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Transport of perfluoroalkyl acids in a water-saturated sediment column investigated under near-natural conditions

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ABSTRACT

The aim of this study was to gain an understanding of the transport of C_{4-10} perfluoroalkyl carboxylic acids (PFCAs) and $C_{4,6,8}$ perfluoroalkyl sulfonic acids (PFSAs) in a water-saturated sediment column representing a riverbank filtration scenario under near-natural conditions. Short-chain PFCAs and PFSAs with up to six C-atoms showed complete tracer-like breakthrough. Longer chain ones were retarded due to sorption to the sediment or due to other processes in the aqueous phase. The study reports the first column derived sediment–water partition coefficients ranging from 0.01 $cm^3\ g^{-1}$ to 0.41 $cm^3\ g^{-1}$ for $C_{4,6}$ PFSAs and from 0.0 $cm^3\ g^{-1}$ to 6.5 $cm^3\ g^{-1}$ for $C_{4,5,6,8,9}$ PFCAs. The results clearly indicate that short-chain PFCAs and PFSAs may pose a problem if contaminated surface waters are used for drinking water production via riverbank filtration.

1. Introduction

Recently, research on per- and polyfluoroalkyl compounds has highly improved our understanding of the risk occurring from the presence of these compounds in the environment (Kannan, 2011). In the beginning, focus of this research has mainly been on C_8 perfluoroalkyl carboxylic acid (C_8 PFCA; perfluorooctanoic acid, PFOA) and C_8 perfluoroalkyl sulfonic acid (C_8 PFSA; perfluorooctane sulfonic acid, PFOS), which was mostly motivated by the high production volumes of these two chemicals in the past 60 years (Lindstrom et al., 2011; Paul et al., 2009; Prevedouros et al., 2006). Today we know that PFOA and PFOS are persistent, bioaccumulative and toxic as defined in international regulations (Vierke et al., 2012; Wang et al., 2009b). Therefore exposure of humans and the environment should be minimised (Vierke et al., 2012; Wang et al., 2009b; Zushi et al., 2012).

Manufacturers are shifting to shorter-chain per- and polyfluorinated chemicals with four and six C-atoms (Buck et al., 2011). Not only PFCAs and PFSAs are part of this short-chain chemistry but also their polyfluorinated precursors. Research is increasingly investigating shorter-chain PFCAs and PFSAs as well as precursors of PFCAs and PFSAs. One example are fluorotelomer alcohols (FTOHs), which were already globally detected in the atmosphere (Dreyer et al., 2009). Degradation intermediates of FTOHs are i.e. fluorotelomer acids (FTCAs) or fluorotelomer unsaturated acids (FTUCAs). These degradation intermediates have already been found in the environment, i.e. in rivers (Li et al., 2011). In contradiction to PFOS and PFOA shorter-chain PFCAs and PFSAs are less toxic and less bioaccumulative (Conder et al., 2008; Ding et al., 2012). Nevertheless, they are still persistent and have already been detected in surface waters and drinking water (Möller et al., 2010; Eschauzier et al., 2010), with wastewater treatment plants and surface runoff being potential sources for these compounds (Furl et al., 2011).

Due to their higher solubility (Rayne and Forest, 2009) these short-chain PFCAs and PFSAs are more mobile, especially in the aqueous environment, than their longer chain homologues. This higher mobility has a direct impact on human and environmental exposure, for instance through drinking water. In many regions drinking water is obtained from surface waters following riverbank

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filtration. In Germany, water from riverbank filtration is the second major source for drinking water after ground water (Kuehn and Mueller, 2000). Riverbank filtration is capable of eliminating a wide range of substances through sorption and degradation or at least diluting peak concentrations (Verstraeten et al., 2003). However, PFCAs and PFSAs with eight and less C-atoms have been detected in riverbank filtrate (Lange et al., 2007) or dune infiltrate (Eschauzier et al., 2010).

Sandy sediments are common substrates in riverbank filtration sites. Sorption of PFCAs and PFSAs on sandy soil quantified within a batch experiment showed that this soil had a capacity to bind the analytes ($K_d = 0.63$ L kg^{-1} to 33 L kg^{-1} for perfluoroheptanoic acid (C_6 PFCA or PFHpA) to perfluorodecanoic acids (C_{10} PFCA or PFDA) and $K_d = 0.07$ L kg^{-1} and 17 L kg^{-1} for perfluorobutane sulfonic acid (C_4 PFSA or PFBS) and PFOS, Enevoldsen and Juhler 2010) and the authors concluded that sandy substrates may therefore be able to protect groundwater (Enevoldsen and Juhler, 2010). So far, the fate of PFCAs, PFSAs and precursors in columns has only been investigated by three laboratory studies, all of them conducted under water-unsaturated conditions using loamy soil (Murakami et al., 2009, 2008) and loamy sandy soil (Gellrich et al., 2012). These studies showed partly competitive sorption between the different analytes and only limited elimination of analytes during soil infiltration, with removal depending on chain length. Furthermore, leaching of PFCAs and PFSAs was investigated in a lysimeter experiment also under water-unsaturated conditions (Stahl et al., 2013), but the fate of chemicals tends to differ between water-saturated and water-unsaturated conditions. So far and to the best of our knowledge, no column study has been conducted under water-saturated conditions in sandy substrates. Besides, available findings from infield studies (Eschauzier et al., 2010; Lange et al., 2007) don't allow for a quantification of the transport of PFCAs and PFSAs during riverbank filtration. Water-saturated conditions are important because they are characteristic for riverbank filtration schemes used as a source for the production of drinking water. The aim of our experiment was to gain an understanding of the transport of $C_{4–10}$ PFCAs and $C_{4,6–8}$ PFSAs in a water-saturated sediment system representing a riverbank filtration scenario and to quantify possible attenuation through the determination of sorption parameters. Furthermore, though not the primary focus, some precursors were also investigated. The results of this study help to assess the potential risk of breakthrough of PFCAs and PFSAs in riverbank filtrate occurring from the presence of these substances in surface waters.

2. Material and methods

Riverbank filtration was simulated under near-natural conditions in a water-saturated sediment column fed with surface water and by applying environmentally relevant concentrations of the analytes. To quantify the sorption of analytes during infiltration, breakthrough was compared to a tracer.

2.1. Chemicals

Table 1 shows the names and abbreviations of analytes which were in the focus of the present study.

Furthermore, methylperfluoro butanesulfonamid (MeFBSA), methylperfluoro butanesulfonamidoethanol (MeFBSE), 2-Perfluorohexyl ethanoic acid (6:2 FTCA), 2-Perfluoroocxyl ethanoic acid (8:2 FTCA), 2-Perfluorodexyl ethanoic acid (10:2 FTCA), 2H-Perfluoro-2-octenoic acid (6:2 FTUCA) and 2H-Perfluoro-2-decenoic acid (8:2 FTUCA) were spiked onto the column. Tables S1 and S2 of the supplementary content list all native as well as mass labelled standards, their acronyms, suppliers, mass transitions and the matching of mass labelled and native standards.

In aqueous media per- and polyfluorinated acids are in equilibrium with their conjugate bases. The fraction of each depends on the pK_a of the acid and the pH value of the media. We analytically detected both the acids and their conjugate bases, whereby the fraction of the base is expected to be higher compared to the fraction of the acids due to the low pK_as of PFCAs, PFSAs and their precursors (Goss, 2008; Vierke et al., 2013b). Therefore, where we name the species as the acids in this study, this always includes both species.

2.2. Water-saturated sediment column

The experiment was conducted on the Federal Environment Agency's facility for the simulation of riverbank and slow sand filtration (SIMULAF) in Berlin, Germany (for details of the site see Grützmacher et al., 2005). The water-saturated column (termed as 'enclosure' in the following; length 1 m, surface area 1 m^2) was embedded in a natural slow sand filter basin and fed by surrounding surface water. The water was pumped continuously through the sediment column at a filter velocity of 1.1 m d^{-1}, which was checked daily. This velocity is in the range of values often encountered in riverbank filtration scenarios (Hijnen et al., 2005; Weiss et al., 2005). Water samples were collected from the supernatant and at a sediment depth of 40 cm and 80 cm depth. A pump was plugged to the sampling ports in 40 cm and 80 cm depth to collect the samples. Grab sampling with a bucket on a stick was used for supernatant sampling. Sample volume was approximately 1 L measured in polypropylen(PP)-bottles. At a flow rate of 0.74 L min^{-1} it was not expected that the removal of 1 L samples would disturb the system. The supernatant was adjusted to a height of 15.5 cm, resulting in a final volume of 155 L. The turbidity of the water in the supernatant amounted to 3 FNU. The pH value of the water in the supernatant, 40 cm and 80 cm depth ranged from 7.4 to 7.9 and water temperature was 14.8 °C–24.9 °C. The oxygen concentration in the columns effluent ranged from 4.7 mg L^{-1} to 8.7 mg L^{-1} during the experiment. Concentrations of dissolved organic carbon (DOC) were highest in the supernatant (3.5 ± 0.3 mg L^{-1}, $n = 4$) and ranged from 2.5 mg L^{-1} to 3.1 mg L^{-1} in the various depths. Ionic strength amounted to 17.5 mmol L^{-1} with a calcium concentration of 4.3 mmol L^{-1}. The column was filled with coarse-grained medium sand (grain size distribution is given in Table S3) followed by 30 cm gravel (Fig. 1). The sand had a content of 0.02% N, 0.07% organic carbon (OC), 0.3% carbonate C and a C/N-ratio of 16.1. The bulk density (ρ_B) of the sediment amounted to 1.57 g cm^{-3}. From the density of the raw material ($\rho_F = 2.65$ g cm^{-3} for quartz sand, Scheffer and Schachtschabel, 1998) a porosity (n) of 0.41 and a void ratio (ε) of 0.7 was calculated. The enclosure and the surrounding pond were located outside and were therefore influenced by natural conditions (i.e. natural microbial community and day–night temperature fluctuations). The experiment was conducted for three weeks in the beginning of September 2011 under environmental conditions.

2.3. Experimental design

Prior to the experiment background concentrations in the enclosure were determined once. Therefore 1 L water samples were collected from the supernatant, from 40 cm and 80 cm depth, respectively.

The supernatant of the enclosure was then spiked with 5 μg of each $C_{4–10}$ PFCAs, $C_{4,6–8}$ PFSAs, MeFBSA, MeFBSE, 6:2, 8:2, 10:2 FTCAs and 6:2 and 8:2 FTUCAs (in total 1.85 ml methanol solution of standards), yielding a target concentration of 32.3 ng L^{-1} for each analyte. 136 ml 25% NaCl solution was added as a tracer and the supernatant was mixed with a stick. Mixing was evaluated by conductivity measurements. As soon as (after approximately 5 min) conductivity changes in the supernatant were minimal (1350 ± 5 μS cm^{-1}) two 1 L samples were taken to determine analyte concentrations right after spiking. One litre water samples were collected from the supernatant and after 40 cm and 80 cm of sediment passage during the following sampling period (in total 53 sampling events at three sampling points of which 70 were analysed). Sampling frequency was reduced in the course of the experiment because high concentration variations were expected mainly in the beginning. At the beginning of the experiment, samples were collected more frequently, i.e. six times per day for the first five days, three times per day in the second week and only once a day in the third week.

Water samples from the supernatant were filtered using glassfiber filters (GFF, Macherey–Nagel, Ø 45 mm, 0.7 μm, heated at 450 °C for 10 h) right after sampling and all samples were stored at 4 °C in PP-bottles until extraction. The effect of filtration on concentrations of analytes was tested with spiked MilliQ water. An aliquot of the water was filtered. Compared to unfiltered water the difference in recovered concentrations were <10% (except for 20% in the case of PFHxA).

Table 1
Name and abbreviations of PFCAs and PFSAs in the focus of the present study.

Name	Abbreviation
Perfluoro-1-butanesulfonicacid	PFBS, C_4 PFSA
Perfluoro-1-hexanesulfonicacid	PFHxS, C_6 PFSA
Perfluoro-1-heptanesulfonicacid	PFHpS, C_7 PFSA
Perfluoro-1-octanesulfonicacid	PFOS, C_8 PFSA
Perfluoro-*n*-butanoic acid	PFBA, C_4 PFCA
Perfluoro-*n*-pentanoic acid	PFPA, C_5 PFCA
Perfluoro-*n*-hexanoic acid	PFHxA, C_6 PFCA
Perfluoro-*n*-heptanoic acid	PFHpA, C_7 PFCA
Perfluoro-*n*-octanoic acid	PFOA, C_8 PFCA
Perfluoro-*n*-nonanoic acid	PFNA, C_9 PFCA
Perfluoro-*n*-decanoic acid	PFDA, C_{10} PFCA