



## Sorption of perfluoroalkyl substances to two types of minerals



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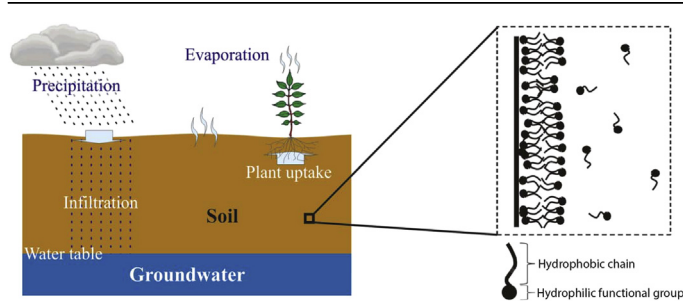
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### HIGHLIGHTS

- PFASs sorbed to alumina but not to silica surface, sorption electrostatically driven.
- The sorbed PFAS layer on alumina was found to be highly hydrated.
- Gentle rinsing with water removed the sorbed PFAS layer from the alumina surface.
- Differences in PFAS solubility is likely to affect environmental behaviour.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The sorption of perfluoroalkyl substances (PFASs) was investigated for two model soil mineral surfaces, alumina ( $\text{Al}_2\text{O}_3$ ) and silica ( $\text{SiO}_2$ ), on molecular level using neutron scattering. The PFASs were selected (i.e. perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), and perfluorooctane sulfonic acid (PFOS)) to examine the role of hydrophobic chain length and hydrophilic functional group on their sorption behaviour. All four PFASs were found to sorb to alumina surface (positively charged) forming a hydrated layer consisting of 50% PFASs. The PFAS solubility limit, which decrease with chain length, was found to strongly influence the sorption behaviour. The sorbed PFAS layer could easily be removed by gentle rinsing with water, indicating release upon rainfall in the environment. No sorption was observed for PFOA and PFOS at silica surface (negatively charged), showing electrostatic interaction being the driving force in the sorption process.

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### 1. Introduction

Organic micropollutants typically have hydrophobic or

lipophilic characteristics which control their sorption behaviour in the environment (Stangroom et al., 2000). In contrast, the perfluoroalkyl substances (PFASs) have both a hydrophobic perfluorocarbon chain and an ionizable hydrophilic functional group, and their environmental behaviour is more complex (Ahrens, 2011). They are also very surface active, with lower surface tension than their C-H analogues (Xie et al., 2007). As a result of their unique properties, PFASs have been widely used, for example as surfactants in textile and paper products and in aqueous firefighting foams

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(AFFFs) (Buck et al., 2011). However, due to the stability of PFASs, they are not readily biodegradable and therefore tend to accumulate in the environment (Higgins and Luthy, 2006; Ahrens and Bundschuh, 2014; Houde et al., 2011). Extremely high concentrations have been found in soil (up to 43  $\mu\text{g g}^{-1}$  dry weight for  $\Sigma\text{PFCAs/PFSAs}$ ) (Houtz et al., 2013) and groundwater (up to 7090  $\mu\text{g L}^{-1}$  for  $\Sigma\text{PFCAs}$ ) (Moody and Field, 1999) near firefighting training sites where PFAS-containing AFFFs have been used. Because of the high levels of PFASs in the environment, in combination with their bioaccumulative and toxic potential (Ahrens and Bundschuh, 2014; Houde et al., 2011), PFASs are receiving increasing public attention.

From contaminated soil, PFASs can potentially leach to the groundwater and contaminate drinking water reservoirs (Eschauzier et al., 2013), surface water (Skutlarek et al., 2006) or can be taken up by plants and soil organisms (Blaine et al., 2014; Higgins et al., 2007). This has led to widespread contamination and shutdown of drinking water reservoirs all over Europe. For example, time-trend analysis of perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs) in blood serum in Uppsala, Sweden, indicated exponential increase over time caused by contaminated drinking water (Glynn et al., 2012). The leaching and availability of PFASs in soil is controlled by the extent of adsorption to particles (Higgins and Luthy, 2006; Ahrens et al., 2010), e.g., the short-chained PFASs generally have a higher leachability, but information on the sorption mechanisms on a molecular level is scarce. The adsorption mechanisms of PFASs to air/liquid interfaces has been investigated (Downer et al., 1999; Eastoe et al., 2003), but there is a great demand for more knowledge about the sorption behaviour of PFASs to solid/liquid interfaces.

The mineral composition of soil is varied, with feldspars ( $\text{KAlSi}_3\text{O}_8$ ,  $\text{NaAlSi}_3\text{O}_8$ ,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) and quartz ( $\text{SiO}_2$ ) being the two most abundant soil mineral materials. Clays are often rich in alumina and other cations (Donahue et al., 1977). The aim of this study was to investigate the sorption of PFASs to two model soil minerals, alumina ( $\text{Al}_2\text{O}_3$ , sapphire) and silica ( $\text{SiO}_2$ , the oxide layer formed on a silicon crystal), using neutron reflection. This technique allows for determinations of surface structures at buried interfaces on a molecular level. The specific objectives were to *i*) determine if the PFASs sorb to the surfaces *ii*) the structure of the adsorbed layer (if present) and the amount of PFASs at the interface, *iii*) to examine the influence of the PFAS functional group and perfluorocarbon chain length on the sorption, and *iv*) to compare the sorption of PFASs on alumina and silica interfaces. This study will enable predictions (e.g. environmental fate modelling) of the leaching, transport and bioavailability of PFASs to soil minerals by gaining a mechanistic understanding of their sorption behaviour.

## 2. Materials and methods

### 2.1. Chemicals

The target analytes included perfluorohexanoic acid (PFHxA,  $\text{C}_5\text{F}_{11}\text{COOH}$ , purity >97%), perfluorooctanoic acid (PFOA,  $\text{C}_7\text{F}_{15}\text{COOH}$ , 96%), perfluorononanoic acid (PFNA,  $\text{C}_8\text{F}_{17}\text{COOH}$ , 97%), and perfluorooctane sulfonic acid (PFOS,  $\text{C}_8\text{F}_{17}\text{SO}_3\text{H}$ ,  $\geq 98\%$ ), and were purchased from Sigma-Aldrich (Schnellendorf, Germany). The analytes thus encompassed three carboxylic acids with varying perfluorocarbon chain length (5, 7 and 8 fully fluorinated carbons) and one sulfonic acid (with 8 fully fluorinated carbons). Their structures and selected physicochemical properties are provided in Table 1.

Bulk solutions of each analyte was prepared separately in both ultra-pure  $\text{H}_2\text{O}$  (obtained from a MilliQ gradient A10 or an ELGA PureLab Option) and  $\text{D}_2\text{O}$  (Sigma-Aldrich, >99.9%) in polypropylene

falcon tubes. All measurements were performed without the use of buffers, i.e. at a pH generally lower than environmental pH values (see Table S1 in the Supplementary material for measured pH values), as buffers increase the ionic strength in the solutions, which in turn lowers the PFAS solubility (3M, 2003). Even so, it was only possible to exceed reported critical micelle concentrations (CMC), at which micelles are formed in solution, in the bulk solution for PFHxA and PFOS. On the other hand, reported physicochemical properties for PFASs are seemingly uncertain (Krafft and Riess, 2015), as demonstrated by the discrepancies between reported CMC and aqueous solubilities as well as between modelled and experimental values (Table 1). The concentrations used in this experiment for PFHxA (25–250 mM, 7850–78510  $\text{mg L}^{-1}$ ), PFOA (0.5–5 mM, 207–2070  $\text{mg L}^{-1}$ ), PFNA (0.06–0.6 mM, 25–250  $\text{mg L}^{-1}$ ) and PFOS (0.9–8.8 mM, 450–4401  $\text{mg L}^{-1}$ ) to enable to identify the structure of the adsorbed layer. These PFAS concentrations were approximately one order of magnitude higher as detected in the aqueous environment contaminated by the application of PFAS-containing AFFFs (Moody and Field, 1999; Houtz et al., 2013) The PFASs are acids and the functional groups carry a negative charge when dissociated. The  $\text{pK}_a$  values are challenging to determine, experimentally as well as by modelling, for these type of strong acids (Goss, 2008), but they are mostly dissociated at environmentally relevant pHs (Vierke et al., 2013). The molecules in our experiment exist in both protonated and dissociated form.

### 2.2. Reflection surfaces

Two different types of polished crystals were used as reflection surfaces in this study. Alumina ( $\text{Al}_2\text{O}_3$ ) crystals (optical *c*-axis (0001) which is perpendicular to the plane of the window) were purchased from Crystran with dimensions  $50 \times 50 \times 10 \text{ mm}^3$ , and silicon (Si) crystals (cut to expose the octahedral (111) face) were purchased from Sil'tronix with the same dimensions. For the silicon crystal, it is the oxide layer (silica,  $\text{SiO}_2$ ) that forms on the crystal that is used in the reflection measurements. The crystals were cleaned prior to measurements with a surface active cleaning agent (Decon90™). After that the reflection face of the crystal was covered with concentrated sulfuric acid (approximately 1 mL 96%  $\text{H}_2\text{SO}_4$  for 5 min) and finally rinsed with extensive amounts of ultra-pure water. All additional components of the experimental set-up in touch with the sample, such as injection tubing and valves, were cleaned with Decon90™ and rinsed with extensive amounts of ultra-pure water prior to use. The charge on a crystal surface will depend on the liquid that it is in contact with. The isoelectric point where the surface carry no net charge for (0001) alumina has been reported to be pH 6 (Zhang et al., 2008). The alumina surface potential was reported to range between 25 and –30 mV between pH 3–11 (Kershner et al., 2004) and is most likely carrying a positive charge in the present study. Silica has an isoelectric point at pH 2 (Papirer, 2000) and would thus carry a negative charge in the present study.

### 2.3. Neutron reflection, experimental information

Neutron reflection experiments were performed at ISIS (U.K.) on the SURF horizontal surface neutron reflectometer (Penfold et al., 1997). Data were collected in time-of-flight mode at several angles in order to collect data over a wide range of momentum transfer,  $Q$  (described below in Section 2.3). The size of the incident beam was chosen so that the illuminated area of the sample was  $30 \times 30 \text{ mm}^2$  in order to avoid any stray scattering from the sample holder. The reflection surfaces were placed in a reflection cell/sample holder (Rennie et al., 2015; Helling et al., 2011) with a

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