.0	4.8	1.1	8.8	12.3	7.3	10.8	1.6
Calcium	[mg kg^{-1}]	38.5	29.5	43.8	23.2	14.1	9.1	69.7	54.0	26.3	46.4	18.0
Potassium	[mg kg^{-1}]	5.2		12.1	1.1	17.1	6.3	25.0	21.8		20.1	1.5
Magnesium	[mg kg^{-1}]	5.7	2.9	4.8	2.6	1.2	1.2	4.8	6.3	3.6	3.1	1.4
Sodium	[mg kg^{-1}]	5.3	6.6	8.9	17.8	9.0	1.9	17.8	10.7	4.0	20.3	2.6
Phosphor	[mg kg^{-1}]	7.7	1.1	8.5	1.9	4.5	0.3	4.3	9.6	2.0	5.8	1.1

The physiochemical properties of the selected sample test set show a wide variation in the respective characteristics. In soil 14a the SOC content is with 3% maximal while in soils 1b, 4a, and 21b it shows a minimum of 0.3%. In two of the eleven samples (5a, 5b), the pH value is below the threshold of 5.5. Therefore, the SOC content has a comparatively higher influence on PFOA sorption than the contents of clay, iron and the respective composition of the ions in the soil solution. The remaining samples have pH values between 5.9–6.7. This suggests that the electrostatic interactions between the surfactant and the soil solution dominate the sorption. The sorption relevant clay contents range between 1.7–11.1% while the amorphous iron contents vary between 0.3–7.3%. In addition, the composition of the total cation and anion contents of the individual samples also varies strongly. For example, the content of calcium ranges from 9.1–69.7 mg kg^{-1} while the sodium content varies only in the range of 2.6–20.3 mg kg^{-1}.

3.3.1 Influences of the pH value

Influence of pH on PFAS sorption in sediments and soils

The Effect of pH on PFAS sorption in soils, sediments and pure mineral phase has been observed several times (Kabiri et al., 2021; Mejia-Avendano et al., 2020; Nguyen et al., 2020). In some studies, PFAS sorption became stronger with decreasing pH values (Higgins and Luthy, 2006; Johnson et al., 2007), while other authors, who studied soils without variable loading, found no or only weak correlations between PFAS sorption and pH (Oliver et al., 2019). Milinovic et al. (2015) for example, found no relationship between pH changes from 4.6 to 8.0 and the sorption of PFOS, PFOA, and PFBS in six sediments. In contrast to that, Kwadijk et al. (2013) found significant sorption increase of PFOS sorption from pH 4.0–6.0. A further pH above 6 resulted only in a small difference in PFOS sorption. In another study by Oliver et al. (2019) the authors found increased sorption of PFOS, PFOA, and PFHxS with decreasing pH values (pH range 2.94–7.91), only when a certain threshold was undertaken. For one soil with low SOC (0.9%), medium clay (30%), and comparably low aluminum (929 mg kg^{-1}) and iron contents (2350 mg kg^{-1}), the threshold was a pH value of 4.5 and for three other soils with higher SOC, clay, and aluminum contents the threshold was between 5–5.5, respectively.

Li et al. (2018b) compiled the available K_D values of PFAS in soils and sediments in literature and could not find any significant correlations between pH and the sorption of PFOS (pH range 2.5–8.5, $R^2 = 0.06$) and PFOA (pH range 4.5–10, $R^2 = 0.07$).

Due to their pk_a values PFASs occur as anions under natural conditions (pH 3-7) (Deng et al., 2012). Thus, it was concluded, that pH changes are influencing the charge of the sorbent rather than the charge of the surfactant (Chen et al., 2009; Higgins and Luthy, 2006; Oliver et al., 2019). Therefore, soil properties must always be included in the sorption of PFAS under different pH conditions. An important indicator in this context is the net soil surface charge. Again Oliver et al. (2019) investigated the role of pH and net soil surface charge for PFAS sorption. The seven examined soils became less negative with decreasing pH values. In sandy soils, pH variation had no effect on PFAS sorption. In two soils, with high sesquioxides contents (kaolin, Al_A, and Fe_A), an increased sorption for PFOS, PFOA, and PFHxS was found, with decreasing pH and lower net negative surface charge. The point of zero charge (PZC) plays an important role in this regard. It varies for several soil compartments and is, for example, low for kaolin (pH 3–4) (Schroth, 1997), while it is high (pH 5–9) for Al_A (Oliver et al., 2019). If the pH of a soil is above the PZC, it will have a negative surface charge, which will cause it to exchange cations. However, if the pH is below the PZC, the soil will retain soil anions electrostatically. This relation shows, that the sorption of PFAS is additionally influenced by electrostatic interactions due to soil pH. However, when the soil pH decreases, the role of surface charge increases, especially in variable charged soils (containing sesquioxides), but the degree of importance is moderated by the content of SOC and oxides (Wen et al., 2020).

A decreased PFAS sorption with decreasing negative surface charges was also observed by Ullberg (2015) and Campos Pereira et al. (2018). The authors additionally found, that the sorption of PFAS also decreased with a reduction in the negative surface charge of the SOM. This effect was observed especially for long-chain PFASs.

A high negative surface charge would be expected to repel the negatively charged functional PFASs head, but, due to the hydrophobic properties of the surfactants, it has been suggested, that they may prefer sorption onto solid surfaces rather than remaining in the water phase (Du et al., 2014). Nevertheless, the sorption of PFAS in soils with high negative surface charge is significantly lower than in soils with low ionic strength (Campos Pereira et al., 2018; Kabiri et al., 2021; Oliver et al., 2019). Thus, PFASs sorption tends to increase with lower pH, because of the reduced negative surface charge

Influence of pH on PFOA sorption in eleven arable soils

Since agricultural soils are subject to constant fertilization, they have different physiochemical properties than, for example, forest or grassland soils, especially regarding the pH value. Therefore, the influence of the pH value on the sorption of PFOA on eleven agricultural soils was investigated in more detail. By adding hydrochloric acid (HCl) and caustic soda solution (NaOH), the pH of the eleven soil samples were manipulated. Due to the high buffering capacity of the soils, a maximum manipulation of one pH unit was achieved. Since the pH value is a logarithmic unit, considerable differences in sorption behavior could still be observed. Further addition of acid or caustic solution would have changed the natural soil solution to such an extent, that the samples would have been rendered unusable for the sorption tests. In order to get an overview of the pH influence on PFOA sorption, the pH-modified soil samples were divided into four pH subgroups (pH<5.5, pH 5.5–6.0, pH 6.0–6.5 and pH 6.5–7.0) (Fig. 2).

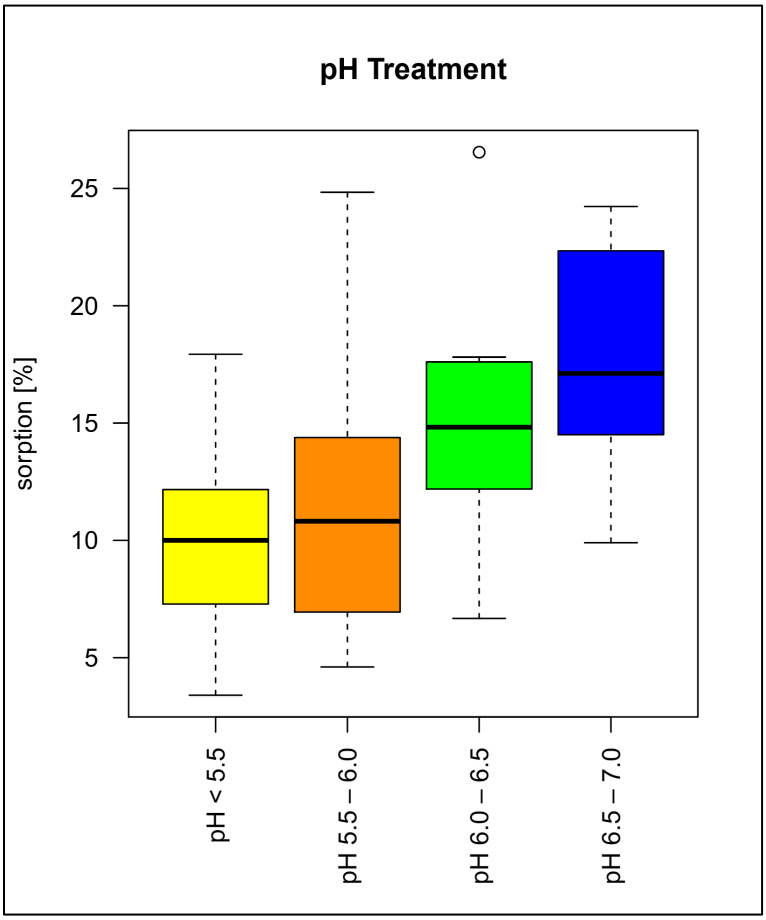


Fig. 2: Boxplot of the PFOA sorption in dependence on the pH value. Every group has a sample size of n=8 except for group pH 6.5–7.0 (n=9).

With increasing pH, the median sorption of the surfactant increased. The findings are in contrast to other studies. Wang and Shih (2011) for example found higher PFOA sorption with decreasing pH values. They studied the sorption behavior of PFOA and two other PFASs, among others, in relation to the influence of varying pH values. The selected pH value range was between 4–7 pH. The authors considered the reason for the decreasing sorption with increasing pH to be the reduction of electrostatic interactions.

However, figure 2 clearly shows that the boxes of the four groups overlap considerably. Therefore, it cannot be assumed that the mean sorption in the groups differ significantly from each other. That is why, a consideration of the pH value changes in the individual soil samples is reasonable beforehand. Thus, all modified mean pH values (n = 3) for each soil sample are presented in figure 3a. The red line marks the threshold value of 5.5. Since the eleven soils each had different pH values after the pH manipulations, the three different manipulation levels are summarized below as low, medium, and high. Within the low group, manipulations were made by adding high amounts of HCl, which lead to an overall decrease of the outgoing pH value. In the high group the pH was changed by the addition of NaOH, leading to pH increases and in the medium group, small amounts of HCl were added, which has led to a slight decrease in the pH values.

Even though the samples could be modified by a maximum of one pH unit, significant differences within the 5% confidence interval can be found in most samples. For the description as well as the discussion of the results, it is necessary to consider, that samples 5a and 5b must be treated separately. The adjusted pH values are below the 5.5 pH threshold. Therefore, it can be assumed that the soil surface is less negative and the sorption of PFOA is less disturbed. Based on the pH values of the two samples, it can be assumed that hydrophobic interactions of the PFOA to the soil organic matter dominate, while electrostatic interactions or precipitation mechanisms control the PFOA sorption behavior in the other samples.

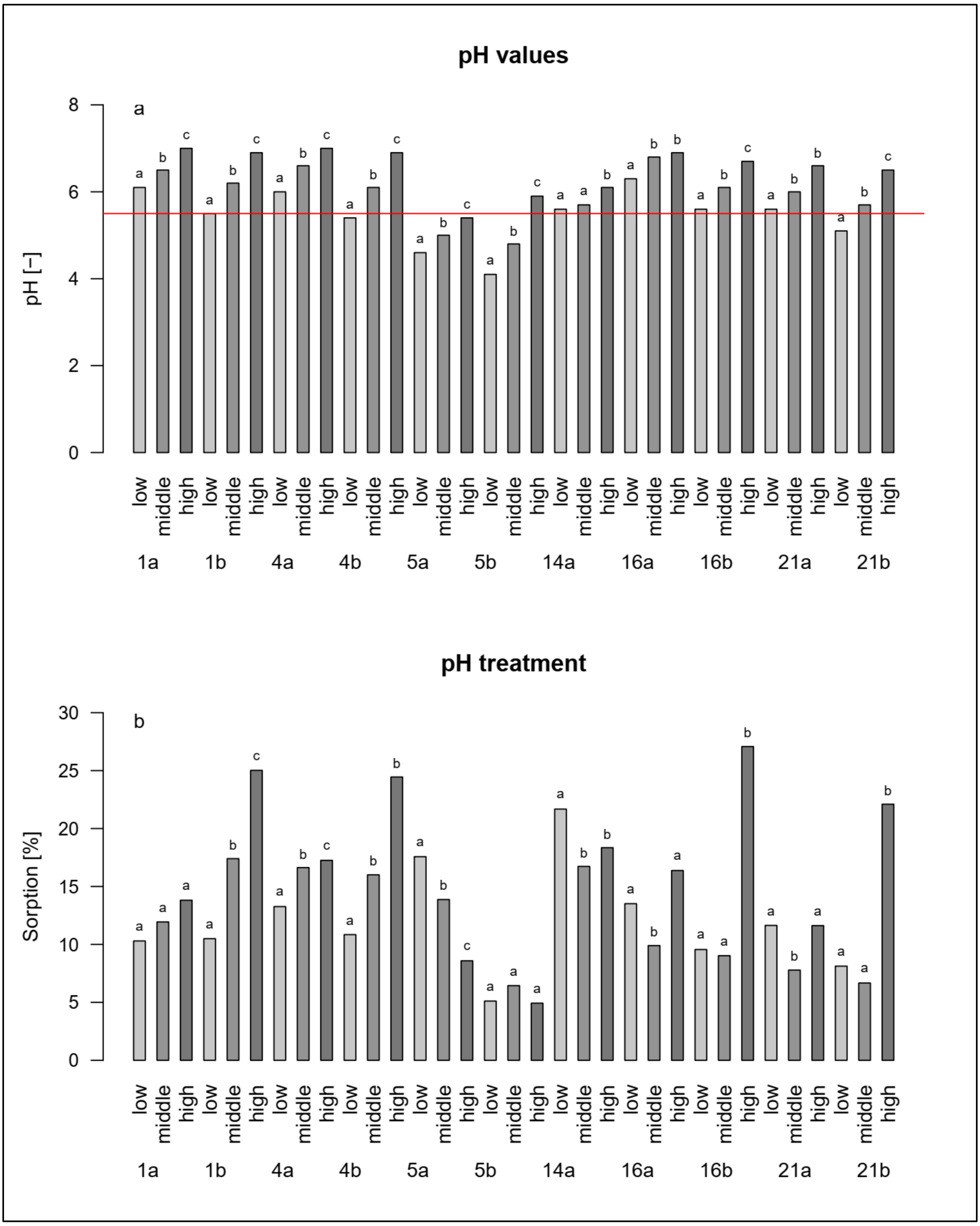


Fig. 3: a) Mean pH values after manipulation with HCl and NaOH (n=3). The red line indicates the threshold pH (5.5) of PFOA sorption in soils. b) Mean PFOA sorption [%] in the different pH-modified soil samples with n=8. Different letters show significant differences within a soil sample (MANOVA, $p < 0.05$).

Except for soil samples 5a, and 5b, sorption of PFOA increases with increasing pH. This relationship is significantly different in eight out of nine cases (Fig. 3). Therefore, the decreasing H^+ ion concentration with increasing pH appears to either enhance precipitation of PFOA in solution or increase electrostatic interactions to the soil solid phase.

As already mentioned, an opposite trend has been described in the literature. However, Oliver et al. (2019) found a much more variable change in sorption with increasing pH values, as described above. In soils with high SOC contents and high contents of sesquioxides, a linear decrease in sorption with increasing pH values was observed. In a sandier soil with relatively high concentrations of sesquioxides, PFOA sorption decreased with increasing pH but increased again after crossing the threshold of 5.5 pH. In the sandy soil with low SOC and sesquioxide contents, sorption increased with increasing pH again above the threshold of 4 pH. Therefore, pH alone does not appear to influence surfactant sorption. Rather, the soil composition also plays a major role here. The hydrophobic binding of PFOA in soils with pH values < 5.5 tends to decrease with increasing pH values, since the functional groups of the organic substance are increasingly protonated (Campos Pereira et al., 2018). In this study, the same relationship was found in sample 5a. Here, the sorption decreased with increasing pH. The three groups are different from each other in the 5% confidence interval and the sorption decreases from 17.6% to 8.6%. The surfactant possesses hydrophobic properties in acidic environments and thus mainly bind to the SOM, resulting in decreasing sorption potentials with increasing pH values (Oliver et al., 2019; Wang et al., 2012). In this context, however, it is noticeable that no significant difference in the sorption of PFOA was found in sample 5b. Nevertheless, the sample has a low SOC content (0.06%), which leads to a generally low adsorption potential. At the same time, the pH change does not affect the sorption, since the hydrophobic binding of the surfactant to the SOM is comparatively weak.

Based on the results, it can be summarized that the sorption of PFOA is mainly determined by the current pH of the soil. In soils with pH values below 5.5, sorption is mainly dominated by the quality and availability of SOC as well as the negative surface charge of the sorbents. At pH values above the threshold, electrostatic interactions and precipitation processes dominate the surfactant sorption. Additionally, as Oliver et al. (2019) described, the texture and content of sesquioxides can shift the threshold, which can lead to an increased sorption with increasing pH. However, this relationship needs further investigation for general applicability.

3.3.2 Effect of cation concentration (ionic strength) on sorption

Influence of ionic strength on PFAS sorption in soils and sediments

Several studies have shown, that the ionic strength in the soil solutions has an effect on the sorption behavior of PFAS (Chen et al., 2012; Higgins and Luthy, 2006; You et al., 2010). Higgins and Luthy (2006) found increased sorption of eight PFAS in five sediments by increased Ca^{2+} concentrations, while the addition of Na^{+} had no effect on the surfactant's sorption. The relation was attributed to the neutralization of the negative sediment surface charge, a decreased electrostatically repulsion and an increased salting-out effect of the rising content of dissolved ions (You et al., 2010). The salting-out effect occurs, when the surfactant molecule becomes more ordered and compressible in the presence of ions and the available cavity volume for the uptake of the neutral solutes decreases (Turner and Rawling, 2001). This leads to a decreased solubility of organic substances with increasing ion concentration (You et al., 2010), which results in precipitation of the surfactants. In the study of Cai et al. (2022) a linear relationship between sorption K_D values of 18 anionic PFAS was found. Further, the soil surface charge became less negative with increasing cation concentrations in the soil solution. Positive correlations between cations and surfactants were found, especially in the presence of polyvalent cations (Ca^{2+} and Mg^{2+}). The effect was more prominent for long-chain PFAS ($C > 10$), which were completely sorbed to the soil at high cation concentrations. It was concluded, that the primary effect of cations is the shielding of negative charges on the head group of PFAS and the realignment of molecules at the interface between the surface of SOM and soil solution, as well as by charge neutralization at the soil surface. The order of effectiveness of cations was $Na^{+} < Mg^{2+} < Ca^{2+}$ for the majority of the long-chain PFAS. Wang et al. (2015b) found the same order of cation effectiveness for the sorption of PFHxS, while

Campos Pereira et al. (2018) also found increased sorption of C5–C8 PFAS in an organic soil horizon in the order: Na^+ (10 mM) = Ca^{2+} (3 mM) < Ca^{2+} (5 mM) < Al^{3+} (2 mM). They further found no relation between cation concentration and sorption of long-chain PFAS (C9–C11), but high K_D values where already attempt at low ionic strength.

Cations in the soil solution can therefore affect PFAS sorption by multiple mechanisms as summarized by Cai et al. (2022): The salting-out effect (Endo et al., 2012), the bridging effect between the anionic functional PFAS head and negative surface charges of soils and sediments (Lath et al., 2019), reduced repulsion between anionic PFAS head groups and decreased charging on different soil surfaces (Chen et al., 2012), which reduces repulsion and enhances hydrophobic interactions between PFAS and organic matter (Ahrens et al., 2010; Higgins and Luthy, 2006; You et al., 2010).

Influence of ionic strength on PFOA sorption in eleven arable soils

In the following, the influence of ionic strength on the eleven agricultural soils of this study is examined in more detail. Since salts are disposed in every environmental sphere through various anthropogenic sources, the salinity of rain, surface and groundwaters is varying extensively (Wang et al., 2012). Sodium and calcium chloride for example are used as a de-icing agent for streets during the winter and can therefore enter wetlands, lakes, rivers, and soils (Shih and Wang, 2013; Wrochna et al., 2010; Xiao et al., 2011). Thus, the monovalent Na^+ and divalent Ca^{2+} cations can play important roles in the adsorption processes of PFOA. Hence, the influence of the two background salts $CaCl_2$ and NaCl was investigated in three different concentrations.

For the sorption and desorption experiments, described above, the background solution consisted of 10 mM $CaCl_2$ solution. This corresponded to specifications in the literature (Chen et al., 2013; Milinovic et al., 2015; Zhi and Liu, 2018). Since this concentration was already set high and there were lower concentrations found in other studies (Higgins and Luthy, 2006; Oliver et al., 2019), 5 mM and 1 mM solutions were used in addition to the 10 mM solution.

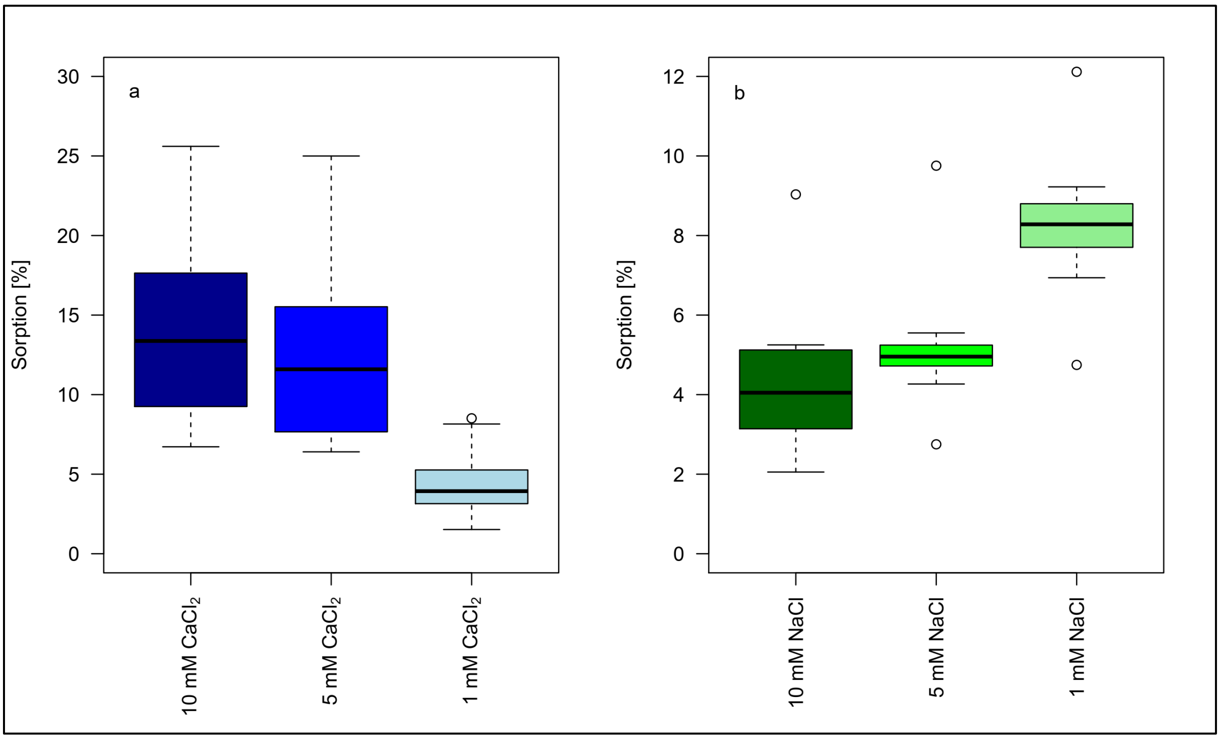


Fig. 4: Boxplot of the PFOA sorption in the 11 selected soil samples within the a) $CaCl_2$ and b) NaCl salt treatment in the concentration steps: 10 mM, 5 mM, and 1 mM. Every group has a sample size of n = 11.

Figure 4 summarizes the results of the sorption experiments in boxplot diagrams. When looking at the medians, it can be clearly seen that the PFOA sorption decreased with decreasing $CaCl_2$ concentration (Fig. 4a). The average decrease of PFOA sorption per unit $CaCl_2$ was 1.11% mM^{-1}. The median concentration of 5 mM does not correspond to this ratio, but the standard deviation in this range is significantly higher than that at 1 mM solution.

An explanation for the influence of Ca^{2+} molecules on PFOA sorption is, that the surfactant is negatively charged in neutral and alkaline soil conditions (Goss, 2008; Zhi and Liu, 2018), which are present in this study. The divalent cation calcium can build bridges between the negatively charged soil surface and surfactant (Higgins and Luthy, 2006; Liu et al., 2020; Oliver et al., 2019). The bridge building effect was also found for other divalent cations like copper and magnesium (Hyun and Lee, 2005). A further influencing factor can be found in the salting out process, which occurs in the presence of solved ions. They compress the water molecules and therefore reduce the cavity volume available to accommodate the neutral solutes (Turner and Rawling, 2001). Thus, the solubility of organic chemicals decreases. The crystallization in turn becomes apparent as increased sorption in the data. Moreover, the electrostatic repulsion is lowered at high Ca^{2+} contents which also leads to an increased sorption of PFOA (You et al., 2010).

Especially, the concentrations 10 mM and 1 mM $CaCl_2$ differ significantly ($p < 0.05$) from each other in most of the soil samples (Fig. 5).

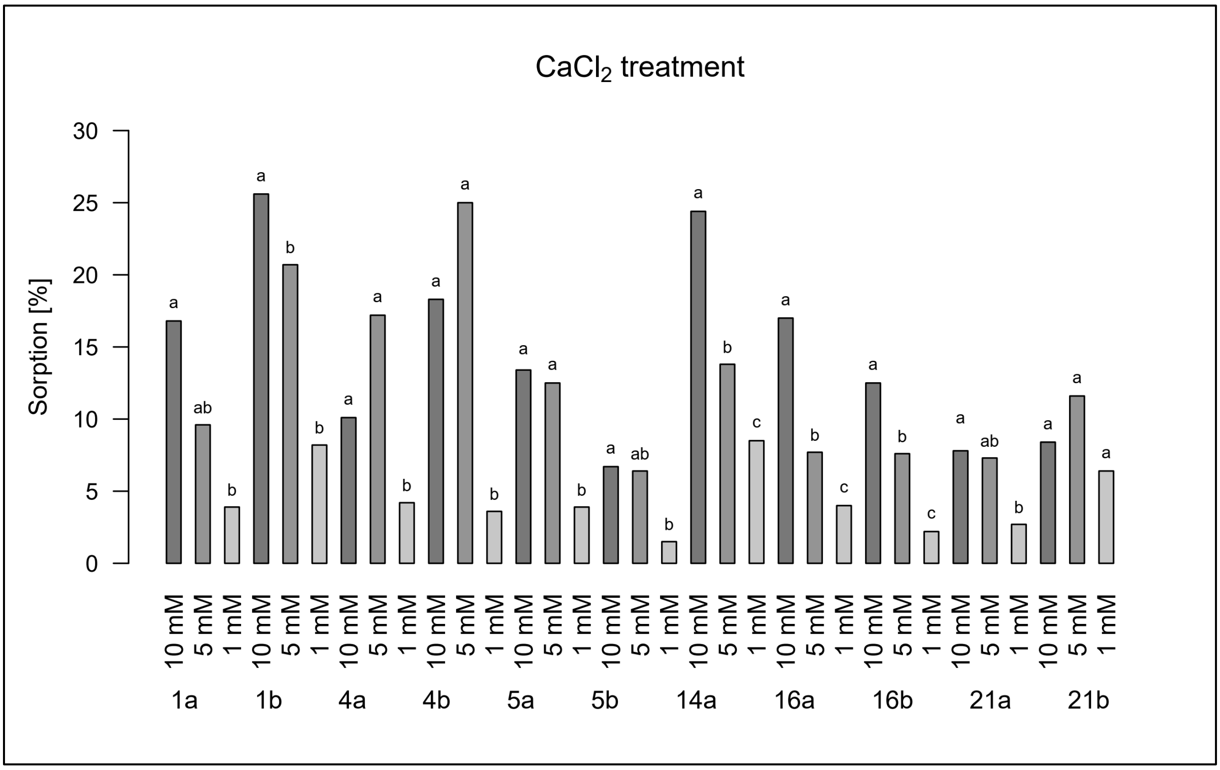


Fig. 5: Mean PFOA sorption [%] in the selected soil samples influenced by $CaCl_2$ concentrations of 10 mM, 5 mM, and 1 mM with n=8. Different letters show significant differences within a soil sample (MANOVA, $p < 0.05$).

Soils 5a and 5b are particularly interesting in this context, due to their pH values. The pH values are below the threshold of 5.5, whereby the hydrophobic binding of the surfactant to the SOM overrides the electrostatic binding to soil ions. Nevertheless, an increase in sorption by a factor of three (1 mM compared to 10 mM) can still be observed with increasing $CaCl_2$ concentration. However, the increase is weaker compared to soils with higher pH values. For example, in soil

16b (pH = 6.3) the sorption of PFOA was increased six-fold by an increase from 1 mM to 10 mM $CaCl_2$.

For the background salt sodium chloride, the conditions were reversed. The sorption increased with decreasing molarity of the solution (Fig. 6). Furthermore, the sorption was on average lower than the PFOA sorption in the $CaCl_2$ solution.

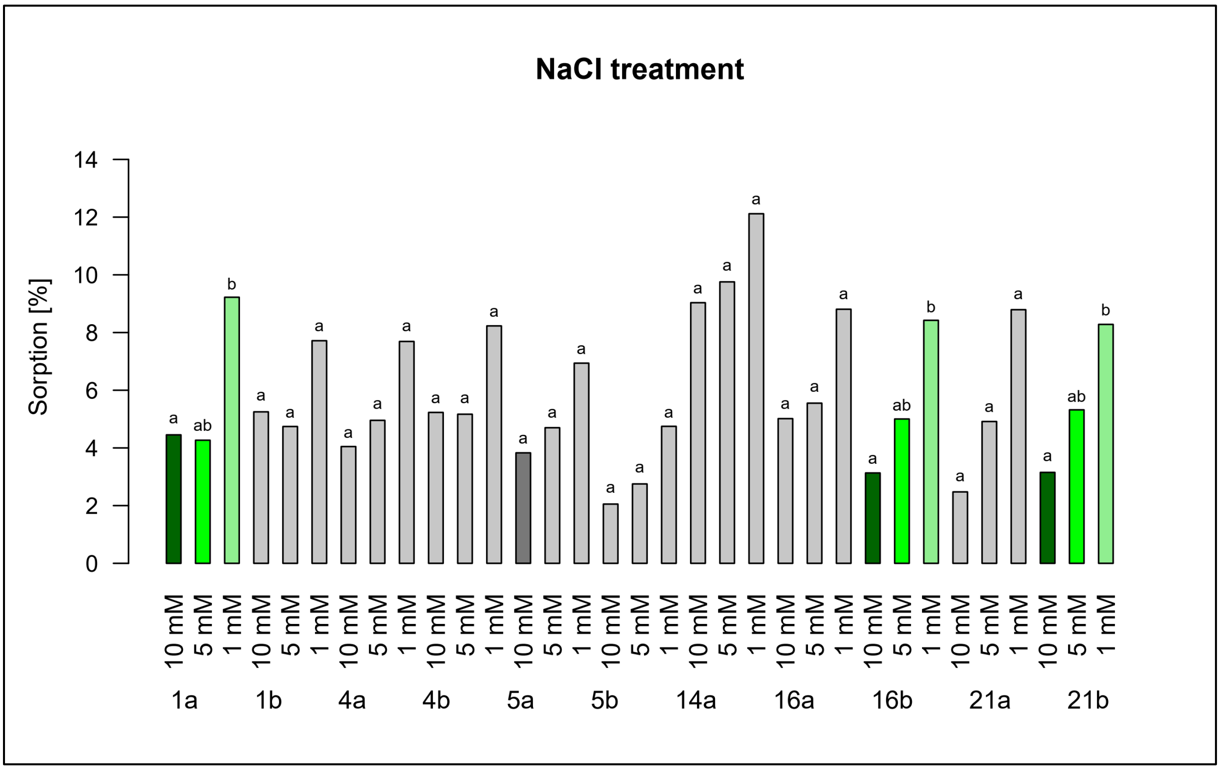


Fig. 6: Mean PFOA sorption [%] in the selected soil samples influenced by NaCl concentrations of 10 mM, 5 mM, and 1 mM with n=8. Different letters show significant differences within a soil sample (MANOVA, $p < 0.05$). Samples in which significant differences could be observed are shown in color.

The NaCl solution showed significant differences in the groups 10 and 5 mM in the 5% confidence interval for three soil samples (Fig. 6). Although the MANOVA identified significant differences in the NaCl groups, the median values were separated by only 4.3% (10 and 1 mM) and 3.3% (5 and 1 mM), respectively. The statistical significance can be explained by the low sample size (n = 11) per group. Therefore, an influence of the NaCl molarity could not be identified. This result coincides with the findings of other researches. Among others (Chen et al., 2012; Higgins and Luthy, 2006; You et al., 2010), Oliver et al. (2019), e.g., found no association between altered NaCl molarity and the sorption of PFOA, PFOS and PFHxS in soils.

In general, PFOA sorption was larger in the 10 mM and 5 mM $CaCl_2$ solution, than in the NaCl solution with the same molarity. This can be explained by the stronger divalent cation binding of Ca^{2+} in comparison to the monovalent Na^+ binding. Which is also an explanation for the positive correlation between PFOA sorption and the CEC (Xiang et al., 2018).

The sorption of PFOA slightly decreased with an increased Na^+ concentration, because the ionic strength in the 10 mM NaCl solution is ten times higher than in the 1 mM solution. Hence, the electrostatic interactions between the positively charged soil surface and the negatively charged PFOA decreased, which led to a decrease in sorption (Wang et al., 2012; Wang and Shih, 2011).

3.3.3 Temperature Influences

Temperature influence on sorption of PFAS in soils and sediments

The influence of temperature on the sorption of PFASs in soils and sediments has not yet been clarified sufficiently. However, it is known that the sorption of anionic surfactants is usually an exothermic reaction. This is the case, for example, for nonylphenol (Yang et al., 2011). The exothermic reaction is prevented by the increasing kinetic energy (Fava and Eyring, 1956; Ziegler and Handy, 1981), resulting in decreased sorption at high temperatures (Tao and Tang, 2004; Zhao et al., 2001). However, this process can also occur in opposite directions, as described by Kamal et al. (2017) and others. For enthalpy-driven sorption (low sorption strength) the sorption increases with increasing temperatures, while for entropy-driven sorption (high sorption strength) the sorption decreases during the same process. Sorption of PFOA and PFOS was described to be endothermic and entropy-driven (Jia et al., 2010; Xiang et al., 2018), which would lead to an enhancement of PFAS sorption at elevated temperatures. Given the special chemical properties of PFASs, it can be assumed, that like ionic strength and pH, the physiochemical properties of the soil will have a major effect on sorption when temperature is involved. Therefore, this relationship is considered in more detail below.

Temperature influence on sorption of PFOA in eleven agricultural soils

Given that so far not much is known about the influence of temperature on the sorption of PFASs in general and PFOA, the influence of temperature on the sorption of PFOA in the eleven described agricultural soils was analyzed in a final study. For this purpose, the temperatures 4, 20, and 30 °C were tested to recreate sorption behaviors for different seasons (Glaser and Riemann, 2009). A diversified investigation was necessary, since the solution behavior of PFOA is temperature dependent. The solubility of PFOA decreases from 9.59 g l^{-1} at 25 °C to 3.49 g l^{-1} at 22 °C (Campbell et al., 2009; Deng et al., 2012). For a first overview the sorption results are shown in figure 7.

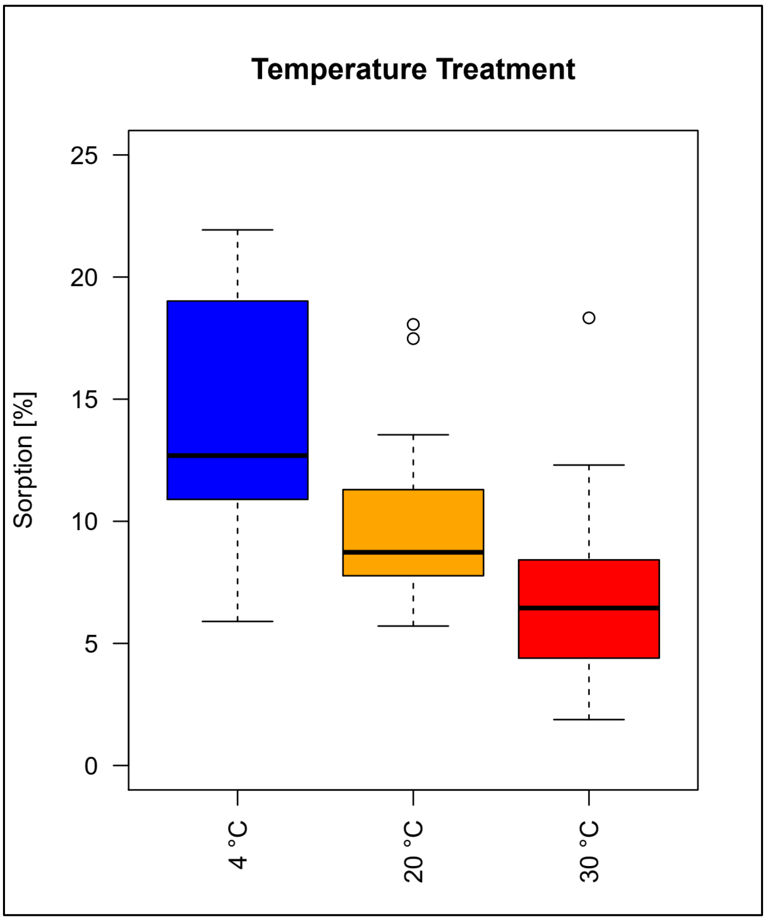


Fig. 7: Boxplot of the PFOA sorption under the influence of different ambient temperatures. Every group has a sample size of n = 11.

Although the minimum and maximum values as well as the quartile limits of the three groups partially overlap, the medians of the boxes indicate a negative trend of sorption with increasing temperature. The results indicated that the solubility of the surfactant has a decisive influence on sorption processes. Furthermore, it can be concluded, that an increased solubility at high temperatures masked the electrostatic interactions with soil minerals. Furthermore, reduced solubility at low temperatures could lead to salting-out effects of the surfactant. These would lower PFOA concentrations in the soil solution, which is subsequently interpreted as increased sorption, since sorption is determined by the difference between the initial PFOA concentration and the concentration in the soil solution.

The temperature influence on the sorption of PFOA in soils has not been researched in sufficient detail, so far. Xiang et al. (2018) tested the sorption behavior of PFOA in a paddy soil

(0–20 cm) on six different soil size fractions, at three different temperatures (15, 25, and 35 °C). For all six soil fractions the temperature increase resulted in a sorption increase, which contrasts with the results of this study. The authors explained their results by stating that PFOA sorption is an entropy-increased endothermic processes. Therefore, the available energy would be greater at higher temperatures, which would lead to a sorption increase. Since this study was performed on one soil sample only, the influence of the physicochemical soil properties was not considered.

However, Belhaj et al. (2019) investigated anionic surfactant adsorption with varying ambient temperatures, but with regard to improved oil recovery. They found decreasing sorption with increasing temperature for anionic surfactants. The authors discussed, that by increasing the thermal energy in the system through rising temperatures, the kinetic energy of the surfactant molecules increases subsequently, which corresponds to the findings of Xiang et al. (2018). But Belhaj et al. (2019) further explained, that the increase in the dynamics of the experimental system results in a corresponding reduction in sorption to the solid phase. In addition, Yekeen et al. (2019) also found increasing surfactant sorption on shale with decreasing temperatures. Another explanation for the decreased sorption with increasing temperatures can be found in the changed surface tension. It is known, that the sorption of surfactants increases with increasing surface tension (Herzfeldt and Kreuter, 1999; Sun et al., 1995). With increasing temperature, the surface tension of the soil-water system decreases, resulting in a reduced sorption rate (Gao and Shao, 2015; Nimmo and Miller, 1986).

In order to be able to finally consider the sorption of PFOA in detail, the results were additionally presented for the individual soil samples (Fig. 8). Significant differences are again marked in color.

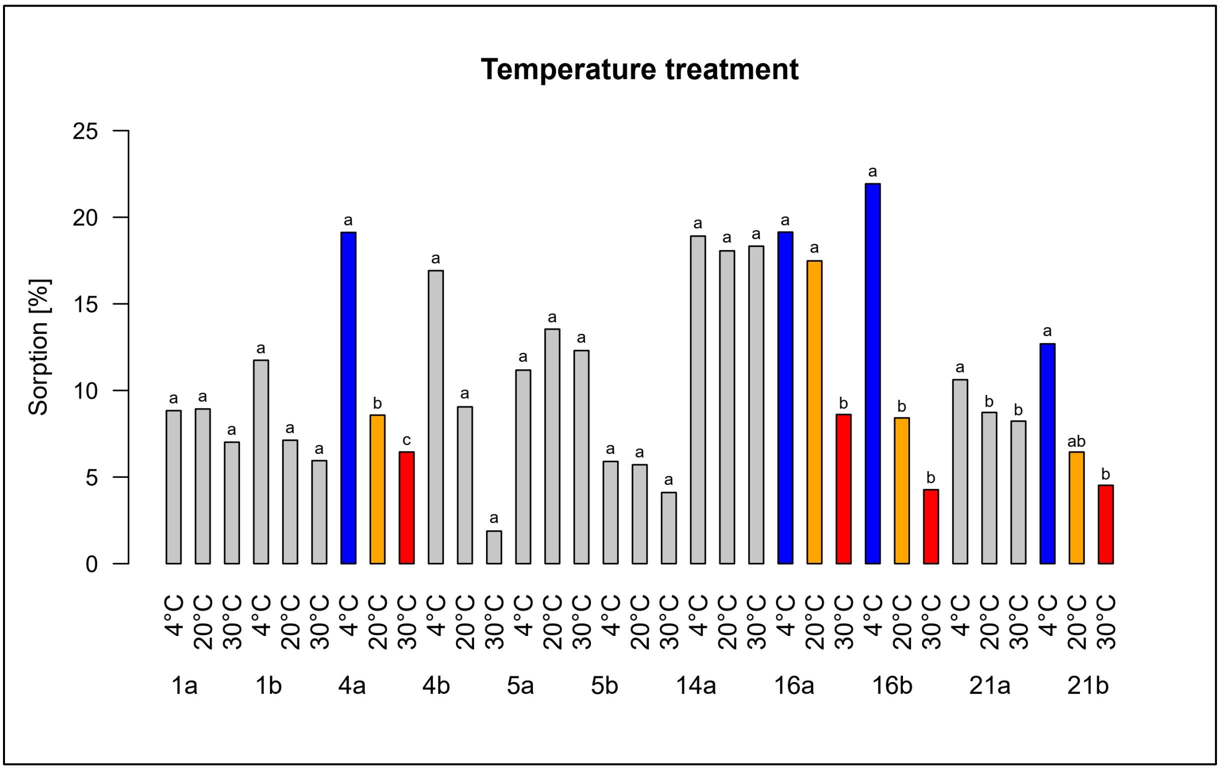


Fig. 8: Mean PFOA sorption [%] in the selected soil samples influenced by three different ambient temperatures of 4°C, 20°C, and 30°C with n=8. Different letters show significant differences within a soil sample (MANOVA, $p < 0.05$). Samples in which significant differences could be observed are shown in color.

As shown in the figure, all samples with significant differences show decreasing PFOA sorption with increasing temperature. This corresponds to the trend shown in figure 7. It becomes clear, that PFOA sorb to less than half the amount at an ambient temperature of 30°C compared to 4°C. In soils 4a and 21b, sorption at 4°C is three times higher than at 30°C. In soil 16b, sorption is even five times higher. Differences in the temperature effect between the samples suggest, that not only the PFOA dynamics but also the dynamics of the respective soil components increased. One such component is dissolved organic carbon. It interacts with the PFOA molecules at high temperatures to different extents in the respective samples.

However, in most of the soil samples no significant and thus systematic differences in the different temperatures were found. An explanation can be found in high variances of the individual measurements especially in the 30°C dataset. Thus, total amounts of outliers in the respective datasets are shown in figure 9.

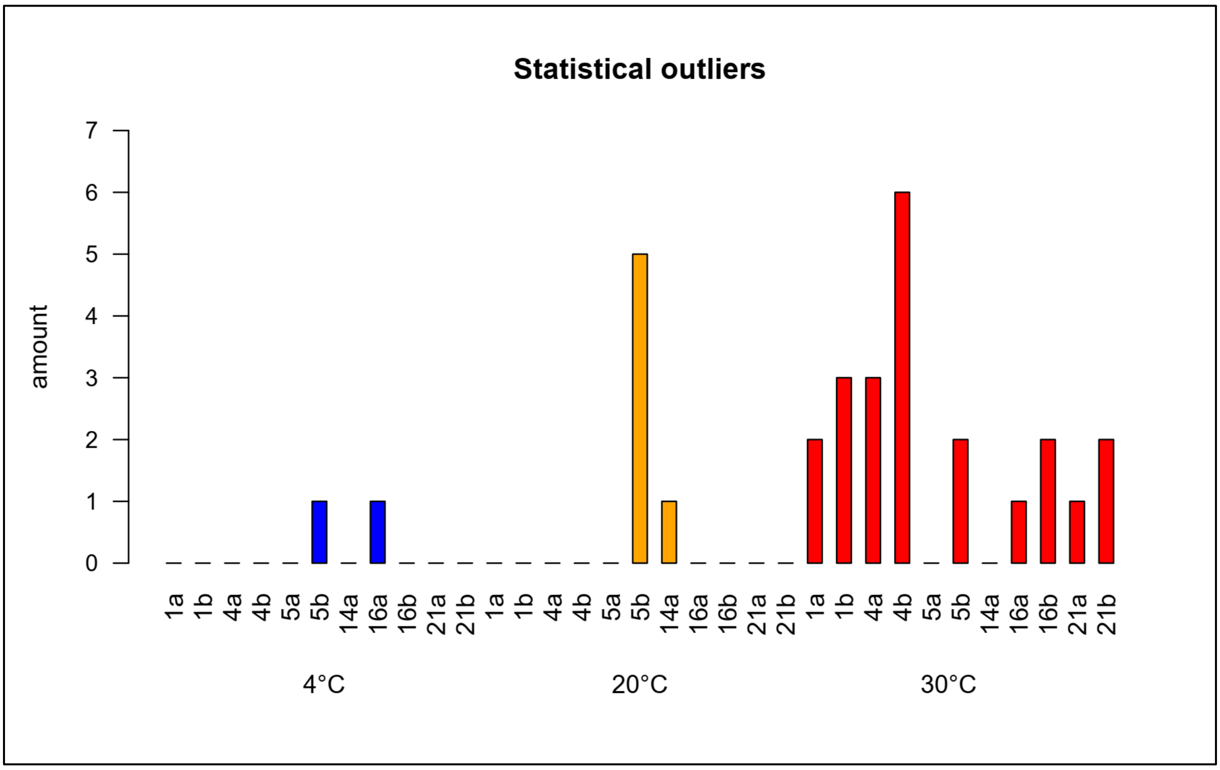


Fig. 9: Number of statistical outliers in the PFOA sorption measurement in the respective soil samples. In each temperature and soil samples eight parallels were considered.

The figure clearly shows that outliers occur especially at an ambient temperature of 30°C. By increasing the thermal energy, the dynamics in the sorption process were changed. This probably prevented the equilibrium state between solution and solid phase from being reached after 24 hours. Therefore, unlike the other two, this data set has a high variance in the results. As already explained, these outliers were not considered for the average calculation, so that in the end a clear influence of the test temperature on the sorption of PFOA can be determined. In summary, the sorption of PFOA is subject to temperature influence. With increasing temperatures, the sorption of the surfactant decreases significantly. This leads to an increased mobility of the surfactant during the summer months. However, the temperature curve in the soil profile must also be considered in this case. Since the temperatures drop further with increasing depth, the leached surfactant of the topsoil may reattach with leachate in colder subsoil layers. Further temperature dependent tests in column trails or in the field are recommended accordingly at this point.

4 Conclusion

Sorption and desorption strength of PFAS in soils is mainly influenced by the respective physiochemical soil and surfactant properties. Since the surfactants are negatively charged under natural pH conditions, pH changes primarily lead to a different chemical composition of the soil solution. Changes in surfactant properties are subordinated in this regard. If the pH value in the soil declines, PFAS sorption increases because the repulsion between the negatively charged soil surface and the negatively charged surfactant is weakened, due to the increase of protons. The availability and quality of SOM and clay minerals positively enhances the binding of PFAS. However, this relation was not found for PFOA in agricultural soils with pH values above a threshold of 5.5. It is assumed, that hydrophobic interactions are becoming less important through the progressive deprotonation of the surfactant with increasing pH. Thereby, electrostatic interactions with the soil ions, especially those of the sesquioxides, determine the sorption of PFOA. In this context, polyvalent cations are of particular importance. They are able to form bridges between the surfactant and the soil surface and thus enable sorption. No clear influence of the Na^+ concentration in the background solution was detectable. However, a decreasing sorption tendency with decreasing Na^+ concentration was observed, which might be caused by a reduction of the electrostatic interference.

When manipulating the ambient temperature, an increase in sorption could be achieved with decreasing temperature. This effect can mainly be explained by the better solubility of PFOA and the decrease in surface tension with increasing temperatures. Therefore, a higher leaching of PFOA in arable soils during the summer months are expected.

It must be pointed out, that for this study the investigations were performed individually. Nevertheless, feedback effects of the individual treatments on each other cannot be ruled out. The manipulation of the salt background concentration, can for example also impact the pH. By adding Ca^{2+} to the solution, the pH decreases, which can in turn increase PFOA sorption (Higgins and Luthy, 2006). The manipulation of one environmental parameter can therefore lead to the simulated variation of other parameters. This relationship should be investigated more closely in future studies.

Acknowledgement

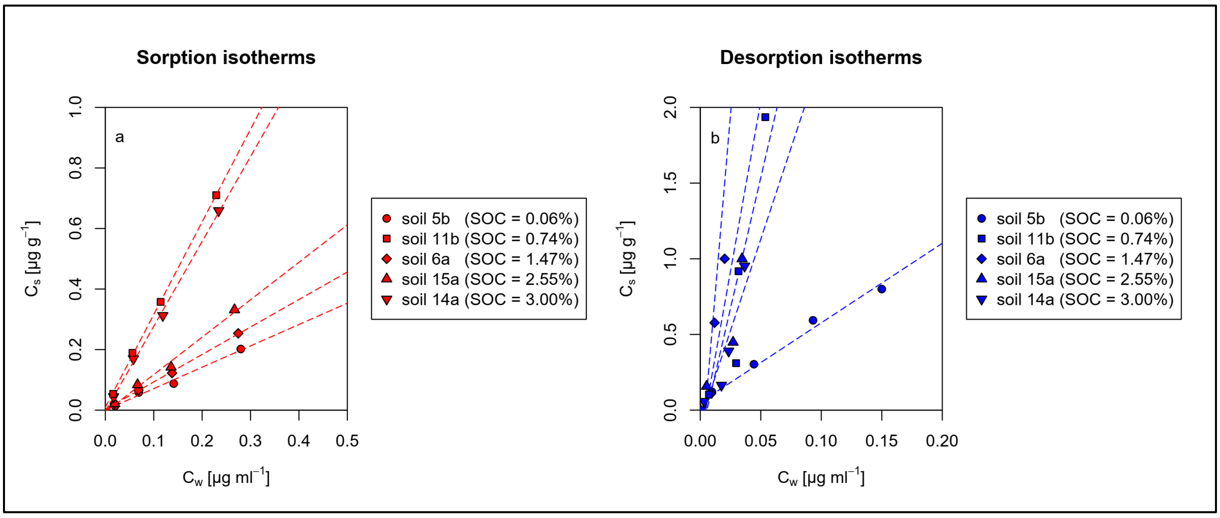
We would like to thank the Geographical Survey NRW and the Ministry for Environment, Agriculture, Conservation and Consumer Protection of the state of North Rhine-Westphalia for providing the soil samples. Special thanks to Mareike Mersmann and Jörg Leisner for the intensive professional exchange and consultation during the project. We would also like to thank the RUBION at the Ruhr-Universität Bochum for providing us laboratories and equipment for working with radioactive chemicals and Heidrun Kerkhoff and Katja Gonschorek for laboratory assistance.

Funding

We acknowledge the funding for this research provided by the Ministry for Environment, Agriculture, Conservation and Consumer Protection of the state of North Rhine-Westphalia.

Appendix

#1



Appendix 1: Linear (a) sorption and (b) desorption isotherms of five representative soils with varying SOC contents.

#2

Appendix 2: Sorption and desorption results of the 39 soil samples.

Soil Properties		Samples (n = 39)			
		Mean	S_D	Min.	Max.
Sorption	[%]	12.13	4.45	5.68	25.60
S_D	[%]	0.64	0.21	0.19	0.97
K_D	[ml g^{-1}]	1.44	0.62	0.60	3.47
Desorption	[%]	42.05	19.38	13.82	85.02
S_D	[%]	1.24	0.56	0.09	2.20
K_D	[ml g^{1}]	19.96	14.67	2.03	62.37
Hysterese	[-]	0.82	0.29	-0.71	0.98

#3

Appendix 3: Pearson correlation coefficients for PFOA sorption [%] and desorption [%].

Soil Properties		Sorption [%]	Desorption [%]
		R^2	R^2
SOC	[%]	0.43**	-0.44**
Sand	[%]		0.5**
Silt	[%]		
Clay	[%]	0.4*	-0.41**
CeC_{eff}	[$mmol_c$ kg^{-1}]	0.33*	-0.5**
Fe_A	[%]	0.34*	
Mn_A	[%]	0.43**	-0.38*
Al_A	[%]	0.42**	
pH	[-]		-0.43**
Conductivity	[µS cm^{-1}]	0.36*	-0.37*
Chloride	[mg kg^{-1}]		-0.47**
Nitrite	[mg kg^{-1}]		-0.46**
Bromide	[mg kg^{-1}]		-0.42**
Nitrate	[mg kg^{-1}]		-0.32*
Calcium	[mg kg^{-1}]	0.36*	-0.53**
Magnesium	[mg kg^{-1}]		-0.46**
Sodium	[mg kg^{-1}]		-0.32*

*indicating p-values <0.05

**indicating p-values <0.01.

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Chapter 5

Synopsis

Summary

Over the past year, the concern about PFAS increased, since they were found ubiquitous in the environment and are potentially toxic to humans, other mammals, and aquatic organisms. After the release of PFASs in the environment, they undergo several degradation and sorption processes, which are controlling their concentrations in soils and aquatic environments. Thus, an understanding of their distribution behavior in soils is essential to improve risk assessments for those substances. Therefore, the aim of this study was to identify the general sorption and desorption mechanisms that control the distribution of PFASs in soils.

Since the group of PFAS consists of more than 4000 individual substances, the experiments were carried out with one of the two lead substances: PFOA. PFOA is either released into the environment through direct utilization, or released as an end product during the mineralization of longer-chain precursor compounds. As the sorption and desorption mechanisms of PFOA in soils were not sufficiently understood, the already widely studied nonylphenol (NP) was co-examined in the same soils. This allowed a better classification and characterization of the obtained results.

This thesis consisted of over 100 series of batch experiments conducted with the radiolabeled surfactants NP and PFOA with a total of 134 different soil samples taken from various sites in Germany. The physicochemical soil properties were analyzed for all soil samples. For 96 samples, grounded and sieved FTIR spectra were measured in order to determine the quality of the SOC. Further, an incubation test was performed to evaluate the microbial degradation of the surfactants within one year. Firstly, results were used to characterize the sorption behavior of the two surfactants in soils depending on the physicochemical soil properties. In a next step, the FTIR data was used to improve the understanding of the sorption behavior of NP and PFOA in soils with low SOC contents (< 0.5%). Following the sorption experiments, desorption experiments were performed on aged samples. Thus, influences on soil aging were depicted. Finally, the influence of changing soil conditions on the distribution of PFOA in soils was analyzed on 39 arable soils. The results contribute an improved understanding of the

sorption and desorption processes of NP and PFOA in soils, as described and discussed in the following.

Sorption and desorption processes depending on the SOC content

The sorption of the two surfactants was fitted by linear regression for all conducted experiments. With log (K_D) values between 1.78–3.68 NP sorption was significantly higher than that of PFOA (log (K_D) = –0.9–1.41). Furthermore, NP was almost completely adsorbed ($\bar{x}$ = 97.4%, SD = 0.15). In topsoils (SOC > 0.5%) the sorption of NP was mainly influenced by the SOC content. Correlation coefficients in individual SOC groups were determined, which varied between 0.8 and 0.9. With increasing SOC, the sorption increased, whereby a saturation was observed at a content of over 4% with about 99.5% sorption. However, in subsoils a significant decrease in the SOC influence (r^2 = 0.4) was observed. Sorption levels remained high ($\bar{x}$ = 95.5%), but a standard deviation increase of 2.4% was observed. By evaluating the sieved FTIR spectra, an increased influence of SOC quality rather than quantity was determined in subsoils for NP sorption. Furthermore, manganese and iron minerals also influenced NP sorption in SOC depleted subsoils.

With a range of 1–68.6%, PFOA sorption varied widely in the first test series. An increased SOC influence with increasing SOC concentrations was measured. Nonetheless, with a maximum r^2 of 0.65, the correlation was less distinct than for NP. In subsoils, a correlation with SOC was not detectable (r^2 = 0.00). In the second test series, PFOA adsorbed with a maximum of 25.74% in a SOC enriched soil (3.56%). The lower overall sorption was caused by higher pH values and lower SOC contents within the data set. Again, there was no measurable correlation with SOC content in this test series.

The desorption potential of PFOA was much higher than that of NP in both SOC depleted and enriched soils. The desorption of NP on aged samples could not be explained with the used method, because the molecules were metabolized during the storage period. However, the low desorption rates (x̄ = 4.2%) indicated, that NP and its metabolites are hardly leachable under natural conditions in aged samples. A low desorb ability of NP in soils was also found on fresh samples. Wang et al. (2019), e.g., observed maximum desorption of 5%, with previously over 97% sorption, in three different soils. The desorb ability mainly depended on the total organic carbon (TOC) content.

The desorb ability of PFOA was approximately equal in both fresh (x̄ = 40%) and aged (x̄ = 46%) samples. The maximum desorption of aged samples was 97.5% compared to 70% for fresh samples. However, this difference may have been caused by the different soil properties. The SOC content had no explanatory relevance for either data set. It only became visible after the aged data set was split into different SOC groups. Here, a negative influence could be detected. The desorption results indicated, that the PFOA leaching risk in soils is high, regardless of how long it has already been in the soil.

The SOC content has thus different influences on the sorption and desorption potential of NP and PFOA. While the distribution of NP is mainly influenced by SOC content, other impact factors play an important role in sorption and desorption processes of PFOA, which will be described in detail in the following.

Influence of other physicochemical soil properties

Despite SOC content, other physicochemical soil properties influenced the sorption and desorption of NP and PFOA in soils. Although NP sorption was mainly determined by the OC content in topsoils, clay, amorphous iron, and aluminum content also had a significant influence. With increasing clay and SOC contents, NP sorption increased, whereas an enhancement of the positively charged particles aluminum and iron led to a decrease in sorption. This can be attributed to a disturbance of the hydrophobic interactions (see chapter 2). In subsoils, however, the influence of clay, iron, and aluminum decreased as well as the explainable variance of the data set, while the influence of SOC remained constant. Through the evaluation of the sieved FTIR data, the subsoils were divided into two clusters using a PCA analysis. One cluster showed a higher SOC quality, which could be detected, e.g., by higher peaks in the range of C-O-H group vibrations (1660 cm^{-1}) or aromatic structures (1410 cm^{-1}, 2850 cm^{-1}, and 2920 cm^{-1}). This leads to the conclusion, that in subsoils not only the content but also the quality of the SOC is important for the sorption of NP. Nevertheless, averaged adsorption rates of over 95% regardless of soil properties indicated, that soils are potential sinks for this pollutant. This is further enhanced by the fact that NP cannot be dissolved out of the soil by the leachate.

The sorption of PFOA was determined by different physicochemical soil properties. In topsoils, high SOC contents dominated hydrophobic sorption processes, but also the content of clay and iron minerals had an influence on the sorption. With increasing pH values, the sorption of PFOA and the influence of SOC decreased steadily. Simultaneously, the importance of clay, iron, and aluminum mineral contents increased. Those minerals influence the electrostatic interactions of PFOA with the soil, which are dominant in pH ranges above 5.5. In subsoils with low SOC concentrations, contents of clay, manganese, and iron minerals dominated PFOA sorption, if present. In mineral and SOC depleted subsoils, sorption processes were not explainable by the used physicochemical properties.

Influence of the physicochemical surfactant properties

One of the main factors influencing the sorption of perfluorinated surfactants are the physicochemical properties of these substances. Due to the low pk_a value of –0.5 (Campbell et al., 2009), the surfactants are completely dissociated under natural conditions. The SOM is also negatively charged, because of the presence of dissociated carboxylic and phenolic acid groups (Kinniburgh et al., 1999; Wan et al., 2013). Therefore, the sorption of PFOA below the threshold value of 5.5 is determined by hydrophobic interactions between the surfactant and the SOM. This explains why the amount of SOC has been determined as the main influencing parameter in numerous studies (Miao et al., 2017; Milinovic et al., 2015), because mainly topsoils with high amounts of SOC and low pH values were analysed (Li et al., 2018; Zhu and Kannan, 2019).

However, if soil pH values are increased, such as in arable soils due to liming, the dissociation of both substances is reduced. This, in turn, led to an increase in the electrostatic interaction between PFOA and charged soil particles like clay minerals or iron oxides (Oliver et al., 2019; Tang et al., 2010). Since the electrostatic bond is considerably weaker than the hydrophobic bond, the sorption potential of PFOA is lower in neutral and alkaline pH ranges.

The change of the physicochemical properties of NP in soils is not expected, since an ionization of the surfactant would only be present in very alkaline soils ($pk_a = 10.7$). Therefore, in natural soils, the hydrophobic interactions dominate the sorption of NP (Düring et al., 2002).

Influence of varying soil matrix conditions

Not only the physicochemical properties of soils and pollutants are influencing sorption processes of pollutants in soils. Changing external conditions of the soil matrix also determine the retention. Influences of varying temperatures as well as concentration and composition of the leachate were therefore investigated in more detail in a final experiment.

Salinity influence

In contrast to the bivalent cation calcium, the monovalent cation sodium had only a minor influence on the sorption of PFOA. With decreasing molarity of Na^+, the sorption of the surfactant increased slightly. This can be explained by the decrease in the ionic strength, as it interferes with the electrostatic interactions in the soil solution. Thus, a reduction of the disturbance leads to an increase in sorption. However, the reduction of Na^+ concentrations by a factor of 10 only led to a sorption increase of 3.1%. Thus, the influence of monovalent cations on the sorption of PFOA is negligible for risk assessments.

Changing Ca^{2+} concentration had a significantly greater effect. With decreasing concentrations, the sorption of PFOA decreased by the factor of 1.11% mM^{-1} Ca^{2+}. This relation was mainly explained by the formation of bridges between the negative surfaces of the soil and the surfactant. This effect was also found for other divalent cations like copper and magnesium (Hyun and Lee, 2005). Besides the effect of bridge building, electrostatic repulsion is lowered at high Ca^{2+} contents, which also leads to an increased sorption of PFOA (You et al., 2010). Finally, the solubility of surfactants decreases at high ion concentrations in solutions since the ions compress water molecules and reduce the cavity volume available to accommodate neutral solutes (Turner and Rawling, 2001). In turn, the crystallization becomes apparent as increased sorption in the data (You et al., 2010).

Therefore, it can be concluded, that changes in the chemical composition of the leachate can have a significant effect on the sorption of PFOA. The sorption is especially high, if high concentrations of polyvalent cations are present in the leachate water and in the soil.

Temperature influence

A temperature increase of 26 °C decreased the sorption of PFOA in the tested soils by 7%, which is a factor of 0.27% $°C^{-1}$. The reduced sorption is explainable by increasing solubility of PFOA with increasing temperatures (Campbell et al., 2009; Deng et al., 2012). It is therefore possible, that low temperatures lead to crystallization of the surfactant. The lowered concentration in the soil solution would again be interpreted as sorption since it is calculated by the difference between the initial PFOA concentration and the concentration after shaking. Furthermore, the temperature change also has an influence on the surface tension of the soil-water system. The sorption of surfactants increases with increasing surface tension (Herzfeldt and Kreuter, 1999; Sun et al., 1995). An increase in temperature leads to a decrease in surface tension, which in turn leads to reduced sorption (Gao and Shao, 2015; Nimmo and Miller, 1986). Therefore, a higher risk of PFOA leaching during the summer months is to be expected.

Microbial decomposition of NP and PFOA in soils

The incubation study was used to test the microbial decomposition of NP and PFOA in four different soils, with varying physicochemical characteristics. Since the samples for the desorption experiments were stored over the period of one year, the incubation time was also set to one year. At present, data from the first half year are on hand.

It was found, that PFOA was not metabolized over the observation period. After half a year, a degradation of 0.4% of the initial contamination was observed. It has been confirmed several times that the strong C-F compounds prevent decomposition of PFOA under natural conditions (Lee et al., 2017; Liu et al., 2017; Liu et al., 2019). A strain of bacteria has already been discovered that is able to destroy PFOA, however, the strains have long degradation cycles, low efficiency, and are not able to decompose PFOA completely (Yi et al., 2019). Thus, they are not able to decompose PFOA in the increasing demand.

In contrast, a degradation of NP could be detected during the observation period. Depending on the available SOC content, up to 32% of the initial concentration was decomposed within half a year. Although sodium azide was used to sedate the microorganisms, decomposition processes could be measured after 27 days of incubation. This is due to the fact that, sodium azide is a bacteriostatic agent and not a sterilant. Thus, microbial communities remained present and the microbial activity was inhibited for a short time only.

Therefore, it can be concluded, that NP is degradable under natural conditions. Different parameters are responsible for the intensity of the degradation rate. The microorganisms must first have a tolerance to the toxicity of the pollutant (Ahmed et al., 2001; Soares et al., 2003). Furthermore, their productivity depends on oxygen supply (Hesselsoe et al., 2001; Topp and Starratt, 2000) and bioavailability (Bosma et al., 1997; Kelsey et al., 1997), as well as the supply of carbon and nitrogen (Heitkotter et al., 2017). Another important influencing factor is temperature. As temperatures rise, the productivity of microorganisms increases, since the available oxygen quantity increases simultaneously (Marcomini et al., 1989; Topp and Starratt, 2000). At temperatures below 4 °C no metabolic activity of NP decomposing fungi could be detected so far (Kollmann et al., 2003).

Synthesis

In all experiments, sorption of NP and PFOA was linear. With log (K_D) values between 1.78–3.68 the NP sorption was significantly higher than the PFOA sorption (log (K_D) = –0.97–1.44). In topsoils, SOC content determined NP sorption. The hydrophobic interactions between the surfactant and the SOC were the most important sorption mechanism. For PFOA a SOC dependence in the topsoil could also be determined, but only in certain pH ranges. In soils with low pH values (< 5.5), the surfactant is almost completely dissociated due to the low pk_s value. Therefore, the hydrophobic interactions between the negatively charged surface of the surfactant and the organic matter are dominating the sorption. If the pH rises above a threshold of 5.5, dissociation decreases to such an extent that electrostatic interactions with positively charged soil components, such as iron minerals, are predominant. Therefore, when considering PFOA sorption in topsoils, not only the SOC content but especially the pH values must be considered in detail.

Overall, the determined log (K_D) values from the first test series corresponded to the literature. Milinovic et al. (2015), who examined six soils with a maximum SOC content of 39%, found log (K_D) values between –0.1–1.69. Furthermore, Knight et al. (2019) tested PFOA sorption on 100 different soils and found log (K_D) values between –0.22–1.17 (SOC range: 0.1–3.5).

In subsoils, the relevance of SOC decreases significantly for both surfactants. For NP, correlations in the range of 0.4 were found, while a correlation to PFOA sorption could no longer be measured. An effect of SOC inaccessibility was not found, but for NP, an increased importance of SOC quality instead of quantity was measured. Thus, SOC aggregation with the mineral fraction was important since aggregation will affect SOC quality characteristics on aggregate surfaces. In soils with low SOC contents (< 0.5%), which have both low concentrations of iron and clay minerals, the behavior of PFOA remained unpredictable. If clay minerals are present in these soils, they dominate the sorption process. This effect increases further with increasing pH values.

The desorption potential of PFOA was much higher than that of NP in both SOC depleted and enriched soils. The desorption of NP on aged samples could not be imaged with the used method, because the molecules were metabolized during the storage period. However, the low desorption rates ($\bar{x} = 4.2\%$) are indicating, that NP and its metabolites are hardly leachable under natural conditions in aged samples. A low desorb ability of NP in soils was also found on fresh samples. Wang 19 observed maximum desorption of 5%, with previously over 97% sorption, in three tested soils. The desorb ability mainly depended on the total organic carbon (TOC) content since the desorption decreased with increasing values.

The desorb ability of PFOA was approximately equal in both fresh ($\bar{x} = 40\%$) and aged ($\bar{x} = 46\%$) samples. The maximum desorption of the aged samples was 97.5% compared to 70% for the fresh samples. However, this difference may have been caused by the different soil samples. About 40% of the variances could be explained for the fresh and aged data sets by multiple regression. The main influencing factor was the clay content in both cases, indicating higher desorption potentials at lower clay contents. In the aged samples, the aluminum concentration and the size of the soil surface were also significant influencing variables. While, chloride and magnesium concentrations were significant in the unweathered data set. The SOC content had no explanatory relevance for either data set. It only became visible after the aged data set was split into different SOC groups. Here, a negative influence could be detected. However, this was only visible for soils with pH values above the 5.5 threshold.

Thus, in both cases, desorption was mainly determined by the clay content and the pH value of the sample. The SOC content had only a minor influence on desorption behavior. The regression models have different explanatory variables, since varying physicochemical properties of the soil were incorporated into the models.

Besides the physiochemical soil properties, the influence of changing soil matrix properties on the sorption of PFOA was investigated in this study. It was found that the concentrations of polyvalent cations, e.g., calcium, has an influence on the sorption behavior of PFOA. The ability of cations to form bridges between the negative surfaces of the soil and the surfactant increases adsorption processes. Since monovalent cations are not able to form these bridges, no clear influence of the concentration of sodium on the sorption behavior of PFOA could be determined. Due to the use of deicing agents on streets in the winter period, an increased amount of calcium chloride can be found in the leachate. This, in turn, leads to an increased adsorption potential of PFOA during this season. This effect is further enhanced by the fact that winter temperatures also lead to a sorption increase. Since low temperatures lead to an increase in surface tensions, this effect is mainly caused by the increase in surface tension, leading to an increase in sorption.

Perspectives

Although this research improved the understanding of the distribution behavior of NP and PFOA in soils, some questions remain unanswered, which should be examined more closely in further studies.

First of all, the sorption processes of PFOA and NP in SOC, clay and iron oxide depleted subsoils could not be fully explained by the determined physicochemical soil properties. Hence, additional parameters should be included for the investigations, such as solved anions and cations. Further data on SOC quality and its microstructure would, e.g., contribute to a better understanding of the sorption behavior of NP in such soils. For PFOA sorption, more differentiated data on clay mineralogy are required. These can have numerous molecular structures and functions, which in turn can interact with the deprotonated PFOA.

By extending the shaking time during the batch experiments, a more realistic picture of the sorption could be covered. As it is well known, sorption takes place in two steps. The relatively fast adsorption is usually completed after 24 h. However, depending on the chain length, the absorption can last several days (UBA, 2020). It is therefore possible that the sorption was underestimated in the conducted experiments. This influence should be determined by sorption measurements at constant time intervals, similar to the investigations of Higgins and Luthy (2006) on PFOS and PFDA sorption.

In order to describe the desorption behavior of NP on aged soils, another method should be used to quantify NP concentration in the batch experiments or soils must be sterilized instead of spiked with sodium azide to avoid microbial activity over the storage period.

Further investigations on the temperature influence on the sorption of PFOA should be performed, as the results obtained partly contradict the literature. In this case, experiments with more soils in all pH ranges should be carried out in order to investigate the influence of the physicochemical soil and surfactant properties on the temperature variance in more detail. This could improve the understanding of the temperature influence on the PFOA sorption. In addition, the changes in the soil matrix should also be tested on additional PFAS compounds.

This would make it possible to determine how the carboxy or the sulfone group has a further influence on the sorption behaviour. It can also be assumed that the change in soil matrix has less influence on molecules with shorter chain lengths. This thesis should also be verified by further experiments.

Since there is an increasing health hazard for living organisms due to the constantly emerging substitutes in the field of PFAS compounds, an understanding of the distribution pathways of these pollutants is particularly important.

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Acknowledgements

First of all, I would like to gratefully thank my supervisor Prof. Dr. Britta Stumpe for the chance to carry out such an interesting research field. I am grateful for her trust, the advises and constructive discussion throughout the research. Furthermore, I appreciate the opportunity, given from Prof. Dr. Marschner, to carry out my laboratory work at the Ruhr-Universität Bochum. I would also like to thank him for his assessment, the scientific exchange and his help throughout the time. I also thank Prof. Dr. Andreas Keil for incurring the examination board without hesitation, his encouragement and his easy-going character. A special thanks goes to Dr. Jannis Heil for his professional advises and for reviewing this work.

I would like to thank the Geographical Survey NRW, the LANUV NRW and Prof. Dr. Jörg Rinklebe for providing the soil samples. A special thanks goes to Mareike Mersmann and Jörg Leisner from the LANUV NRW, for the numerous professional exchanges and interesting discussions about the environmental behavior and use of PFAS and the financial support.

I am indebted to Michael Siewert, Stephan Spöllmann and Tommy Lenders from the Central Isotopic laboratory at the Ruhr-Universität Bochum for the chance to execute my laboratory work, for their help, funny talks and for providing me with endless galore of scintillating cocktails. Further I am grateful for the assistance of Heidi Kerkhoff and Katja Gonschorek from the Physical Geographical lab. For countless hours spent determining soil properties, for funny coffee breaks, for their creativity when it comes to trying out new test regulations and their good spirit and never-ending support. This work benefited by the wonderful help of our student assistants. Special thanks go to Fritjof Obermann for his tireless, always friendly and inquisitive encouragement in the laboratory.

This work would not have been possible without the help, discussions, support, and open ears of my friends and coworkers Katharina Schwarz and Anne Neuser. Thank you for the endless coffee and fresh air breaks and for your friendship. Further I would like to thank Jonas Birke for his assistance and the numerous joint lectures and Christoph Jörges for the mathematical advice, the shared office hours and his support. I would also like to thank my valued colleagues from the department of Geography, Nikolas Meintz, Nina Heuke, Mira Fassbender, Jutta Bedehäsing, Ina Jeske, Stefan Padberg, Ursula Steffen and Rene Schmidt, who have always backed me during this time.

Finally, I would like to say a special thanks to my friends and family who always believed in me and have always supported me. My mother, who is always there for me and always had my back, my siblings who always encouraged me to give my best, my friends Kathrin, Daniel, Christian, Judith and Lara for always being there for me, my dear Margot for her know-it-all attitude and her sisterhood and last but not least my best friend and husband Dennis who is always there for me and motivates me at the right moment. Thank you so much, I will never forget what you have done for me during this time.