



# Behavior of perfluorinated compounds in soils during leaching experiments

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## ABSTRACT

Perfluorinated compounds (PFCs) can be detected worldwide in both, soil and water. In order to study the leaching behavior of this heterogeneous group of compounds in soil, flow-through column experiments have been conducted. Ten perfluoro carboxylates and four perfluoro sulfonates ranging from C4 to C14 in chain length, and contaminated sewage sludge, have been used to spike a standard soil. The aqueous column effluent was analyzed using liquid chromatography tandem mass spectrometry (LC-MS/MS) with direct injection. The observed percolation velocity seems to be strongly correlated with the length of the perfluorinated chain. Other factors that additionally contribute to the leaching behavior are the functional group of the PFC, the organic carbon content of the soil and the presence of other adsorbates. A mass balance calculation showed that perfluorobutanoic acid can adsorb strongly to the soil, when no PFC with longer carbon chain are present. Only about 60% of the added perfluorobutanoic acid could be detected in the percolate water. The missing amount started to elute again when longer chain PFC or stearate were added to the soil. Thus it would appear that larger and more lipophilic molecules can displace shorter PFC from their binding sites in the soil.

The results of a monitoring study using 32 surface water samples and 150 groundwater samples confirm that the PFC with the highest concentrations in groundwater are the short chain PFC with less than 7 (fluorinated) carbon atoms. The dominating PFC in surface waters are perfluorooctanoic acid and perfluorooctane sulfonic acid.

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## 1. Introduction

Perfluorinated compounds (PFCs) are a diverse group of anthropogenic chemicals which are used because of their exceptional surface active properties (Kissa, 2001) as stain repellents, in fire-fighting foams and as polymerization aids. Their persistence (Saez et al., 2008), toxicity (Kudo and Kawashima, 2003) and bioaccumulation potential, indicate both, an ecological and human toxicological risk (Lau et al., 2009). Several regulations now exist restricting the use of PFOS (for abbreviations see Table 1), PFOS-related products and PFOA ("Significant New Use Rule" (US EPA, 2000), 3 M phase out (US EPA, 2009)). Use of PFOS in most application areas in the EU has been banned since 2008 (EU, 2006). Thus alternatives to PFOS and PFOA have to be found. As substitutes in many application areas, the C4 analogues, e.g. perfluorobutane sulfonate (OECD, 2006; 3M Company, 2009) or C6 telomer products can be used (Daikin Industries, 2009; Dupont, 2009).

The short chain PFC (less than seven carbon atoms) are reported to be less toxic than the long chain PFC (as PFOS and PFOA), show a

higher mobility in the environment and have a lower bioaccumulation potential (Das et al., 2008; Newsted et al., 2008). As they have been used for a relatively short time there is very limited data on their fate in the environment. Recent data (Eschauzier et al., 2010; Möller et al., 2010) indicate that PFBS and PFBA are the dominant compounds in water in the River Rhine and the River Scheldt.

To obtain more information about the fate and behavior of PFC in soil, a long term laboratory study was initiated 2 years ago simulating and studying the transfer from soil to groundwater. The aim of this study was to examine the sorption properties of the PFC, their mobility and leaching behavior, e.g. the velocity and efficiency of leaching, and the relationship to the chain length and functional group. The different possible fates of long chain PFC (as PFOS and PFOA, which are already used for several decades) and short chain PFC (increasingly used in the recent years as alternatives) in the soil have been examined. This new data is essential for the assessment of the acute and long-term exposure of groundwater to PFC. The adsorption- and remobilization potentials of the different PFC may have important implications for the retention and release of these chemicals in the aquatic environment.

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**Table 1**  
Names and descriptions of the experimental approaches.

Name	Percolating velocity (mL week <sup>-1</sup> )	PFC added	Number of tubes
MIX <sub>100</sub>	100	14 PFC <sup>a</sup> , 2 µg each	2 <sup>b</sup>
C4 <sub>100</sub>	100	PFBA and PFBS, 10 µg each	2 <sup>b</sup>
C4 <sub>35</sub>	35 <sup>c</sup>	PFBA and PFBS, 10 µg each	2 <sup>b</sup>
Sewage sludge 1 <sub>35</sub>	35	About 20 µg total PFC <sup>d</sup> in sewage sludge 1 <sup>e</sup>	2
Sewage sludge 2 <sub>35</sub>	35	About 20 µg total PFC <sup>d</sup> in sewage sludge 2 <sup>e</sup>	2
PFOS <sub>35</sub>	35	PFOS (with impurity <sup>f</sup> ), 1 mg	3
PFOA <sub>35</sub>	35	PFOA, 1 mg	3
Blank <sub>35</sub>	35	None	1
Blank <sub>100</sub>	100	None	2

<sup>a</sup> Perfluorobutanoic acid (PFBA), Perfluorobutane sulfonic acid (PFBS), Perfluoropentanoic acid (PFPeA), Perfluorohexanoic acid (PFHxA), Perfluorohexane sulfonic acid (PFHxS), Perfluoroheptanoic acid (PFHpA), Perfluorooctanoic acid (PFOA), Perfluorooctane sulfonic acid (PFOS), Perfluorononanoic acid (PFNA), Perfluorodecanoic acid (PFDA), Perfluorodecane sulfonic acid (PFDS), Perfluoroundecanoic acid (PFUnDA), Perfluorododecanoic acid (PFDoDA), Perfluorotetradecanoic acid (PFTeDA).

<sup>b</sup> Chloride was added to one of the tubes.

<sup>c</sup> 35 mL per week and tube complies with the average Hessian precipitation.

<sup>d</sup> Sum of the 14 PFC.

<sup>e</sup> Sewage sludge was applied wet calculated as 100 g dry weight per kg soil.

<sup>f</sup> The technical PFOS standard contains about 10% PFBS as impurity.

In parallel we present the results of a monitoring study of over 180 Hessian water samples which has been performed in order to assess the present state of aqueous PFC contamination.

## 2. Methods

### 2.1. Standards and reagents

All standards and internal standards for quantification and for the “MIX”- and “C4”-tubes (see Table 1) were purchased from Wellington Laboratories (Guelph, Canada) with a stated purity of ≥98%. PFOS and PFOA for spiking were provided by Sigma Aldrich (St. Louis, MO, USA) and were specified as ≥96% purity. In the PFOS standard, branched and linear PFOS isomers could be detected, as it is typical for a technical mixture. Analysis also revealed about 10% PFBS and minor concentrations of PFHxS. In the PFOA standard, no other PFC or branched isomers were detectable. Methanol, water and ammonium acetate for UPLC (ultra performance liquid chromatography) were provided by Biosolve BV (Valkenswaard, The Netherlands). Water for rain simulation in the laboratory experiment was a mineral water from a source known for negligible PFC-concentrations (Erbeskopf spring, Malborn, Germany).

### 2.2. Study design

Plastic tubes (PP, 5 cm diameter and 60 cm long) were filled with a standard soil (loamy sand provided by LUFA Speyer, standard soil 2.2, see supporting information.) to a height of 50 cm and set up vertically in the laboratory. At the bottom, the tubes were capped with a close meshed net to retain the soil but allow the water to pass. Watch-glasses were placed on top of the tubes to minimize evaporation. The wetted soil was spiked with aqueous PFC-solutions or sewage sludge, (see Table 1). In order to be able to assess the percolation velocity, 0.12 mg chloride (as NaCl) was added to selected tubes (Table 1) as a tracer. Four to five times a week, water was added to each tube, simulating precipitation leading to a percolation velocity of 35 ml water/week and of 100 ml water/week indicated with the subscript “35” and “100”

respectively (see Table 1). 35 mL water per week and tube complies with the average Hessian precipitation.

Each column eluate was collected, via a funnel, in a 100 mL PE bottle. Every week (for the tubes MIX<sub>100</sub>, C4<sub>100</sub> and blank<sub>100</sub>) or every 3 weeks (for the other tubes, see Table 1), the bottles were replaced, the volume of the water collected was measured and the bottles stored at 8 °C until analyzed.

All materials used were tested to ensure that they did not release any PFC.

### 2.3. Sample preparation

The collected percolate water was analyzed by direct injection. Therefore, 200 µL of water were mixed with 50 µL internal standard solution (10 µg L<sup>-1</sup> of each internal standard (PFBA, PFHxA, PFOA, PFOS, PFNA, PFDA; all <sup>13</sup>C labeled) in methanol) and filtered through 0.2 µm syringe filters (PET 20/15 MS; Machery-Nagel) before injection. For matrix calibration, water from the “blank” tubes was spiked.

For the water samples, 100 mL of water was spiked with 50 µL of the internal standard solution and filtered under vacuum through SPE-cartridges (Strata X AW; Phenomenex). Prior to extraction, the cartridges were conditioned with 3 mL methanol and 3 mL water. After application, residual water was removed by vacuum and 0.5 mL methanol. The compounds were eluted with 2 mL 0.1% ammonia in methanol. The extracts were evaporated to dryness at 39 °C under nitrogen and reconstituted with 250 µL of methanol:water (1:1; v:v).

### 2.4. UPLC-MS/MS

A Waters Aquity UPLC system was used with a BEH C<sub>18</sub> column (1.7 µm; 2.1 × 50 mm; waters, Eschborn, Germany) with a precolumn (BEH C<sub>18</sub>; 1.7 µm; 2.1 × 5 mm, waters). The injection volume was 10 µL. The chromatographic separation was performed using a linear gradient starting with 55% A (20 mmol NH<sub>4</sub>Ac in methanol) and 45% B (20 mmol NH<sub>4</sub>Ac in water), increasing to 90% A within 5 min, followed by another ramp to 100% A at 5.10 min and returned to 55% A (from 6 to 7 min), and then holding initial conditions for 2 min. The flow rate was set at 0.4 ml min<sup>-1</sup> and the column temperature was 40 °C. The UPLC was connected to a Waters TQ mass spectrometer, operated in negative electrospray and MRM (multiple reaction monitoring) mode. For more information concerning the MS-acquisition see supporting information.

Six internal standards and a calibration curve with at least five concentration levels were used for quantification. The calibration curves linear correlation coefficients were generally between 0.980 and 0.999.

The validity of this method was verified by participation in inter-laboratory comparisons (LANUV NRW S-01 2008, unpublished, and LHL 2008, unpublished). The recovery rates were between 81% and 130% and the standard deviation of the mean ( $n = 5$ ) was between 2% and 8% (with the exception of PFTeDA). Quality control solutions measured regularly with the samples assured the stability of instrumental parameters.

## 3. Results and discussion

This study was designed to give information about the sorption and desorption behavior of PFC in standardized soil, in order to estimate future developments of PFC concentrations in groundwater and soil. By analyzing the seepage water of this flow-through column experiment, the mobility of the different PFC can be assessed. As these laboratory experiments were conducted under controlled settings, the results cannot be transferred directly to

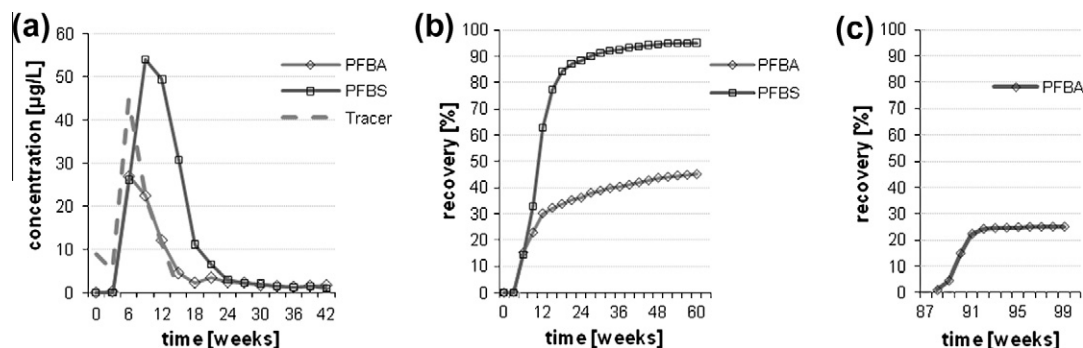


Fig. 1. Breakthrough curves of PFBA and PFBS: (a) as through flow and (b) as sum, in the C<sub>435</sub>-tubes; 10 µg of each PFC, (c) breakthrough of PFBA after the addition of 50 µg magnesium stearate;  $n = 2$ .

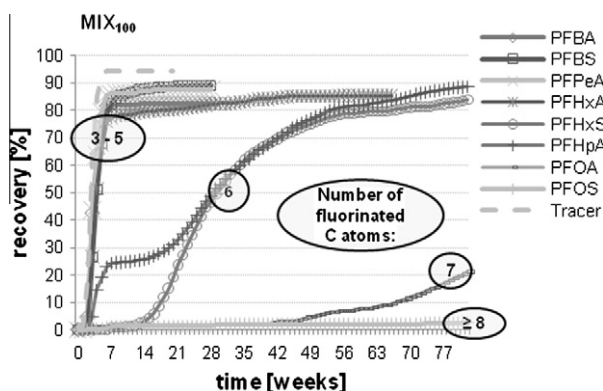


Fig. 2. Breakthrough curves of the MIX<sub>100</sub>-tubes; 2 µg of each of the 14 PFC;  $n = 2$ .

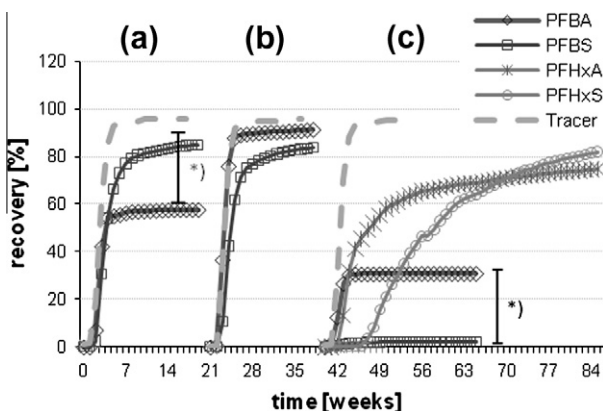


Fig. 3. Breakthrough curves of the C<sub>4100</sub>-tubes with three sequenced additions: (a) week 0: 10 µg PFBA and PFBS, (b) week 21: 10 µg PFBA and PFBS, (c) week 40: 10 µg PFHxA and PFHxS, (\*) the missing amount of PFBA from the first addition is desorbed after addition of PFHxA and PFHxS (details see text); 10 µg of each PFC;  $n = 2$ .

natural conditions in the environment, but this new data provides essential evidence of the long-term behavior of PFC in soil. Besides monitoring the velocity and behavior of leaching, a mass balance was calculated. By measuring the volume of the percolated water the total eluted mass of the PFC can be compared with the mass initially added.

### 3.1. Leaching behavior

Both investigated short chain PFC, PFBA and PFBS coelute under the given conditions from the C<sub>435</sub>-tubes simultaneous with the

mobile tracer chloride (Fig. 1a). However, as it can be seen in Fig. 1b, only the C-4 compound PFBS elutes close to 100%, whereas about 55% of the added C-3 compound PFBA did not elute. (see also, 3.2.)

During a similar experiment, when PFBS was co-spiked as impurity of technical PFOS, similar breakthrough curves out of the PFOS<sub>35</sub>-tubes were obtained (data not shown). In this case even the amount of PFBS was about ten times higher than in the C<sub>435</sub>-tubes.

After the first year of spiking, no PFOS could be detected in the percolate of the PFOS<sub>35</sub>-tubes. Only after 70 weeks, elution of the branched PFOS isomers in the percolate of the PFOS<sub>35</sub>-tubes was detected.

From the PFOA<sub>35</sub>-tubes (figure not shown) the first breakthrough of PFOA was 18 weeks after the breakthrough of chloride. After a further 52 weeks all PFOA added was eluted.

Some batches were studied with a higher flow rate of percolation (MIX<sub>100</sub> and C<sub>4100</sub>) in order to assess regularities more easily and to be able to perform tests during an appropriate period of time.

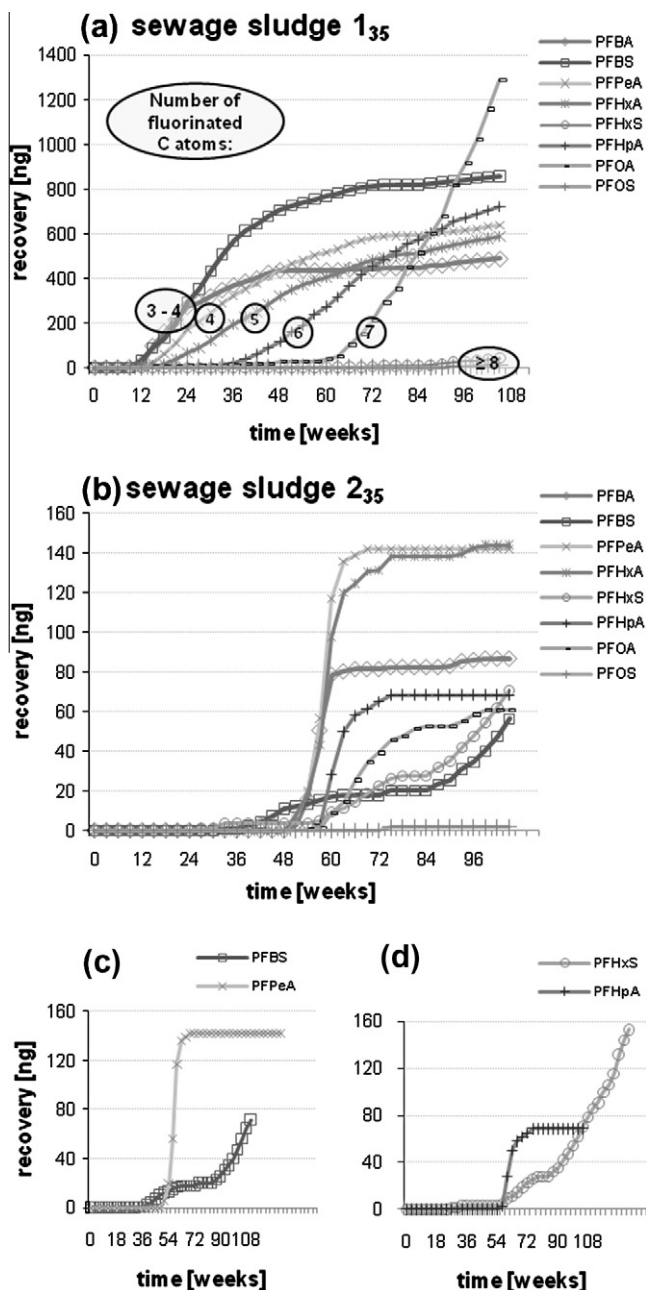
The breakthrough curves of the C<sub>4100</sub>-tubes (Fig. 3) agree with those of the C<sub>435</sub>-tubes. For mass balance considerations, further tests were conducted, see 3.2.

In the MIX<sub>100</sub>-tubes (Fig. 2) PFBA, PFBS, PFPeA, and PFHxA were not retained and eluted together with the tracer. PFHxS and PFHpA, which have the same fluorinated carbon chain length, elute with similar breakthrough curves over a period of more than 70 weeks. For PFHpA, a fast first desorption has been observed followed by a slower second desorption.

The desorption of PFOA from the MIX<sub>100</sub>-tubes commences after 33 weeks. PFOS and PFC with longer carbon chains could not be detected in the percolating water after 140 weeks. Thus the desorption appears to be slow from the soil. These results indicate a strong dependency of the leaching behavior on the chain length. The longer the fluorinated carbon chain, the stronger it is retained, which agrees with the findings of Higgins and Luthy, 2006, that each CF<sub>2</sub> moiety increases the adsorption potential, measured as  $K_{oc}$  (Higgins and Luthy, 2006). Under the conditions used, PFC with a chain length of up to five fluorinated carbon atoms show a fast elution, whereas the longer ones are retained to some degree. The sorption potential increases with every CF<sub>2</sub> moiety. The results of the C<sub>4100</sub>-tubes (Fig. 3c) support this finding. PFHxA elutes marginally slower than PFBA, and the elution of PFHxS has a delay of 5 weeks from PFHxA and of 6 weeks from PFBA.

In addition to the soil spiked with known amounts of PFC, some tubes of soil were spiked with real sewage sludge. The breakthrough curves of the sewage sludge 1<sub>35</sub>-tubes (Fig. 4a) also confirm the dependency of the elution order on the chain length. The elution of PFC out of the tubes with sewage sludge starts after





**Fig. 4.** Breakthrough curves of tubes with sewage sludge;  $\Sigma$  total PFC about 20  $\mu\text{g}$ ;  $n = 2$ : (a) sewage sludge 1<sub>35</sub>; (b–d) sewage sludge 2<sub>35</sub>; (c and d) excerpts of (b) showing only PFC with the same fluorinated carbon chain length.

9 weeks with PFBA and PFBS. Subsequently the elution of PFPeA, PFHxA and PFHpA commences according to their chain length. PFOA starts to elute after 1 year and again, PFOS and PFC with longer carbon chains could not be detected in the percolating water after 120 weeks. The breakthrough of PFBA and PFBS appears to be complete after 1 year. Thus complete elution takes twice the time taken for the other tubes with the same flow velocity. The PFC show a stronger adsorption to the sewage sludge, probably due to a higher content of organic carbon, which is a factor for the degree of adsorption to soils or sediment. This sludge had a content of organic carbon of 7%, whereas the soil used had only 2%.

In the percolated water from the sewage sludge 2<sub>35</sub>-tubes (Fig. 4b) no PFC could be detected in the first 50 weeks. This can be attributed to the high organic carbon content of 14%. PFBA, PFPeA, and PFHxA, eluted with sharp narrow breakthrough curves

from week 50 to week 70. The elution of PFHpA and PFOA, again, starts 10 weeks later. PFOS and PFC with longer carbon chains could not be detected in the percolating water after 120 weeks. The concentrations measured were only about a fifth of those measured from the sewage sludge 1<sub>35</sub>-tubes. For this sludge, the PFC did not only elute according to the chain length as it did for the other sewage sludge, but there are clear differences concerning the functional group. As illustrated in (Fig. 4c and d), the sulfonic acids show a different leaching behavior than the carboxylic acids of the same fluorinated chain length. The desorption starts later for all of them, but then the perfluorinated carboxylic acids (PFCAs) elute faster than from sewage sludge 1, whereas the perfluorinated sulfonic acids (PFSAs) elute only slowly and erratically. This agrees with the findings of Higgins and Luthy (2006) and Enevoldsen and Juhler (2010), who showed in batch experiments that the PFSAs adsorb more than their corresponding PFCAs. The leachates of other tubes than the sewage sludge 1<sub>35</sub>-tubes revealed no differences between PFSAs and PFCAs. The elution thus seemed to be dependent solely on the chain length (hydrophobic interaction) with the functional group (the head – electrostatic interaction) playing no part in retention. The higher organic carbon content and perhaps other properties of this sewage sludge caused another leaching behavior.

When interpreting the results with respect to environmental conditions, it must be considered that the soil column lengths used in these experiments was very short. The PFC concentrations applied did range from low loads (2  $\mu\text{g}/\text{kg}$ ) to very high concentrations (1 mg/kg), much higher than found in the environment (except near point sources). Considering that and the fact that PFOS did not elute until after 2 years of regular application of water, it can be assumed that the remobilization of PFOS in the environment is likely to take several decades.

### 3.2. Mass balance

Calculation of the total eluted mass revealed that the recovery of most PFC is between 80% and 90% of the added mass. PFBA is an exception. In the MIX<sub>100</sub>-tubes, the recovery is 82% (Fig. 2), but if only PFBA and PFBS are added (C<sub>4100</sub> and C<sub>435</sub>) the elution of PFBA is incomplete (Fig. 1b and a). About 40–55% of the added PFBA seem to be irretrievable. To examine this phenomenon, the same amount of PFBA and PFBS was added a second time to the C<sub>4100</sub>-tubes (Fig. 3b). The elution of PFBA was complete with about 90% recovery. This strongly suggests that there are available binding sites of the soil which have been permanently blocked by the first addition and the new PFBA percolates through completely. Within the MIX<sub>100</sub>-tubes these binding sites might be occupied by other PFC so that PFBA has no opportunity to adsorb. To investigate this possibility, PFHxA and PFHxS were added to the C<sub>4100</sub>-tubes (Fig. 3c). A week later, PFBA started to elute again (although it was not added this time) and within 4 weeks the amount of PFBA that was missing after the first addition reappeared. In an additional experiment, magnesium stearate was added to the C<sub>435</sub>-tubes, and again, PFBA started to elute (Fig. 1c). Thus it would appear that the longer and more lipophilic PFC (here PFHxA or PFHxS and stearate) can displace shorter PFC (here PFBA) from their binding sites in the soil. Further research is needed on how these mobile PFC are adsorbed or bound to the soil. Within the time span of our experiments, this type of adsorption, which could be desorbed by other adsorbates, did only occur with short chain perfluorinated carboxylates.

### 3.3. Comparison with monitoring results

The experimental results show that the mobility of PFC in soil is heavily dependent on the chain length. The short chain PFC,

**Table 2**

Statistical evaluation of a monitoring study with Hessian ground- and surface water samples from 2008 and 2009. LQ: limit of quantification: 1 ng/L.

	PFBA	PFBS	PFPeA	PFHxA	PFHxS	PFHpA	PFOA	PFOS	PFNA	PFDA	PFDS	PFUnDA	PFDoDA	PFTeDA
<i>32 surface water samples</i>														
Percentage of results >LQ	78	72	72	81	72	72	91	84	78	59	0	0	0	3
Median (ng/L) <sup>a</sup>	12	7	7	11	5	5	20	17	2	2	–	–	–	–
<i>150 groundwater samples</i>														
Percentage of results >LQ	17	7	9	14	13	10	27	21	2	1	0	0	1	1
Median (ng/L) <sup>a</sup>	3	2	8	4	2	2	3	3	–	–	–	–	–	–

<sup>a</sup> Only calculated if percentage of results >LQ is higher than 3%.

increasingly used in the recent years as alternatives for PFOS and PFOA, can pass through the soil without retention and are likely to be carried away easily with surface runoff. This will happen more readily if some binding sites are already occupied by for example other PFC. Thus, the increased use of these substances should soon be reflected by water monitoring data. Table 2 shows the results of a monitoring program with 32 surface water samples and 150 groundwater samples from Hesse. The short chain perfluorinated carboxylic acids were found in similar or even higher concentrations as PFOA in the ground water samples. Although especially PFBS is discussed as an alternative PFC, the concentrations found are not as high as those of the other short chain PFC.

PFC with more than eight carbon atoms are not commonly found in groundwater. They are more prevalent in surface water, but only at very low concentrations. This observation correlates with the results of the leaching experiments. The long chain PFC are held back by the soil on their way to the groundwater because of their strong adsorption.

The interpretation of this monitoring study shows that PFOA and PFOS, although the most frequently studied of PFC, are not necessarily the ones with the highest concentrations or the ones most often found in ground water. In ground water the short chain PFC, e.g. PFPeA and PFHxA, were detected at higher concentrations possibly because their transport through soil to groundwater is more rapid so the accumulation there is faster. The longer the fluorinated carbon chain, the more this translocation is retarded. In the beginning of the use of PFC, the emission of short chain PFC was marginal and only due to their presence as impurities in the used products. Long chain PFC were used and hence could accumulate in the environment since several decades. Today, short chain PFC are increasingly used and can reach the ground water fast. The remobilization of the long chain PFC from solid phase to water can take very long (or even does not occur at all, depending on the chain length), consequently their current presence in the aqueous phase is outnumbered by the short chain PFC. Despite the restricted use of PFOS and PFOA it is likely that their concentrations in water and other environmental matrices will increase in the next decades because of three sources: (1) most PFOS and PFOA in the environment is still bound to soil and will only be desorbed slowly, (2) slow degradation of precursors of these compounds in environmental compartments (Frömel and Knepper, 2010) and (3) they are still used in application areas as the galvanic industry, where there is, as yet, no replacement.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2012.02.011.

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