

Perfluorinated compounds (PFCs) in groundwater and aqueous soil extracts: using inline SPE-LC-MS/MS for screening and sorption characterisation of perfluorooctane sulphonate and related compounds

Rasmus Enevoldsen · René K. Juhler

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Abstract Perfluorinated compounds (PFCs) have been recognised as emerging pollutants of global relevance. A fully automated method with inline solid-phase extraction coupled to electrospray ionisation liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS) is presented and used for characterisation of soil adsorption and desorption for six PFCs: perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorobutane sulphonate (PFBS), and perfluorooctane sulphonate (PFOS). The method reduces sample turnaround time and solvent consumption and is suitable for low volume sampling. The only sample preparation necessary for water samples was sedimentation by centrifugation. The method has a total runtime of 21 min including inline sample cleanup (2 min for injection and SPE, 14 min for the chromatographic separation, 5 min for reconditioning). Negative AP-ESI with selective reaction monitoring (SRM) was used and the method was documented for quantification of the six environmentally important PFCs in subsoil matrix and related aqueous matrixes (groundwater and drainage water). Linearity was demonstrated in the range 5 to 2,500 ng/l and the LOD was between 2 and 8 ng/l in

groundwater. Adsorption was characterised by linear Freundlich isotherms for all six compounds in two agricultural top soils (A horizon, sandy and clayey soil). Variability in sorption characteristics for soil types as well as compound properties were found, and correlation between the organic carbon normalised sorption coefficient (K_{OC}) and PFC molecular weight was demonstrated. The K_d values were in the range 0.1 to 33 (l/kg), and 0.3 to 65 (l/kg) for sorption and desorption respectively.

Keywords Fluorinated hydrocarbons · Inline SPE tandem mass spectrometry · Fluorochemical FC

Introduction

Reports on widespread occurrences of perfluorocompounds (PFCs) in the environment have caused concern. Even though many aspects of toxicology and distribution in biota, sea and surface waters have been addressed in studies and reviews [1–10], there is only limited knowledge on the presence and fate of these compounds in the subsoil environment. The lack of quick and sensitive methods for quantitative analysis of these compounds in the soil and groundwater has been a barrier for the generation of knowledge on the comprehensive fate characterisation of PFCs.

In general, the PFCs are considered to be anthropogenic [11], and these fluorinated compounds are used in numerous industrial and domestic products and in may 2009 perfluorooctane sulphonate (PFOS) and salts was added to the persistent organic pollutants (POPs) listing of the Stockholm convention [12]. The overall structure of PFCs is a hydrophobic, perfluorinated aliphatic carbon chain which at

R. Enevoldsen · R. K. Juhler (✉)
Department of Geochemistry, Geological Survey of Denmark
and Greenland (GEUS),
Øster Voldgade 10,
1350K Copenhagen, Denmark
e-mail: rkj@geus.dk

Present Address:
R. Enevoldsen
Novo Nordisk A/S,
Hallas Allé,
4400 Kalundborg, Denmark

one terminal contains a more hydrophilic functional group, e.g. a simple sulphuric acid, a carboxylic acid, an alcohol or more complex derivatives hereof. The length and branching of the carbon chain is variable, and numerous PFC structures can be synthesised. The formation of poly- and perfluorinated acids from biodegradation of fluorotelomer alcohol has been demonstrated [13], a conceptual model for the formation of PFC from microbial degradation of a fluorotelomer polymer has been published [14] and the Organization for Economic Co-operation and Development (OECD) has made a list of more than 200 perfluorinated compounds and groups of compounds, which all potentially can degrade to either the perfluorinated sulphuric acid or the perfluorinated carboxylic acid [15]. Due to the multitude of structures, a considerable span in effects and parameters related to fate (bioavailability, transport, sorption characteristics, etc.) is anticipated, e.g. bioconcentration and bioaccumulation of some perfluorinated acids, have been correlated with the length of each compound's fluorinated carbon chain [8]. The multitude of compound characteristics also represents a challenge, when developing analytical methods for PFCs.

Due to the widespread use and concerns, there is a need for knowledge on the 'typical' compound PFOS as well as other PFCs in the total environment, including soil and groundwater. The global distribution of PFCs in the environment and occurrences of point sources, have been documented [6, 16], and a mass balance model and aspects of global fate and transport pathways have been published [17]. Worldwide PFCs, primarily perfluorooctane sulphonate and perfluorooctanoic acid, but more recently also precursors like fluorotelomers, have been found in both urban and more remote areas. PFCs have also been detected in numerous matrixes, e.g. in human and animal liver, serum and tissue samples [3, 18–22], rainwater [23], freshwater [24, 25], seawater, groundwater [16], soils, sediments, WWPT sludge, and in the atmosphere [3, 6, 17, 26]. The ecotoxicology of the compounds has been evaluated [27–30], and recently it has been suggested, that PFOS may be linked to reproductive effects in polar bears [31], transcriptional effects [32], and may possibly reduce fecundity in humans [33, 34]. In many countries, surface water is the source of drinking water and studies on PFC content in this type of drinking water have been published [25, 35, 36]. In Denmark, the drinking water supply originates from ground water, causing an increased concern for risk of contamination of soil and ground water resources. This is contrasted by the lack of data on PFCs in subsoil environments including groundwater.

For assessment, fate characterisation and risk analysis some basic characteristics of the compound are needed. Adsorption is a core parameter, but data characterising adsorption of PFCs on natural soils is scarce. In an early

publication by Higgins et al., it was suggested that some PFCs may adsorb strongly to solids [37] and a number of studies have been made for developing strategies and technologies to remove PFC from sludge and wastewater. Yet, the identification of suitable treatment methods is still a challenge [1]. A number of mass balance studies on waste water treatment plants have been published [38, 39], and the sorption of some PFCs has been studied on various matrices, e.g. oil and black carbon [40], soils [41], sludge, and minerals [37, 40, 42], freshwater sediments and mudflats [37, 41, 43, 44].

Whereas studies have been carried out on environmental solid matrices [37, 43, 45–47], adsorption data for PFCs based on natural soil samples are limited. In a study on the sorption of 8:2 fluorotelomers in soil, linearity between the partition constant (K_d) and the fraction of organic carbon in the soil was described [48]. The company 3M investigated the sorption of perfluorooctane sulphonate in different soils, and K_d values between 10 and 35 l/kg were reported in a report published by 3M [49]. Higgins and Luthy investigated the partition of several PFCs in the sediment/freshwater compartment, showing linearity between the fraction of organic carbon in the sediment, and the measured partition coefficient [43]. Reported findings of four perfluorinated surfactants in samples of groundwater from wells around a fire-training area [50], and levels of PFOS in municipal wells at or above the state's health-based value (information obtained from the company website of 3M, [51]), have revealed the need for clarification of possible PFC contamination of soil and groundwater. Even if data is starting to emerge, there is a need for extended knowledge for use in risk evaluation and fate characterisation. To meet these needs, fast and sensitive analytical methods are required. The use of inline cleanup and LC-MS/MS can meet this challenge. By linking the knowledge of laboratory adsorption and fate studies with real world monitoring, the knowledge needed for assessment can be established.

The availability of liquid chromatography-tandem mass spectrometry (LC-MS/MS) equipment with inline cleanup provides an opportunity to improve existing methodologies, e.g. reduce solvent consumption, turn-over time, and labour resources. Such fully automated online solid-phase extraction coupled directly to LC-MS/MS, has been used for quantification of other xenobiotic substances in aqueous matrices, e.g. antibiotics and pesticides [52–58].

The purpose of the present study was to generate further insight into the occurrences and fate of PFCs in the subsurface environment. This was achieved by (1) developing a fast and labour-saving solid-phase extraction coupled to electrospray ionisation liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS) method suitable for the analysis of PFCs in the soil and groundwa-

ter matrices (2) describing the sorption characteristics of six PFCs in real soils using the method developed.

Materials and methods

Chemicals and standards

Perfluorobutane sulphonate (PFBS, CAS-RN. 375-73-5), pentadecafluorooctanoic acid (PFOA, CAS-RN. 335-67-1), and PFOS (CAS-RN. 1763-23-1), was obtained from Sigma-Aldrich. Perfluoroheptanoic acid (PFHPA, CAS-RN. 375-85-9), perfluorononanoic acid (PFNA, CAS-RN. 375-95-1), and perfluorodecanoic acid (PFDA, CAS-RN. 335-76-2), was obtained from ABCR GmbH & Co KG, Karlsruhe Germany. 1*H*,1*H*,2*H*,2*H*-perfluorooctane sulphonic acid (THPFOS, CAS-RN. 27619-97-2) was supplied by Apollo Scientific, Cheshire. Ammonium acetate, calcium chloride and high-performance liquid chromatography (HPLC)-grade solvents (acetonitrile, methanol and ethanol) were purchased from WVR Bie and Berntsen, Rødovre Denmark. HPLC water (Type 1 MilliQ water, resistivity >18 m Ω cm,) was made from tap water treated in a Millipore system (Billerica, MA). Prior to use, all glassware were soaked for 24 h in 0.1 M hydrochloric acid, washed with five volumes of MilliQ water, and baked at 300 °C for 16 h. Standard stock solutions of individual analytical standards were prepared at concentration level 5,000 mg/l or 500 mg/l in acetonitrile according to solubility. From these standard stock solutions, working standards with a concentration of 100 mg/l where made in acetonitrile. Standards and mixtures at concentrations lower than 100 mg/l where all made in MilliQ water on a day to day basis. All standards were kept in the dark at 4 °C until usage.

Inline cleanup and chromatography

The only sample preparation needed before injection was the addition of internal standard, sedimentation by centrifugation at 10,000 $\times g$ for 10 min in 2-ml vials, and transfer of the supernatant to the analytical vial using a finnpipette. The inline SPE extraction and analysis of the PFCs was made using a Thermo Scientific Equan LC-MS/MS system (Thermo Scientific, San Jose, CA). The system was equipped with two separate pumping systems, one Surveyor plus LC pump and one Surveyor plus MS pump, additional an HTC PAL auto sampler and a total of two six-port valves for automated inline cleanup. Each run consisted of three steps [52]: (1) injection and SPE loading, (2) SPE enrichment and (3) SPE column elution, analysis and detection.

The inline SPE extraction and enrichment was made using a 2.1 \times 20 mm Hypersil Gold Silica based C18 column with a particle size of 12 μ m (Thermo Scientific). A study on column suitability for PFC analysis has been published [59], and a C18 stationary phase was found to provide the highest analytical sensitivity. In agreement with this finding, the analytical separation in the current method was made using a 2.1 \times 50 mm Hypersil Gold Silica based C18 column with a particle size of 3 μ m (Thermo Scientific). The analysis, including inline SPE cleanup, was carried out using a two-solvent gradient elution: A, 1 g/l ammonium acetate in MilliQ water and B, 50:50 methanol:acetonitrile. At injection and SPE column load, the eluent was 100% A (1 ml/min for 2 min). For SPE elution back flushing of the SPE column with the analytical gradient was used. Thus at 2 min after the start of the SPE loading, the analytical gradient started with a 1.5-min of isocratic run at 55:45, followed by gradient settings A:B to 5:95 at 11 min, and maintaining this eluent composition until 14 min returning to starting conditions 55:45 A:B at 15 min and maintaining this composition 5 min for reconditioning the analytical column at 0.3 ml/min. The volume injected was 1 ml, and between each run the SPE column was conditioned by flushing with eluent B for 2 min at 0.5 ml/min followed by 1 min of eluent A at 0.5 ml/min.

Mass spectrometry conditions

The mass spectrometric detection was made using a Finnigan TSQ Quantum Discovery Max from Thermo scientific. The initial method development, was made using the build-in syringe pump, injecting a 2-mg/l standard solution at 10 μ l/min into a mobile phase pumped at 0.2 ml/min and consisting of 50:50 MilliQ:methanol. The mass spectrometric conditions were optimised using the automated tune utility of Xcalibur™ software. Initially, spray voltage, stealth gas, auxiliary gas, and tube lens where optimised in MS mode, giving optimal ionisation of each of the six compounds for making [M-H]⁻ ions. Subsequently, the fragmentation of each of the [M-H]⁻ compounds was optimised, and the most abundant fragment ion and collision energy was established for the quantitative method.

The optimised MS and MS/MS conditions were: ion source polarity, ESI(-); spray voltage, 4000 V; vaporizer temperature, 275 °C; sheath gas pressure, 50 units; auxiliary gas pressure, 10 units; scan type, SRM; Q1 and Q3 peak width, 0.5 Da; collision gas pressure, 1.5 units. The MS/MS ion trace, used for each PFC, is shown in Table 1. The limit of detection (LOD) was calculated from the standard error (S_{St1}) of 7 analytical runs made at the lowest concentration of the calibration

Table 1 Instrument settings and ion traces for MS/MS detection and quantification of the six compounds included in the method

Compound	Mw	Parent ion [M-H] ⁻	Quantification [F] ⁻	CE	Verification fragments
	g/mole	<i>m/z</i>	<i>m/z</i>	kV	<i>m/z</i>
PFBS	300.10	298.94	79.98	36	98.9; 118.8
PFHpA	364.06	362.97	318.99	15	168.7; 118.5
THPFOS	428.17	426.97	406.85	28	212.6; 168.8
PFOA	414.07	412.97	368.85	16	169.1; 218.7
PFNA	464.07	462.96	219.00	21	418.7; 168.9
PFOS	500.13	498.93	98.93	31	279.6; 129.8
PFDA	514.08	512.96	469.03	17	318.9; 218.7

Also, the optimised fragmentation conditions are shown for the compound THPFOS that was initially evaluated for inclusion in the method. In addition to the primary fragment used for quantification additional fragments suitable for verification is shown

curve (Eq. 1, $t_{0.995}$ is the t distribution fractile at probability 0.995):

$$\text{LOD} = \frac{S_{St1} \times t_{0.995}}{b} \quad (1)$$

The method limit of quantification (LOQ) was calculated as three times LOD or set equal to the lowest standard in the calibration curve whichever is the highest (Eq. 2).

$$\text{LOQ} \geq C_{St1} : \text{LOQ} \geq \frac{3 \cdot S_{St1} \cdot t_{0.995}}{b} \quad (2)$$

Soils

Soil sampling methods and principle for adsorption experiments have previously been described [60]. Sorption characterisation was made using two different soil types (Table 2), sampled from the B horizon (depth 20–40 cm), at two agricultural field-sites in Denmark [61]: Jyndevad in Jutland (sandy soil) and Sj. Odde on Zealand (clay soil). Soil samples were stored at -18°C until use, at which point it was homogenised and sieved, using a 2-mm mesh size. The initial water-content in the soil was measured by baking 100 g of soil for 24 h at 105°C , and the water-content was determined to 9.4 and 19.8 w/w% for the sandy and clayey soil respectively.

Adsorption and desorption

Sorption at several concentrations was measured in batch experiments. Sorption isotherms were estimated using the Freundlich equation, where K_F and n_F are the Freundlich parameters [62, 63]. When the Freundlich constant n_F equals 1, the isotherm is linear and K_F equals K_d .

The applied adsorption/desorption procedure was a modified version of the OECD guideline 106 [62]. For each soil, sorption isotherms were determined, by measuring the partition at eight initial concentrations, in the interval 0.02 to 1 $\mu\text{g/l}$, and the soil sorption coefficient was estimated using the intercept of the isotherms. At each concentration level, a control sample without soil was included. All experiments were carried out using 10-ml glass centrifuge tubes with aluminium-sealed screw caps. Two different soil-to-water ratios were used. For PFBS and PFHPA a soil-to-water ratio of 12:25 was used, and for PFOS and PFDA a soil-to-water ratio of 3:14 was used, while both ratios were evaluated for PFOA and PFNA. Homogenised soil samples of 4.8 or 1.2 g (depending on the soil-to-water ratio), were transferred to a glass tube and added 9.0 and 5.0 ml, respectively, of 100 mM of calcium chloride in MilliQ water. The CaCl_2 solution was used as the aqueous solvent phase to improve centrifugation and minimise cation exchange [62]. Prior to the spiking procedure slurries were equilibrated in a head-to-head shaker for 24 hours at 10°C , and 30 rpm. After

Table 2 Physical and chemical properties of the soil sampled from the two Danish sites, used for adsorption experiments

	Sand 20–2000 μm %dw	Silt 2–20 μm %dw	Clay <2 μm %dw	Organic C %dw	CaCO_3 %dw	pH	Al_{cbd} mg/kg	Fe_{cbd} mg/kg
Jyndevad	94	1	5	1.00	-	6.1	2632	2729
Sj. Odde	41	22	37	0.42	0.4	7.6	1294	8119

Fe_{cbd} and Al_{cbd} is citrate-bicarbonate-dithionite extractable Fe and Al. Relative content is given as percent of dry weight (%dw)

equilibration, a solution of the PFC compounds in 100 mM of calcium chloride was added to the slurry (1.0 and 0.6 ml, respectively). Thus, the total liquid volume used for 4.8 and 1.2 g soil was 10.0 ml and 5.6 ml respectively. Subsequent to spiking, the tubes were equilibrated in a head-to-head shaker at 10 °C and 30 rpm for 96 h. The incubation time used for the sorption experiments was selected based on pilot experiments, where the sorption was followed for several weeks, and no development in the sorption state was observed after 4 days (results not shown)

After 96 h the sorption tubes were centrifuged for 15 min at 10,000×g. Using a finnpipette, 1.9 ml of the supernatant was collected and transferred to a 2-ml micro spin vial, and after measuring the pH of the solution the remaining supernatant was discharged. The volume collected was centrifuged for 15 min at 10,000×g and 1.6 ml of the supernatant was collected using a finnpipette and transferred to a vial that was capped and stored in darkness, at 4 °C until analysis.

For estimation of desorption, the sorption tubes were refilled with 100 mM of CaCl₂ in MilliQ water 4 ml for the tubes with a soil-to-water ratio of 12:25 and 5 ml for the 3:14 ratio. CaCl₂ was used in the desorption experiments as to maintain the same ionic strength as used for the sorption experiment. Subsequently the tubes were shaken vigorously by hand to re-suspend the soil. The slurry was placed in a head-to-head shaker for 96 h, incubated at 10 °C, and centrifuged following the same procedure as for the sorption. Any remaining sorption-water was determined by the weight difference of the sorption tubes and soil, before and after the sorption experiment, the result was used for calculating the initial conditions of the desorbing-experiment.

The quantification of the compounds was made by external calibration using linear fitted curves (no weighting of the calibration function). For documentation of instrument linearity, each sample sequence was initiated and ended by a set of standards (five levels plus blank) spanning up to three orders of magnitude. Having demonstrated linearity the actual samples were quantified using boxed standards (e.g., a high-level standard followed by five samples, a low-level standard followed by five samples, a high-level standard, etc.) and high and low levels were adjusted to the relevant levels of the samples. To promote matrix-matched calibration the standards used for quantification were made in water, which had equilibrated with the soil for 24 h prior to standard addition. For calculation of the soil-to-water distribution coefficients K_d , the method of aqueous loss was used [43, 62]. Using this approach, the concentration of compounds was analysed in the aqueous phase, using the SPE-LC-MS/MS method developed, and the soil concentration was calculated, using the difference between the initial theoretical concentration and the measured concentration in the aqueous phase.

Results

As prerequisite for the fate studies of PFC compounds a quantitative method was developed for determination of six of simple perfluorinated compounds; four carboxylic acids, with carbon chain length of 7 to 10, and two sulphuric acids with a carbon chain length of 4 and 8. The matrices were aqueous soil extracts, ground water and drainage water. The soil/water partition of these six environmentally important PFCs was characterised using two Danish topsoils selected to represent a sandy soil, and a more clayey soil.

Inline cleanup, chromatography and mass spectrometry

The LC-gradient method developed gave baseline separation of all six compounds within 10 min (Fig. 1). The total run time was 21 min, including inline SPE extraction, chromatographic separation, MS/MS detection, and reconditioning of the two columns. From intercomparison studies on analytical methods, it is known that quantification of PFCs in various matrices is a challenge [64–68]. In a recent comparison of methods used for PFCs in blood and similar matrices [64], it was found that the use of matrix-matched calibration was essential for quantitative work to reduce the possible effects of both ion suppression and enhancement using LC-MS/MS. In accordance with this, the calibration standards used were spiked into aqueous soil extracts (24-h shaking) sampled at the same two sites as used in the sorption experiments. Specific issues related to detection and quantification of PFCs at low concentrations in soil, as well as the use of ¹³C standards has been evaluated [69]. It was concluded, that due to the variability in the matrix of soil extracts ¹³C-PFOA was less suitable for use as a general internal standard. In agreement with this, the present study used an external and a compound identical standard for each PFC, and matrix-matched solutions were used for quantification. Thus, the analytical method was calibrated and validated using standards in MilliQ water (0.005–1 µg/l) and spiked groundwater samples (0.005–2.5 µg/l). For both the MilliQ and groundwater standards, linear calibration using the method of least squares gave R^2 of 0.990 or better, indicating a good linear fit of the calibration curve (Table 3).

The optimised chromatographic procedure provided baseline separation of all six compounds and $W_{1/2}$ peak widths was 0.5 min or less for all compounds (Fig. 1). Perfluorooctane sulphonate eluted as three tops in the chromatogram. This was probably caused by the method used for synthesis of the standards, i.e., both straight and branched carbon chains are formed [70].

The detection and quantification limit of the individual PFCs in groundwater is given in Table 3. Overall, linearity was demonstrated within the interval 5 to 2,500 ng/l and the

Table 3 Detection and quantification limit of the individual PFCs in MilliQ water and groundwater the inline SPE LC-MS/MS method

Compound	t_R min	Spiked MilliQ water		Spiked groundwater	
		R^2	LOD ng/l	R^2	LOD ng/l
PFBS	3.43	0.9974	6.4	0.9988	5.2
PFHpA	3.98	0.9968	3.7	0.9977	4.6
PFOA	4.86	0.9992	6.5	0.9988	8.3
PFNA	6.53	0.9997	2.7	0.9991	6.2
PFOS	7.91	0.9985	7.1	0.9980	2.4
PFDA	8.68	0.9924	6.8	0.9968	6.2

Retention time (t_R) and limit of detection (LOD) is shown for each compound using 1 ml injection volume and inline cleanup. The square of the sample correlation coefficient (R^2) of the linear calibration is given for the interval from 5 to 2,500 ng/l (11 levels used)

LOD were between 2 and 8 ng/l. In general, only one major MS/MS transition was obtained using the optimised conditions of the method and this ion trace was used for quantification. A higher limit of detection and quantification would have been the result of including additional secondary transitions in the quantification. In the event that further verification is needed, it is recommended that

alternative instrument settings are optimised for improved intensity of the fragments of secondary transitions for verification purposes. Such secondary MS/M fragments are included in Table 1 for each compound. When using inline cleanup there is no straightforward way to measure the extraction recovery rate, but injecting the same amount of analyt in 10 μ l direct injection and in 1 ml with inline cleanup, gave comparable areas in the chromatograms, indicating a high extraction recovery. Also, control of breakthrough conditions is of essence when integrating SPE in line with LC. In the present study, a 1-ml injection was used whereas breakthrough experiments demonstrated that volumes up to at least 5 ml could be used (data not shown), i.e. even lower LODs could be achieved if required.

Comparing the LODs of the present method (Table 3) to the short-term provisional health advisory values for PFOA and PFOS of 0.4 and 0.2 μ g/l, respectively, as set by EPA in 2009 [71] the method meets the need for a quantitative method for monitoring of groundwater and drinking water resources. Also, as demonstrated in the present study, the method is suitable for studying adsorption and desorption processes in the subsurface environment.

The PFCs included in the present study are widely used and there is a risk for contamination of blank samples. Developing and implementing methods for PFC analysis in this aspect is a matter of concern [72–74]. In the present study, two compounds, PFOA and PFOSH demonstrated a background level. Initially PFOSH was a candidate for an internal standard and the analytical conditions for detection are included in Table 1. However, the impurity leaching from the LC pump/auto sampler system was varying between runs, from levels of no consequence to levels comparable with the 0.1 μ g/l and for this reason it was not possible to use the PFOSH compound as an internal standard. A rather steady PFOS background level indicated that the problem may be related to the MS pump. In contrast, PFOSH was characterised by a peak even in blank samples. This would indicate a source within the LC pump and/or auto sampler system causing a band concentration on the SPE column. Switching the two LC pumps resulted in turning the problem around, giving a high steady background of PFOSH and a PFOA top at the corresponding retention time. The problem of PFOA was probably related to tubes and fittings inside the pump made of Teflon® (polytetrafluoroethylene, PTFE). This is a well-known problem in several common LC systems [4, 75]. One way to minimise the problem would be to exchange all Teflon® parts in the pumping system with non-PFC parts. Powley et al. solved the problem by inserting more retentive HPLC columns between the pump and the injection system, shifting the eluting time of the interfering compounds away from the analyt [45]. In the present study, it was estimated that the PFOA background did not

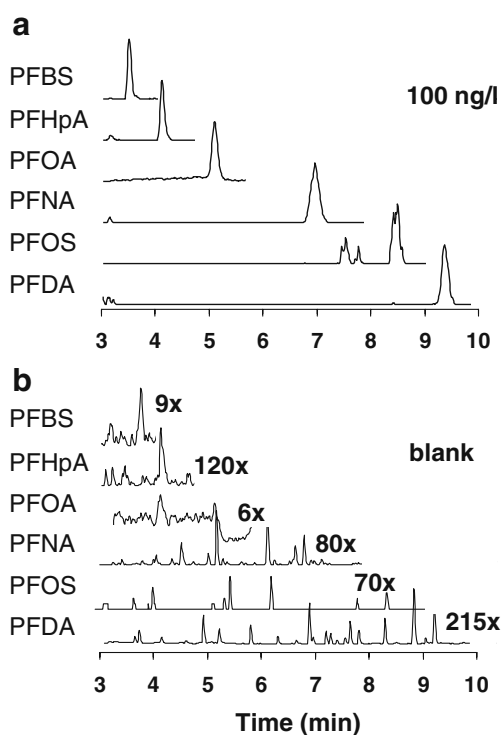


Fig. 1 Ion traces of the chromatogram **a** the six compounds spiked in groundwater to level 100 ng/l and **b** a blank groundwater sample. The scale of the ion traces in part **b** has been amplified relative to traces in **a**, as indicated for each trace. The injection volume was 1 ml on the inline SPE

inflict the sensitivity of the method (Fig. 2) and no further action was taken. However, this part of the method development confirmed the need for awareness and focus on possible background interference when analysing PFCs.

Optimisation of fundamental elements of the analysis of PFCs has been made in various studies, e.g. soil extraction [76] chromatography conditions, eluent composition and columns [59, 77] and comparison of MS techniques [78]. Reviews have been published on analytical methods for PFCs in environmental matrices [11, 68, 79, 80]. In general, the LODs are in the ng/l range, whereas large volume extractions can be used for studies where the pg/l level is addressed [23, 81]. A frequently cited study on PFOA and PFOS in the Tennessee River reports LODs at 25 ng L⁻¹ [24]. The direct quantification of PFCs has been made using direct injection MS and with LODs in the µg/l range [82], but in current methods cleanup procedures are normally applied. In conventional methods, cleanup is made offline and typically include operations such as filtration, centrifugation, SPE and LLE [83]. In an offline cleanup method for river water based on a 100-mL sample volume, 12 perfluorinated surfactants could be quantified to a LOD of 2 ng/l [25]. Using offline SPE or LLE and 900-mL water samples the LOD was 0.26 to 0.62 ng/l [84]. In a study of five short-chain perfluorocarbon carboxylic acids the general LOD was 25 ng/l in water [85] and the LC-MS/MS analysis of PFCs in groundwater was possible down to a LOD of 360 to 620 ng/l [86].

Other inline cleanup methods have been published. However, these methods have been developed for other matrices (e.g. PFOS, PFOA and PFOSA in human blood serum and milk [87–89]) or only a single or a few PFCs have been included in the method. One of the first methods for online extraction and quantification of PFOS in river water was developed using turbulent flow chromatography [90]. Injecting 1 ml of sample, a LOD at 5 and LOQ 17 ng/l could be obtained for PFAO.

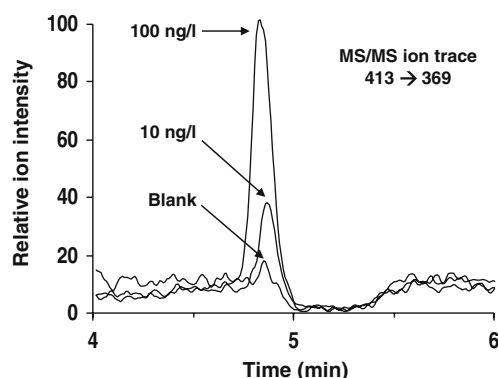


Fig. 2 Detection of PFOA in groundwater. Ion traces are shown for a blank and two spiked levels (10 and 100 ng/l). Inline SPE and 1.00 ml injection were used

In summary, the LODs of the inline cleanup approach developed in the present study is comparable to and in some cases better than PFC methods based on offline cleanup. Further, the inline approach used offers added value, e.g. reduced sample handling, small sample volume, and reduction of solvent use and using inline SPE, the column can be used for more than 200 samples (depending on the nature of the sample), whereas in offline SPE the cartridges is for single use only.

Sorption

The method developed was used for characterisation of PFC adsorption and desorption in a soil/water environment. Linear as well as Freundlich adsorption isotherms were evaluated. Linear isotherms (i.e. Freundlich adsorption isotherms with exponent $n=1$) was found for all six compounds with R^2 values close to 1, the lowest value being observed for PFOS ($R^2 \approx 0.85$), and the K_d values estimated were in the range 0.007 to 33 l/kg (Table 4). For all PFCs, the percentage of sorbed compound was in the range 10% to 75% except for two compounds where sorption on soil from Sj Odde was used: PFNA in ratio 12:25 where 97% was sorbed (using 3:14, this compound was also within the optimal range) and PFBS where 8% was sorbed on the soil.

Considering desorption of PFC from soil linearity was found for all compounds (except for PFOA in Jynde vad soil:water ratio 3:14 giving a low value $R^2 \approx 0.59$, where the values are included in the table for reference only, and a low $R^2 \approx 0.74$ was found for PFOS 3:14 using soil from Jynde vad). The desorption was characterised by K_{des} in the range 0.33 to 65 l/kg. The Freundlich isotherms are exemplified in Fig. 3. In previous studies, K_f for PFOS was in the range 36 to 61 for activated carbon, 31.8 on high-silica zeolite and 0.9 to 1.9 on sludge [42].

Based on the organic carbon content determined in the soil samples the values of K_{OC} were estimated using the OECD guideline 106 procedure [62]. A linear relationship was observed for log K_{OC} relative to the molecular weight in the sandy soil, a non-linear curve could be fitted for the clay soil (Fig. 4). A strict functional relationship may be less likely between the two measurands plotted as the plot is a second-order function between a non-transformed and a log-transformed one. If the relationship between log K_{OC} and MW could be verified using other soils and compound combinations it would rule out any 'second-order relationship by accident' considerations and point to a sorption related controlling mechanism coupled to the MW of the molecule.

In the experimental approach used, the concentration in the solid phase was estimated based on the measurements of the water phase, i.e. the amount of compound not

Table 4 Adsorption and desorption characteristics of PFC in two soil types

	Jyndevad			Sj. Odde		
	R^2	K_d	K_{oc}	R^2	K_d	K_{oc}
Adsorption						
PFHpA 12:25	1.00	0.63±0.01	0.63	0.85	0.63±0.07	1.5
PFOA 12:25	0.99	1.1±0.04	1.1	0.89	1.5±0.21	3.6
PFOA 3:14	0.98	1.5±0.07	1.5	0.93	1.8±0.21	4.3
PFNA 12:25	0.99	4.2±0.14	4.2	n.a.	n.a.	n.a.
PFNA 3:14	0.96	5.2±0.30	5.2	0.990	7.7±0.31	18.
PFDA 3:14	0.99	30±1.0	30	0.99	33±1.2	79
PFBS 12:25	0.99	0.41±0.02	0.41	0.99	0.07±0.02	0.2
PFOS 3:14	0.85	15±1.9	15	0.96	17±1.2	40
Desorption						
PFHpA 12:25	1.00	2.0±0.11	2.0	0.94	1.5±0.41	3.6
PFOA 12:25	0.95	1.8±0.21	1.8	0.86	4.1±3.7	9.8
PFOA 3:14	0.59	2.2±1.9	2.2	1.00	15±0.50	36
PFNA 12:25	1.00	6.4±0.06	6.4	n.a.	n.a.	n.a.
PFNA 3:14	0.99	17±1.0	17	0.98	32±4.8	76
PFDA 3:14	0.92	51±33	51	0.91	65±21	155
PFBS 12:25	0.99	1.2±0.10	1.2	0.81	0.33±0.17	0.8
PFOS 3:14	0.74	36±46	36	0.87	46±38	110

Compounds and soil:water ratio is shown. Linear isotherms were used for estimation of the Freundlich adsorption coefficient (K_d) and the desorption coefficient (K_{des}). The squared correlation coefficient (R^2) for linearity of log-transformed values, confidence level for the estimated function (\pm), and the organic carbon normalised adsorption coefficient (K_{oc} , cm^3/g) is given
n.a. not available

recovered from the water phase was assumed to be adsorbed in the soil matrix [43, 62]. In principle, a complete mass balance would be preferable, but using unlabeled compounds this approach is generally used due to the lack of exhaustive extraction procedures need for total mass balance calculations. As a precaution, the possible adsorption on the vessel surface, laboratory equipment, etc. was ruled out by including water samples spiked with PFC but without soil. In spite of all such measures, there is a potential for bias in the estimation of the soil sorption process when using the aqueous loss approach, i.e. sorption to soil could be systematically overestimated due to other dissipation processes (e.g. sorption to glass or lab material, degradation, etc.). Yet, inclusion of blanks and the slow degradation of PFC compounds reduce the risk for such bias in the present results.

Currently, the controlling parameters for PFC sorption are under debate [6, 46]. For example, dependence on pH was investigated and the results indicated that adsorbents was mainly dominated by the electrostatic interaction [91], and a study of adsorption of PFOA on powdered activated carbon indicated that the process was mainly controlled by particle diffusion [44]. The observation of a molecule size relation of K_{oc} for the PFC in the present study (Fig. 4) confirms previous publications describing correlation between chain length and adsorption characteristics. Thus, it has been shown that the partitioning behaviour is depending on physicochemical characteristics of PFCs as well as on sediment-specific parameters [43]. In the present study,

the correlation was observed even if the two sulphonic acids displayed small $\text{p}K_a$ values relatively to the four carbonylic acids, i.e. a general level of -3.3 vs. 2.8 , respectively [92, 93]. This observation indicates a minor importance of the functional group and possibly larger effect of carbon chain length within each soil. Also, the difference in curvature of the fitted function for the two soils demonstrates a clear relation between PFC sorption and partitioning characteristics and soil properties.

Discussion

In recent years several papers dealing with analysis of PFCs in natural samples have been published, and two primary principles for cleanup and sample concentration has been used: liquid/liquid extraction with counter ion [94] and more recently SPE [22–24, 75]. To our knowledge, the present study is the first to implement an automated cleanup and enrichment approach integrated inline with the LC-MS/MS system, for the analysis of PFCs in ground water samples and aqueous soil extracts.

Analysing compounds in natural samples by conventional methods sample cleanup and enrichment is laborious and often more time consuming than the quantitative analyses itself and can be the limiting factor of the number samples that can be analysed in a laboratory. The present inline SPE method dramatically reduces the sample turnaround time.

Fig. 3 Adsorption (*plus sign*) and desorption (*filled circle*) on soil as exemplified by isotherms. The adsorption of the PFC on the solid phase (C_s , $\mu\text{g/kg}$) is plotted against the concentration in the aqueous phase (C_{aq} , $\mu\text{g/l}$). Correlation coefficients and other details are given in Table 4. **a** PFHpA (Jynnevad, soil-to-water ratio 12:25), **b** PFOA (Jynnevad, soil-to-water ratio 12:25), **c** PFNA (Sj. Odde, soil-to-water ratio 3:14), **d** PFDA (Sj. Odde, soil-to-water ratio 3:14), **e** PFBS (Jynnevad, soil-to-water ratio 12:25), **f** PFOS (Sj. Odde, soil-to-water ratio 3:14)

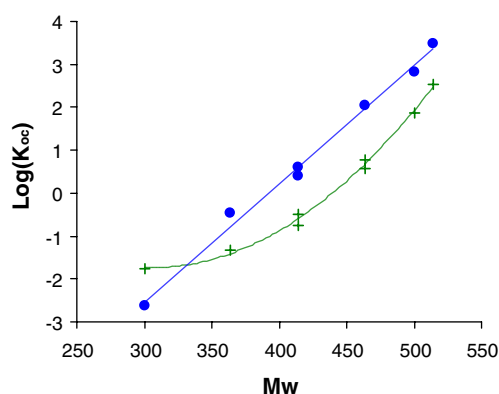
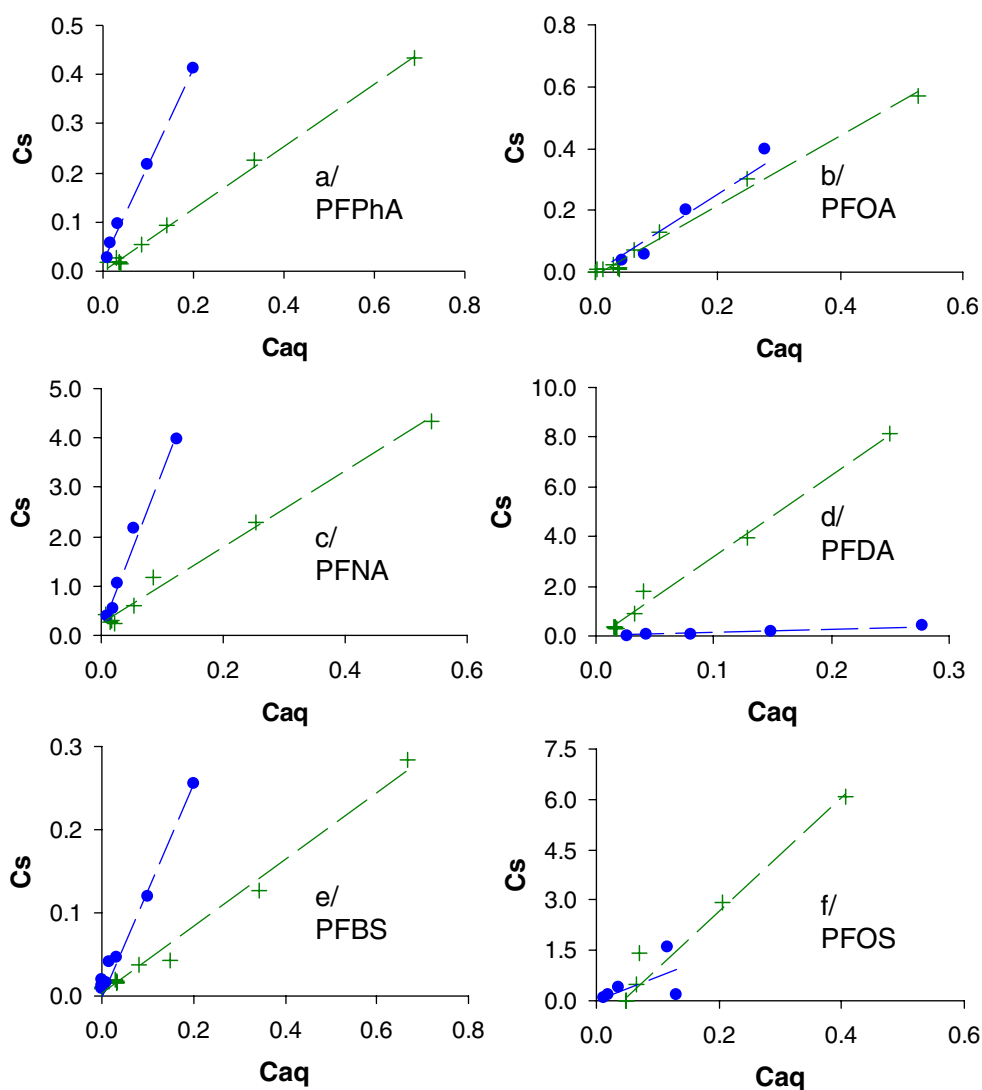


Fig. 4 Molecular weight and adsorption characteristics. Correlation was found for both soils between the logarithm to the distribution coefficient (K_{OC} , kg/l) and the molecular weight of the individual PFCs. The soils used were sampled at Jynnevad (*plus sign*, sandy soil, linear fit *green line*, $y=0.0275x-R^2=0.9928$) and Sj. Odde (*filled circle* clay soil, polynomial fit *blue line*, $y=1E-04x^2-0.0593x+7.3$ $R^2=0.9956$)

In addition to being time-saving, inline cleanup methods are characterised by using minimal volumes of organic solvents for sample cleanup and analyte pre-concentration. In a standard SPE method for analysing PFCs, the amount of organic solvent used in the SPE procedure (conditioning, wash and elution) can be up to 140 ml [75]. For comparison, the volume used in the present method is approximately 1 ml. Further, small sample volumes can be used, a great advantage for monitoring programmes and field experiments, e.g. in field studies where ceramic lysimeters are used in the vadose zone. Combined with reduced need for manual labour, turnaround time, method complexity and cost and the benefits of a fully automated procedure from sample to data, the inline approach is very suitable for fate studies and monitoring programmes where many samples are to be processed and quantified for content of PFCs.

From previous studies it is known that sorption of PFCs is influenced by a number of factors, e.g. soil carbon

content, pH and presence of surfactants [95], and inorganic components and electrostatics of the matrix [43, 96–98]. However, the mechanism, kinetics and controlling parameters are not fully characterised at present, as exemplified by the discussion on possible carbon effects on adsorption of PFCs [40, 46, 97]. It has been reported that PFC structural characteristics effect adsorption, e.g. the effect of chain length on PFC enrichment was studied in sediment cores [99]. Short-chain perfluoroalkyl carboxylic acids ($C < 8$) were found exclusively in pore water, while long-chain ($C > 10$) were found in sediment only. Enrichment of PFCs on sediment increased with increasing organic matter and decreasing pH. Likewise, in a pioneering study the of sorption of eight PFCs on five natural freshwater sediments of varying iron oxide and organic carbon content, it was concluded that the dominant characteristics influencing sorption was PFC perfluorocarbon chain length and sediment carbon content [43]. For sorption to sludge, this finding has been elaborated and it was suggested that protein fractions may be the dominant sludge parameter [46]. This demonstrates that the generation of knowledge on freshwater sediments and sludge is detailed to an extent that by far exceeds the insight into processes in natural soil status.

From Fig. 4, it is clear that the sorption characteristics vary for the two soils. Also, differences between adsorption and desorption curves slopes can be seen and such hysteresis points to the presence of two or more types of adsorption sites within soil matrix [100]. In the present study, a linear relationship was observed for $\log K_{oc}$ relative to the molecular weight in the sandy soil, whereas a non-linear curve could be fitted for the clay soil. Relative to the sandy soil (Jyndevad), the clay soil (Sj. Odde) had a high iron and low carbon content (Table 2). In a study of PFOS sorption on various geological materials, it was observed that electrostatic attraction may play a role when organic carbon is not present in the matrix [98]. Due to the complexity of the natural soils as used in the current study, it is difficult directly to compare this observation to studies made on standardised material. With this aspect in mind, it is interesting that the low carbon soil is more in line with other K_{OC} studies made, whereas the high carbon, low iron soil displays non-linearity. Log–log linearity has also been found for K_{OC} and chain length for fluorotelomer alcohols in a soil/water system [101] and $\log K_{air/water}$ coefficients [102].

The two soils used in the present study were neutral to slightly acidic (Table 2). Decreasing solution pH has been reported to increase sorption capacity and induce non-linearity of PFOS adsorption in experiments with black carbon [40]. Thus, the linearity of the adsorption isotherms observed may not be attributable to acidic soils. Soil acidification can occur due to, e.g. inherent soil characteristics, use of acid-forming fertilisers, mining activities, presence of conifers or hardwood trees, and use of a soil

additive. It would be informative to compare the results of the present soil sorption experiments to more acidic soils; such soils may have reduced sorption capacity and increased risk for leaching of PFCs. Also, considering the adsorption/desorption characteristics of the PFCs investigated, the possibility of solid-bound residue transport through the unsaturated zone should be considered. The method developed is suitable for such studies and also for monitoring programmes.

Conclusion

A method suitable for quantitative analysis of six simple perfluoro compounds was developed, and the obtained detection levels are suitable for studies of these compounds in the subsoil environment. The combination of inline SPE cleanup and LC-MS/MS showed useful when analysing simple environmentally important PFCs in natural samples, like ground and drainage water. The method is labour-saving and cost effective, as the SPE column can be reused more than 300 times (depending on the characteristics of the samples). The inline SPE method would be particularly suitable in studies where only limited sample material is available, as the sample volume was as low as 1 ml. Also, compared to more conventional methods, the present inline SPE method is using very small amounts of solvent for sample cleanup, and the method is less labour-intensive.

The sorption and desorption characteristics of the PFCs were characterised contributing to a more detailed understanding of PFC fate in the subsurface environment. The adsorption and desorption data indicate that the soil may have a capacity store PFCs due to high adsorption and low desorption, i.e. the soil matrix may act as a protective barrier towards extensive groundwater contamination. However, as demonstrated by findings of PFCs in groundwater in areas with industry and fire-fighting training areas, the leaching of PFCs is possible. The current results need to be matched by studies on soils from other parts of the world, i.e. extension of the soil types, in particular in relation to texture, carbon, pH and iron characteristics and the potential for bound residue transport through the unsaturated zone needs clarification.

Using the combination of inline SPE and an analytical LC-MS/MS method, it was possible to make automated analysis of natural water samples, with a minimum of sample handling and cleanup procedures. The overall time from the raw sample to the analytical result was less than half an hour, making this method ideal for studying PFCs in natural water samples, such as ground and drainage water, and quantitative analysis at the sub- $\mu\text{g/l}$ level is possible.

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