



Sorption behaviour of perfluoroalkyl substances in soils

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HIGHLIGHTS

- Sorption isotherms of PFOS, PFOA and PFBS in soils are linear.
- Sorption affinity of PFASs increases with the hydrophobicity of the compound.
- Sorption reversibility decreases when the hydrophobicity of the PFAS increases.
- Sorption K_d correlates to the soil organic matter content.
- K_{OC} values are obtained from the K_d -organic matter correlation.

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ABSTRACT

The sorption behaviour of three perfluoroalkyl substances (PFASs), perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and perfluorobutane sulfonic acid (PFBS), was studied in six soils with contrasting characteristics, especially in the organic carbon content. Sorption isotherms were obtained by equilibrating the soil samples with 0.01 mol L⁻¹ CaCl₂ solutions spiked with increasing concentrations of the target PFAS. The sorption reversibility of PFASs was also tested for some of the samples. Liquid chromatography coupled to tandem mass spectrometry was used to quantify the target PFASs in the solutions. Both the Freundlich and linear models were appropriate to describe the sorption behaviour of PFASs in soils, and enabled us to derive solid-liquid distribution coefficients (K_d) for each compound in each soil. K_d values increased from 19 to 295 mL g⁻¹ for PFOS, from 2.2 to 38 mL g⁻¹ for PFOA and from 0.4 to 6.8 mL g⁻¹ for PFBS, and were positively correlated with the organic carbon content of the soil. K_{OC} values obtained from the correlations were 710, 96 and 17 mL g⁻¹ for PFOS, PFOA and PFBS, respectively. Whereas K_d values decreased in the sequence PFOS > PFOA > PFBS, desorption yields were lower than 13% for PFOS, from 24 to 58% for PFOA, and from 32 to 60% for PFBS. This shows that the physicochemical characteristics of PFASs, basically their hydrophobicity, controlled their sorption behaviour in soils, with PFOS being the most irreversibly sorbed PFAS.

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1. Introduction

Perfluoroalkyl substances (PFASs) are characterised by a fully fluorinated hydrophobic alkyl chain of varying length, attached to different hydrophilic groups, such as sulfonate or carboxyl. Due to their exceptional surface-active properties, these compounds have been widely used in many applications such as stain- and water-resistant textiles, food packaging, fire-extinguishing formulations, pesticides, paints, personal care products and surfactant agents (Lau et al., 2007). Strong C–F bonds make PFASs extremely resistant to hydrolysis and to thermal, microbiological and photolytic degradation. As a consequence, they are ubiquitous in diverse environmental matrices, including water

(Taniyasu et al., 2003; Ahrens et al., 2009), sewage sludge (Yoo et al., 2009; Sun et al., 2011), soils (Strynar et al., 2012; Wang et al., 2013) and sediments (Bao et al., 2010; Yang et al., 2011). In recent years, PFASs have come to public and scientific attention because of their high bioaccumulation, extreme persistence, and toxic properties, such as endocrine disrupting activity and carcinogenesis (Kannan, 2011).

Of all the PFASs, perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) show the highest accumulation in the environment (Ellis et al., 2004). These compounds have been directly released or generated by the microbial degradation of other PFAS precursors (Paul et al., 2009). In 2009, PFOS and its salts were added to the Stockholm Convention's list of persistent organic pollutants, and hence their production and use in most applications was prohibited in the EU (UNEP, 2009). Recently, perfluorobutane sulfonic acid (PFBS) has been commercialised as a homologous compound of PFOS in a

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variety of applications (OECD, 2006). PFBS also has a sulfonate hydrophilic group, but a shorter carbon chain, which makes it less bioaccumulative than PFOS (Newsted et al., 2008).

Data on the concentrations of PFASs in soils are scarce in the literature. PFASs were found at ng g⁻¹ levels in ten soil samples from several countries (Japan, Mexico and the USA), with the highest concentrations found for PFOS and PFOA, which were 10 and 30 ng g⁻¹, respectively (Strynar et al., 2012). Li et al. (2010) reported similar concentration levels of PFOS and PFOA in soils from Shanghai, China, directly related to the manufacturing and usage of perfluoro-containing products, which is still permitted in this country (Wang et al., 2010; Wang et al., 2013). However, not only the total amount of PFASs in soils, but also their distribution between the solid phase and the soil solution is of great importance, as it influences their environmental fate. Whereas some studies have reported sorption parameters such as the solid-liquid distribution coefficient (K_d) of PFOS and PFOA in sediments, as appear in the review of Zareitalabad et al. (2013), to date, only limited data are available for sorption experiments carried out in mineral soils (Enevoldsen and Juhler, 2010; Chen et al., 2013) and pure phases of soils (Johnson et al., 2007). In these studies, K_d values varied by up to two orders of magnitude. This suggests that various factors influence the sorption pattern of PFASs in soils, and the most important appears to be soil organic carbon. Nevertheless, there is a lack of information on PFASs in soils with a relatively high amount of organic matter as well as on the reversibility of the sorption process.

In order to better understand the distribution of PFASs in soils, particularly soils with a significant amount of organic matter, we evaluated the sorption behaviour of PFOS, PFOA and PFBS, which have different physicochemical properties, in six soil samples with a broad range of organic carbon content. Sorption isotherms were obtained for the target PFASs in a wide range of concentrations, and K_d values were derived from fitting the isotherms to appropriate simple models (Freundlich and linear). The main soil characteristics, as well as the physicochemical properties of PFASs, were considered to explain their sorption mechanisms. Furthermore, the sorption reversibility of each compound was determined and compared.

2. Experimental part

2.1. Reagents and standards

Milli-Q double deionised water (18.2 MΩ cm⁻¹) was obtained from a USF PureLab Plus water purification system (Spain). Water, ammonium acetate and acetonitrile, all of them gradient grade for liquid chromatography, were supplied by Merck (Germany). Analytical standards of perfluorooctanesulfonate (PFOS, potassium salt, 98%) and perfluorooctanoic acid (PFOA, 99.2%) were purchased from Sigma-Aldrich (Germany), and perfluorobutanesulfonate (PFBS, tetrabutylammonium salt, 98%) was purchased from Sigma-Aldrich (Switzerland). The main physicochemical properties of the PFASs selected for this study are shown in Table 1 (Deng et al., 2012). Of the three PFASs, PFBS is the most soluble in water and is more likely to be transported into aqueous environments than PFOA and PFOS, which are less soluble in water. Moreover, the three PFASs have very low pK_a values ($pK_a < 0.1$), and thus all of them will be dissociated into anionic species in the soil solution, whose pH value is usually higher than 4.

With respect to the octanol–water partition coefficient (K_{ow}) of PFASs, literature values show considerable variability, due to the fact that the determination of this parameter for hydrophobic organic compounds is highly operational (Linkov et al., 2005). Here, the values of Deng et al. (2012) are considered for the interpretation of results. Comparing PFOS and PFOA, they contain equal number of carbon atoms in the molecule, but PFOS has more C–F units than PFOA, which has a carboxyl group. As a consequence, PFOS is more hydrophobic than PFOA. In the same way, PFBS, which has the shortest perfluorinated chain, is the compound that shows the lowest hydrophobicity.

Stock standard solutions of PFOS, PFOA and PFBS of 1 g L⁻¹ were prepared individually in acetonitrile. Working solutions of PFASs for the sorption experiments were prepared by dilution of stock standards in acetonitrile. All solutions were stored at -18 °C in 20 mL glass vials with polyethylene caps (Sigma-Aldrich, Germany).

Isotopically labelled standard solutions of sodium perfluoro-1-[1,2,3,4,-¹³C₄]-octane sulfonate (MPFOS) and perfluoro-n-[1,2,3,4,-¹³C₄]-octanoic acid (MPFOA), both at concentrations of 50 µg mL⁻¹, were purchased from Wellington Laboratories (Canada). Working solutions of MPFOS and MPFOA were prepared by 50-times dilution of standard solutions in acetonitrile. The solutions were stored at -18 °C in chromatographic vials of 2 mL (Waters, USA).

2.2. Sample characterisation

Six soil samples with contrasting characteristics, especially in relation to the organic matter content, were selected from an already existing soil collection. ASCO, ALM, GOLOSO, DELTA2, and OVI01 were natural and agricultural soils originated from the Iberian Peninsula collected in a sampling campaign carried out in a previous work (Gil-García et al., 2008). The sixth soil, DUBLIN, was a peat soil originated from a wet meadow of Belarus. All soils corresponded to the top layer (0–10 cm depth) of plain soils. Soil samples were air-dried and sieved through a 2 mm mesh. Prior to analysis, samples were homogenised with a roller table and stored at room temperature. A summary of the main soil parameters is shown in Table 2.

Main soil parameters were previously determined as already described elsewhere (Gil-García et al., 2008). Briefly, the pH of the soil samples was measured in Milli-Q water, using a solution-to-soil ratio of 2.5 mL g⁻¹. The cation exchange capacity (CEC) was determined from the sum of the extractable bases (Ca + Mg + K + Na) plus the extractable acidity obtained by displacement with BaCl₂–triethanolamine (TEA) solution buffered at pH 8.2 (Burt, 2004). The particle size distribution was determined by the pipette method, based on the varying settling velocity in a fluid medium according to the particle size (Burt, 2004). Organic carbon (OC) was determined using a Thermo EA 1108 elemental analyser (Thermo Scientific, Milan, Italy). Samples were pre-treated with 2 mol L⁻¹ HCl in order to eliminate carbonates, and then analysed in tin capsules using V₂O₅ as additive (ISO, 1995). The carbonate content was determined by using the calcimeter Bernard method (Mueller and Gastner, 1971).

The dissolved organic carbon (DOC) was measured in the solutions obtained by equilibration of soil samples with 0.01 mol L⁻¹ CaCl₂ (10 mL g⁻¹). A total organic carbon analyser TOC-5000A (Shimadzu, Tokyo, Japan) was used, with previous acidification of solutions to pH 3 with HCl to remove carbonates.

Table 1
Physicochemical properties of selected PFASs.

PFC name (molecular formula)	Abbreviation	Molecular weight (g mol ⁻¹)	Water solubility (g L ⁻¹) ^a	pK_a^a	log K_{ow}^a
Perfluorooctane sulfonic acid (C ₈ HF ₁₇ SO ₃)	PFOS	500.1	0.57	-3.3	5.26
Perfluorooctanoic acid (C ₈ HF ₁₅ O ₂)	PFOA	414.0	3.4	-0.2	4.59
Perfluorobutane sulfonic acid (C ₄ HF ₉ SO ₃)	PFBS	300.1	46.2	0.1	2.73

^a Deng et al. (2012).

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