



Robust trace analysis of polar (C₂-C₈) perfluorinated carboxylic acids by liquid chromatography-tandem mass spectrometry: method development and application to surface water, groundwater and drinking water

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Abstract

A simple and robust analytical method for the determination of perfluorinated carboxylic acids (PFCAs) with C₂ to C₈ chains, based on solid-phase extraction (SPE) and liquid chromatography-tandem mass spectrometry (LC-MS/MS), was developed, validated and applied to tap water, groundwater and surface water. Two stationary phases for LC (Obelisc N and Kinetex C₁₈) and two materials with weak anion-exchange properties for SPE (Strata X-AW and Oasis WAX) were evaluated. Robust separation and retention was achieved with the reversed phase column and an acidic eluent. Quantitative extraction recoveries were generally achieved for PFCAs with C > 3, but extraction efficiencies were different for the two shortest chained analytes: 36 to 114% of perfluoropropanoate (PFPrA) and 14 to 99% of trifluoroacetate (TFA) were recovered with Strata X-AW, while 93 to 103% of PFPrA and 40 to 103% of TFA were recovered with Oasis WAX. The sample pH was identified as a key parameter in the extraction process. One-step elution-filtration was introduced in the workflow, in order to remove sorbent particles and minimise sample preparation steps. Validation resulted in limits of quantification for all PFCAs between 0.6 and 26 ng/L. Precision was between 0.7 and 15% and mean recoveries ranged from 83 to 107%. In groundwater samples from sites impacted by per- and polyfluoroalkyl substances (PFASs), PFCA concentrations ranged from 0.056 to 2.2 µg/L. TFA and perfluorooctanoate were the predominant analytes. TFA, however, revealed a more ubiquitous occurrence and was found in concentrations between 0.045 and 17 µg/L in drinking water, groundwater and surface water, which were not impacted by PFASs.

Keywords Trifluoroacetate (TFA) · PFAS · PFCA · Water analysis · Solid-phase extraction · Liquid chromatography-tandem mass spectrometry · Water pollution · Water quality

Introduction

Perfluoroalkyl carboxylic acids (PFCAs) and their salts represent a special class of chemicals within the group of per- and

polyfluoroalkyl substances (PFASs), because they have not only been directly used in technical products (Kissa 2001) but they have also been identified to be dead-end products of fluorotelomer (FT) precursor degradation in the environment (Lee and Mabury 2014). Due to unique features, such as high thermal and chemical stability or the ability to repel both water and oil, PFASs are used in numerous industrial and domestic applications e.g. in coatings for paper, leather or textiles or as surfactants in fire-fighting foams, cleaning agents and paints (Kissa 2001; Trier et al. 2011; Dinglasan-Panlilio and Mabury 2006; Place and Field 2012). Thus, their widespread use has opened various direct and indirect pathways into the environment for these chemicals, and, in consequence, they have been detected in many environmental compartments (Lee and Mabury 2014; Ahrens 2011; Gawor et al. 2014) and organisms (Giesy and Kannan 2001; Houde et al. 2011). Due to its persistence, toxicity and bioaccumulation

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potential, perfluorooctanesulfonate (PFOS) and its derivatives have been widely banned in Europe (Commission of the European Communities 2006). Further administrative and voluntary efforts have been made to reduce or even eliminate other long-chained PFASs from emissions and products (United Nations Environment Programme 2010; US EPA 2006), resulting in increased importance of alternatives like polyfluorinated compounds (e.g. FT substances and polyethers) (Wang et al. 2013).

These substitutes are characterised by fluorinated molecular substructures with shorter fluorinated carbon-backbones than legacy products and are classified—including their potential degradation products—as less bioaccumulative and less toxic compared to long-chained PFASs (Stahl et al. 2011; Ding and Peijnenburg 2013). If released into the environment, FT-based substances are subject to degradation processes, leading to PFCAs with shorter carbon chains than the original molecules (Lee and Mabury 2014). Most analytical methods for PFCAs target analytes with a minimal carbon chain length of four (i.e. perfluorobutanoate, PFBA) (Ahrens 2011; Villagrasa et al. 2006, Jahnke and Berger 2009, Deutsches Institut für Normung e.V (DIN) 2011). However, considering the trend to smaller fluorinated building blocks in modern PFAS products, environmental degradation may lead to even shorter PFCAs with C₃ (perfluoropropanoate, PFPrA) or C₂ chains (trifluoroacetate, TFA). In this context, TFA is a special PFCA, since it has been shown to emerge also from other potential precursors like hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) (Solomon et al. 2016). Other compounds containing trifluoromethyl groups, like pesticides or pharmaceuticals, can also be considered as potential TFA precursors. For instance, TFA is specified as a key metabolite of the herbicide Flurtamone (Lewis et al. 2016).

Although many physicochemical properties of PFASs are still discussed controversially (Ding and Peijnenburg 2013), there is broad consensus that many intrinsic properties of PFCAs, like dissociation constants, aqueous solubility or partitioning behaviour, are closely related to their chain length. Hence, in several studies, short-chained PFCAs (C < 7) were mainly detected in the aqueous phase, while their longer-chained homologues (C₇–C₁₁) showed an increasing tendency to adsorb to solids like suspended particulate matter (Ahrens et al. 2010), soil (Gellrich et al. 2012) or sediments (Vierke et al. 2014). This underlines the higher mobility of the short-chained homologues in water. The increasing occurrence of short-chained PFASs in the aquatic environment (Ahrens et al. 2010; Gellrich et al. 2012; Chen et al. 2016) also supports that the hydrosphere is the major sink for these polar, persistent contaminants and emphasises the need for a method for simultaneous analysis of all water-relevant PFCAs, including TFA and PFPrA.

A gas chromatography-mass spectrometry (GC-MS) method for PFCAs (C₂–C₁₀) in rain and surface water achieved

detection limits of 0.5 ng/L and used rotary evaporation of the original sample, liquid-liquid extraction with ethyl acetate, derivatisation with difluoroaniline and clean-up on activated silica gel (Scott et al. 2006). Major PFCAs in Lake Ontario samples were TFA with 100 ng/L and PFBA (> 5 ng/L). TFA concentrations in environmental samples were generally approx. 10 times higher than the other PFCAs.

Numerous analytical methods have been published, in which high performance liquid chromatography (HPLC) has been utilised for the separation of PFASs on reversed phases (RPs) (Trier et al. 2011; Skutlarek et al. 2006; Villagrasa et al. 2006; Jahnke and Berger 2009). Most of such studies targeted PFBA and larger molecules with non-polar molecular parts, which enable retention on RPs. Due to its shorter alkyl chain length, the ability of TFA for non-polar interactions is much weaker. A liquid chromatography-tandem mass spectrometry (LC-MS/MS) method for TFA and other short- and long-chain PFASs in rain water achieved limits of quantification (LOQs) between 0.5 ng/L (e.g. TFA) and 0.1 ng/L (e.g. C₃–C₁₆ PFCAs) (Taniyasu et al. 2008). Solid-phase extraction (SPE) on a weak anion exchanger (WAX), HPLC separation on a mixed-mode ion-exchange column and tandem mass spectrometry were applied. From LC separation experiments with RP columns, the authors concluded that C₁₈ columns are not suitable for the analysis of short-chain PFCAs. In rain water samples of two cities in Japan, the dominating short-chain PFCAs were TFA and PFPrA at 76 and 10 ng/L, respectively (Taniyasu et al. 2008). However, further studies using this LC-MS/MS method for aqueous samples with different matrices (e.g. marine water (Ahrens et al. 2010), river water (Chen et al. 2016), groundwater (Chen et al. 2016), tap water (Mak et al. 2009) and waste water (Zhang et al. 2013)) did not include TFA and only in one case (tap water) considered PFPrA.

Most reports of TFA concentrations in groundwater have been published more than 15 years ago e.g. up to 0.32 µg/L was reported in a study investigating spring water samples of different ages (Jordan and Frank 1999). Scott and Mehran estimated the TFA concentration of a groundwater sample taken southwest of Toronto to be 0.18 µg/L (Scott and Mehran 1998). In a recent study from China, current TFA levels in environmental waters were compared with concentrations, which have been determined 10 years earlier with samples taken from the same sampling sites. The authors reported TFA levels elevated by a factor of up to 17 (Zhai et al. 2015); median concentrations in the current samples were 643, 155 and 282 ng/L in surface water, tap water and snow, respectively. TFA levels in river water samples from Europe, South Africa, Russia and Brazil have been reported to range between < 15 and 630 ng/L (Jordan and Frank 1999).

Background contamination of groundwater with PFASs due to diffuse inputs usually provokes low concentrations (e.g. < 50 ng/L for Σ PFAS), whereas point sources can cause considerably higher concentrations in the microgram per litre

scale. For instance, industrial emission and subsequent infiltration of contaminated surface water into an aquifer used for drinking water production in Bavaria, Germany, led to PFOA levels of up to 4.3 $\mu\text{g/L}$ in 2006 (Eschauzier et al. 2012). Fire-fighting training sites, where aqueous film-forming foams (AFFF) had been used, have also been identified as potential PFAS hot spots impacting groundwater reservoirs (Backe et al. 2013; Alder and Voet 2015; Hu et al. 2016). Samples from a drinking water catchment close to a fire brigade's training area near Cologne, Germany, contained concentrations of up to 4.0 $\mu\text{g/L}$ (Σ PFAS) with PFOS being the predominant (> 80%) and PFCAs the minor components (< 5%) (Eschauzier et al. 2012). Other potential PFAS point sources include wastewater treatment plants, landfill leachate firefighting training sites and the agricultural use of contaminated materials like biosolids or ameliorant (Skutlarek et al. 2006; Alder and Voet 2015; Hu et al. 2016).

The aim of this study was to establish and validate a robust analysis method for short-chain PFCAs ($\text{C}_2\text{-C}_8$) in different types of aqueous samples. We started with the method of Taniyasu et al. (2008) and optimised sample extraction by SPE as well as LC separation. Finally, we applied the analytical method to aqueous samples from surface water, groundwater and drinking water with a focus on the occurrence of TFA compared to other PFCAs ($\text{C}_3\text{-C}_8$). To our knowledge, this is the first study simultaneously investigating the PFCAs with $\text{C}_2\text{-C}_8$ in these matrices.

Materials and methods

Details about the chemicals and materials used in this study are given in the electronic supporting material (ESM, section 1).

Samples

Water samples for validation purposes were taken from the in-house water supply (tap water), from a well in Karlsruhe (groundwater), from the Rhine river close to Karlsruhe (surface water) and bought at a supermarket (natural spring water), respectively. Surface water and groundwater samples were taken by TZW staff using amber glass bottles and were collected from the rivers Rhine (Lower Rhine, Middle Rhine, Upper Rhine), Danube, Neckar and Dreisam, from Lake Constance and its tributaries and from groundwater sampling sites in northern, central and southern Baden-Württemberg. Tap water samples were collected either in amber glass bottles or polypropylene bottles and were collected from private and public taps in northern and central Baden-Württemberg. Glass bottles were cleaned successively by rinsing with methanol (MeOH) and demineralised water and by pyrolysis at 550 °C (Carbolite LHT 6/120, Hope, UK). Polypropylene

bottles were rinsed with MeOH and demineralised water. Samples were stored at 4 °C up to a maximum of 3 weeks before analysis.

Sample preparation

The optimisation of SPE recoveries involved an evaluation of two extraction sorbents (Oasis WAX (Waters, Eschborn, Germany) and Strata X-AW (Phenomenex, Aschaffenburg, Germany)) at different sample pH levels (3.0, 4.0, 5.0 and 6.0). For each combination of SPE material and pH level, natural spring water samples were spiked in triplicate (100 ng/L), adjusted to a specific pH level with hydrochloric acid (HCl) and sodium hydroxide (NaOH) and extracted with each sorbent. Preconditioning of SPE cartridges, elution, drying and solvent-exchange was performed as described below. Absolute extraction recoveries were quantified using matrix-matched calibrations (one blank, five concentration levels), prepared from blanks (same spring water, pH level and SPE sorbent as the corresponding recovery samples), which were spiked after the extraction procedure.

The optimised SPE method was used for the analysis of surface water, groundwater and drinking water: 50 mL of a water sample were given into a 100-mL flask (amber glass, conical shoulder, wide mouth). After addition of internal standards (12.5 ng of isotopically labelled TFA (TFA-M1) and 2 ng of each other isotopically labelled PFCA) and 0.25 mL MeOH to the sample, the pH was adjusted to 3.9 ± 0.1 using solutions of HCl (5%, 0.5%) and NaOH (0.6 mM). SPE cartridges (Oasis WAX, 6 mL, 150 mg) were placed on a vacuum manifold (VacMaster 20, Biotage, Sweden) and preconditioned with 2×3.0 mL of 0.2% ammonium hydroxide (NH_4OH) in MeOH (v/v), 3.0 mL MeOH and 3.0 mL ultrapure water ($\text{H}_2\text{O}_{\text{mQ}}$) adjusted to $\text{pH } 3.0 \pm 0.1$ with HCl. After connecting 60 mL polyethylene reservoirs (Supelco, Bellefonte, USA) onto the cartridges, the sorbents were loaded with samples (ca. 1.0–1.5 mL/min flow rate). The sorbents were dried in a gentle stream of nitrogen. Before elution of the analytes, the SPE cartridges were connected to regenerated cellulose syringe filters (Chromafil Xtra RC-45/13; 0.45 μm , Macherey-Nagel, Düren, Germany) and placed on a vacuum manifold, which did not contain any fluoropolymer parts (Chromabond, Macherey-Nagel, Düren, Germany). Elution of the SPE material was done with 2×3.0 mL of 0.2% NH_4OH in MeOH (v/v) and residual solvent was drawn out of the SPE cartridge by vacuum of a water jet pump. The eluates were collected in 20-mL glass vials and blown down to dryness under a gentle stream of nitrogen at 33 to 34 °C in a heating block (Techne DB-3). The residues were dissolved in 0.4 mL of $\text{H}_2\text{O}_{\text{mQ}}$ /MeOH solution (7:3, v/v) and transferred into 1.1 mL conical crimp glass vials for further analysis.

Liquid chromatography-mass spectrometry

All analyses were performed using an LC-MS/MS system consisting of a model 1260 Infinity HPLC instrument (Agilent Technologies, Waldbronn) coupled to a model API 5000 triple-quadrupole mass spectrometer (AB Sciex, Darmstadt) via a two-position diverter valve (Valco Instruments). The MS was equipped with a Turbo V electrospray ionisation (ESI) source.

Chromatographic separation was carried out using a Kinetex C₁₈ column (100 × 3 mm, 2.6 μm, 100 Å; Phenomenex, Aschaffenburg, Germany) equipped with a 3-mm SecurityGuard Ultra precolumn (Phenomenex, Aschaffenburg, Germany). For the final method, a binary gradient (eluent A: 2 mM ammonium formate and 0.2% formic acid in H₂O_{mQ}/MeOH (4:1, v/v), eluent B: 2 mM ammonium formate in MeOH) was applied at a flow rate of 0.25 mL/min and the following time programme: 1-min pre-injection equilibration time (87.5% eluent A). After injection, eluent A was kept at 87.5% for 2 min following a decrease over 3 min to 25%, and further decrease to 2.5% within 6 min. 2.5% eluent A was held for 4 min, before switching back to the initial eluent ratio and holding it for 5 min. The column effluent was directed to the MS detector between 1.0 and 14 min of the time programme.

Additional LC separation experiments were performed with an Obelisc N column (150 × 2.1 mm, 100 Å, 5 μm; SIELC Technologies, Wheeling, USA) including an Obelisc N guard column. According to manufacturer information, Obelisc N is zwitterionic and combines retention mechanisms of ion (IC), hydrophilic interaction (HILIC) and normal-phase chromatography. The final IC/HILIC separation included a binary gradient (eluent A: 2.5 mM ammonium acetate and 0.3% acetic acid in H₂O_{mQ}/ACN (3:2, v/v), eluent B: 20 mM ammonium acetate in H₂O_{mQ}/acetonitrile (ACN; 1:9, v/v)) at a flow rate of 0.7 mL/min. The time programme started with 95% eluent A for 3-min pre-injection equilibration. After injection, eluent A was kept at 95% for 1 min then decreased to 90% over 1 min. From 2 to 15 min, eluent A was further decreased to 55% and then over 2 min to 5%, which were kept constant for 6 min. After that, eluent A was raised to 95% and held 5 min for equilibration. The diverter valve directed the effluent to the MS detector between 0.5 and 16 min of the time programme. Further details about method development and experiences with the Obelisc N column are given in the ESM (section 2c).

For both LC methods, an injection volume of 10 μL was used, the oven temperature was held at 35 °C and MS interface parameters were set as follows: curtain gas 25 psi, collision gas 5 psi, interface temperature 500 °C, nebulizing gas 60 psi, heater gas 75 psi and ion-spray voltage – 4500 V. The MS was operated in scheduled MRM mode in order to record at least 12 data points across the chromatographic peaks with MRM

detection windows set to 90 s. The compound-specific MS parameters, which were used in the acquisition methods, are summarised in the ESM (Tab. S 1).

Validation and quality control

In quantitative analysis, common strategies for the compensation of matrix effects are matrix-matched calibration and the use of isotopically labelled standards. In this study, both strategies were applied. For each analyte, except for PFPrA, a corresponding isotopically labelled standard was used. PFPrA was quantified using the isotopically labelled PFBA (PFBA-M4) as internal standard. Since groundwater and surface water were expected to contain considerable amounts of TFA, natural spring water was used as calibration matrix (background contamination ≈ decision limit (LOD)). For this purpose, natural spring water samples were spiked and prepared according to the described method. For each analyte, two overlapping calibration functions with at least five points were used: in a low (TFA: 10 to 250 ng/L, other analytes: 1 to 150 ng/L) and a high concentration range (TFA: 200 to 1500 ng/L, other analytes: 100 to 1500 ng/L).

The working ranges for the analytes were estimated by direct injections of calibration standards prepared in H₂O_{mQ}/MeOH solution (7:3, v/v). However, due to observed matrix effects, the ‘total method’ working ranges, linearity and analytical limits were determined using calibration standards prepared in spring water matrix; spring water aliquots were spiked at different analyte levels and the whole sample preparation procedure was applied. Linearity was evaluated applying least squares regression on ten equidistant concentration levels spanning the whole working range. The determination of LODs and LOQs was according to DIN 32645 using ten calibration standards (also equidistant levels) in the lower working range (1.0 to 200 ng/L for TFA, 0.1 to 20 ng/L for other analytes). After linear regression, LOD and LOQ were deviated considering the residual standard deviation, method standard deviation and confidence levels of 95%. The analyte signals were used without blank correction in these calculations.

In the analysis of environmental samples, each series of 12 samples contained one procedural blank (demineralised water) for detection of blank contamination and at least one spiked spring water, tap water, groundwater or surface water sample for recovery measurements (control sample). Procedural blanks and recovery control samples were treated like real samples. The instrumental performance was monitored by repeated injections (after every series of 12 samples) of another control sample and was considered acceptable as long as the deviation was less than 10% relative standard deviation (RSD).

Matrix effects were determined by preparation of a series of six “blank” samples of each matrix, five of which were spiked

after the elution step with equidistant ($\Delta = 100$ ng/L) concentration levels. The resulting calibration curves were used for the calculation of relative matrix effects based on slope ratios (Matuszewski et al. 2003) relative to a calibration curve with the same spiked concentration levels prepared in demineralised water.

Depending on their chain lengths and functional groups, PFASs dissolved in aqueous liquids have varying degrees of tendency to adsorb onto vessel walls e.g. glass or polypropylene (Berger et al. 2011). Impairment by such effects was not observed for the investigated analytes under the conditions described above.

SQS software was used for evaluation of LOD and LOQ (SQS2010 1.3, 2010, J. Kleiner). Marvin was used for drawing, displaying and characterising chemical structures (Marvin 15.1.12, 2015, ChemAxon). Igor Pro was used for preparation of graphs (Igor 6.37, 2015, WaveMetrics).

Results and discussion

Solid-phase extraction

Two different polymer-based, WAX materials (Strata X-AW and Oasis WAX) were evaluated for extraction of the seven PFCAs from water samples. Both materials offer non-polar and ionic interactions with primary and secondary alkylamine groups (Strata X-AW) or an *N*-arylpiperazine moiety (Oasis WAX). The partial structures of the sorbent materials and calculated pK_a values of the functional groups are shown in the ESM (section 3a). Since pH is a crucial parameter for ion-exchange interactions, SPE recoveries for both materials were tested with spiked spring water samples at pH 3.0, 4.0, 5.0 and 6.0 at a level of 100 ng/L for each PFCa. The absolute extraction recoveries were quantified by eight individual matrix-matched (same water, pH level and SPE material) calibrations in order to exclude matrix effects on the analyte quantification during this experiment. The results are shown in Fig. 1.

The RSD was below 10% ($n=3$) in all cases. For Strata X-AW, the absolute extraction recoveries ranged between 14 and 133% and for Oasis WAX between 40 and 106%. The recoveries of C_4 to C_8 PFCAs were almost independent of the sample pH and between 76 and 133% for both SPE materials. However, the extraction efficiencies for TFA and PFPrA were substantially dependent on the sample pH. Recoveries of PFPrA using Oasis WAX were between 93 and 103% for all pH values, while recoveries achieved with Strata X-AW were acceptable in the pH range between 3.0 and 5.0 (94 to 114%), but decreased to only 36% at pH 6.0. Considering the recoveries for TFA, the effect of sample pH on the SPE process is most evident: With Oasis WAX quantitative extraction recoveries were achieved between pH 3.0 to 5.0 (95 to 103%), but only 40% was recovered at pH 6.0. With Strata X-AW, 99% of

TFA was recovered at pH 3.0, but at higher sample pH levels, decreased extraction recoveries were observed: 80% at pH 4.0, 50% at pH 5.0 and 14% at pH 6.0. This behaviour can be explained by the predominance of ionic interactions compared to non-polar interactions for TFA and PFPrA with the SPE materials. Since the pK_{as} of TFA, PFPrA and all other PFCAs are still below 3.0—the lowest pH value used for extraction—they are still extracted in their anionic form. Low pH values, however, help to protonate the functional groups of the sorbents and, most importantly, reduce competition effects with bicarbonate anions. At pH 4.3, about 99% of bicarbonate anions are neutralised to carbonic acid (according to its label, the natural spring water used has 248 mg/L bicarbonate). Other competing anions like sulphate or chloride will not be eliminated at pH levels between 3.0 and 6.0. The preconcentration of these anions is shown in Table 1 (details ESM, section 3b).

In favour of method robustness and quantitative recovery of PFCAs, we selected Oasis WAX as SPE material for the final method and adjusted samples to a pH between 3.8 and 4.0 before extraction.

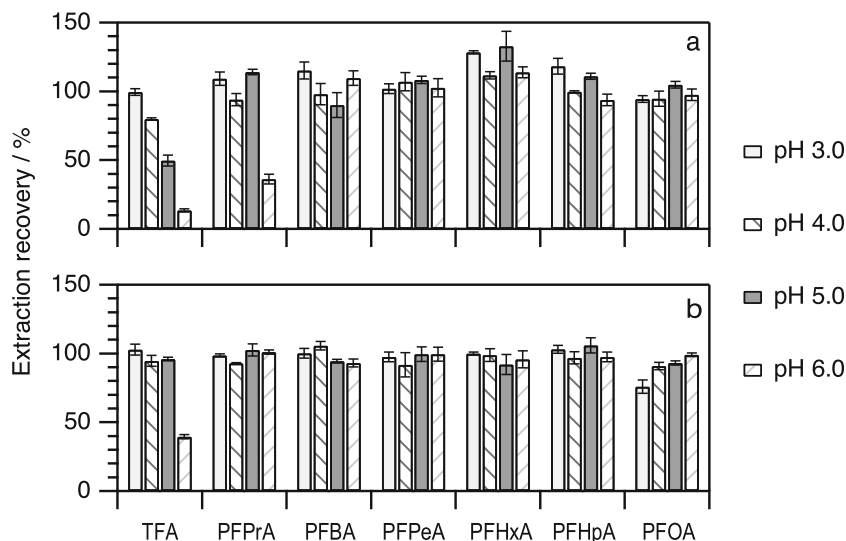
Characterisation of particles in eluates

SPE with Oasis WAX cartridges led to considerable amounts of particles in the eluates, which was a minor but remarkable observation. First, it was assumed that these were precipitated salts, which were insoluble in the ammonia-methanol solution used for elution. This hypothesis was rejected, because the dried residues could not be entirely resolved in $H_2O_{mQ}/MeOH$ (7:3, v/v) and the particles also appeared, when demineralised water was used as sample matrix. As described in the ESM (section 3c), Raman microspectroscopy revealed that the particles were identical with the sorbent material in the cartridges. WAX material present in a solvent with high water content can negatively affect the recoveries of PFCAs due to adsorption processes i.e. the time period, during which elution and particle separation steps are conducted, affects the reproducibility of the analyses. Aiming for reduced effort during sample preparation, syringe filters (regenerated cellulose) were attached to the cartridges before elution. Hence, particles mobilised during this preparation step were separated immediately, preventing additional adsorption processes. Subsequent filtration or centrifugation was not necessary.

Liquid chromatography-tandem mass spectrometry

To cope with the rather polar character of the short-chained PFCAs, we evaluated a mixed-mode phase offering both, ion exchange and HILIC (Obelisc N), and a core-shell RP column (Kinetex C_{18}) for chromatographic separation. As demonstrated in Fig. S 4 of the ESM, a chromatographic separation of the investigated PFCAs in pure water could be achieved using a

Fig. 1 Extraction recoveries of the analytes at four sample pH levels using two different SPE materials: Strata X-AW (a) and Oasis WAX (b). Error bars indicate the standard deviation ($n = 3$)



binary gradient on the Obelisc N column. However, the separation was seriously disturbed by co-extracted matrix of environmental samples (Fig. S 5). Therefore, we used the Kinetex C₁₈ column for PFCA separation in the further course of the study. The RP phase provided a more robust separation i.e. it did not exhibit such matrix effects on retention times as were observed with Obelisc N. In RP separations of PFASs with a chain length of $\geq C_4$ usually neutral eluents are used, which is not suitable to retain very polar PFCAs. However, the retention of TFA, PFPrA and PFBA could be increased substantially on the Kinetex C₁₈ column, when the eluents were acidified with formic acid (ESM, Fig. S 1)—an unexpected effect comparing the low pK_a of TFA (0.3) (O’Neil 2013) to typical pH ranges of diluted formic acid (ca. 2.7 for a 0.1% solution), which may be attributed to enhanced retardation by the stationary phase due to protonation of residual silanolate groups. A similar effect was observed during the validation study of the DIN 38407-42 method for the analysis of selected PFASs in water samples (NA 119-01-03-02-19 AK PFC in Wasser, Klärschlamm und Boden 2011). Though, in our final method, we added formic acid only to eluent A to improve retention of TFA and PFPrA. In eluent B, formic acid was avoided, since longer-chained PFCAs exhibit sufficient retention due to non-polar interactions and their detection may be

affected by signal suppression due to the presence of formic acid in negative ESI (Mallet et al. 2004). The optimised separation of the analytes on the Kinetex C₁₈ column and the retention times for both LC methods (Obelisc N and the Kinetex C₁₈), as well as the compound-specific MS parameters, which were used in the acquisition methods, are summarised in the ESM (Tab. S 1 and Fig. S 2). For all analytes, the corresponding anions ($[M-H]^-$) were selected as precursor ions. The $[M-COOH]^-$ mass fragments were selected as quantifiers, which is typical for LC-MS methods analysing PFCAs (Villagrasa et al. 2006). For PFBA and higher homologues, a second mass transition was available, optimised and included as qualifier. The small molecules TFA and PFPrA only produced one single mass fragment $[M-COOH]^-$.

Method validation

LODs, LOQs and working ranges were determined for the individual PFCAs, as well as matrix effects, precision and mean recoveries in four different water matrices. Table 2 summarises LODs and LOQs determined according to DIN 32645 for demineralised water and spring water together with reporting limits (RL), working ranges and linearity values, expressed as coefficients of determination. The RL were set considering the LOQ and precision data.

LODs and LOQs of PFBA and higher homologues are similar in both matrices, ranging from 0.1 to 1.0 ng/L (LOD) and from 0.6 to 4.6 ng/L (LOQ), respectively. Elevated baselines for TFA and PFPrA resulted in lower signal-to-noise ratios and caused higher LODs and LOQs compared to the other PFCAs. A further factor to be considered is the isotopically labelled TFA-M1, as discussed in detail in the ESM (section 4). TFA traces in the TFA-M1 standard contribute to the TFA signal in the range of 1 to 2%. On the other side, the

Table 1 Concentrations of inorganic anions in a synthetic water sample, in permeate, and concentrate after application of the optimised SPE procedure

Sample	Concentrations/(mg/L)	
	SO ₄ ²⁻	Cl ⁻
Original water sample	112	253
SPE permeate	63	226
SPE concentrate	730	607

Table 2 Method performance parameters: LOD and LOQ determined according to DIN 32645, reporting limit, working range and linearity

Compound	Demineralised water		Natural spring water		RL / (ng/L)	Working range / (ng/L)	Linearity
	LOD / (ng/L)	LOQ / (ng/L)	LOD / (ng/L)	LOQ / (ng/L)			
TFA	3.3	15	5.5	26	30	10–1500	0.998
PFPrA	1.0	4.6	0.9	4.3	5.0	1–1500	0.998
PFBA	0.2	1.0	0.2	1.0	1.0	1–1500	0.998
PFPeA	0.2	1.0	0.1	0.6	1.0	1–1500	0.998
PFHxA	0.1	0.7	0.2	0.8	1.0	1–1500	0.999
PFHpA	0.6	2.7	0.4	1.8	3.0	1–1500	0.992
PFOA	0.3	1.5	0.5	2.5	3.0	1–1500	0.998

LOD decision limit, LOQ Limit of quantification, RL reporting limit

naturally occurring ^{13}C isotope of TFA contributes to the TFA-M1 signal with 1.1%. The interdependent influences of native TFA and TFA-M1 on the respective mass traces were found to be acceptable with regard to the lower limits of native TFA calibration and the spiked concentration of TFA-M1 (0.25 ng/L). Background contamination of the used spring water also contributes to a higher LOQ of TFA in this matrix compared to demineralised water. However, the TFA concentration in the spring water was < LOQ (estimated to be approx. 6 ng/L using an extrapolated calibration curve in the lower working range). Linear regression of the method calibration resulted in acceptable linearity values above 0.99.

Matrix effects in different types of water were examined by comparing the slopes of respective calibration curves, which were prepared by spiking five SPE extracts at equidistant concentration levels using intervals of 100 ng/L. This concentration interval was found to be appropriate for distinguishing the added substance from the background concentration and at the same time not exceeding the linear range (max. 1500 ng/L). Figure 2 illustrates the matrix effects on the analyte signals occurring in extracts of natural spring water, tap water,

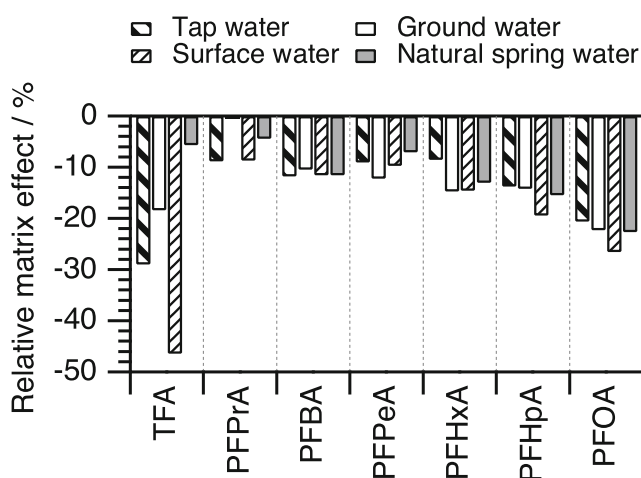


Fig. 2 Matrix effects in four different water types relative to the analyte signals in solvent

groundwater and surface water relative to the signals in pure solvent.

For all PFCAs considered in this study, co-extracted matrix causes signal suppression, the lowest for PFPrA in groundwater (0.2%) and the highest for TFA in surface water (46%). Comparing the signal suppression for the individual analytes, it is striking that PFPrA and longer-chain PFCAs show variations between the different matrices below 9%, while the variation is 41% for TFA. This indicates substantial differences in the amounts of polar, early eluting matrix components co-extracted from the investigated water types. An adequate internal standard is, therefore, essential for a reliable quantification of TFA i.e. for correction of matrix effects and recoveries. For PFPrA, we selected PFBA-M4 as an internal standard for PFPrA, because the variation of matrix effects of PFPrA was similar to that of PFBA, compared to that of the closer eluting TFA.

Precision and bias in tap water, groundwater and surface water were studied in repeatability and intermediate reproducibility experiments. *Repeatability* was determined using five aliquots of a sample (per matrix), which were spiked at the same concentration levels and prepared the same day. For determination of *intermediate reproducibility* (within-laboratory reproducibility), several variations were considered: Different days of sample preparation, different spiking levels and different real samples, which were used for spiking. The results are summarised in Table 3, expressed in mean recovery and RSD.

Repeatability experiments resulted in mean recoveries ranging from 83 to 104% and precisions between 0.7 and 6.2% RSD for the analytes in the different water matrices. The mean recoveries resulting from the intermediate reproducibility experiments range between 87 and 107% and the precisions range between 1.2 and 15% RSD. The data used for calculation of the intermediate reproducibility in Table 3 were used together with results from corresponding spiking experiments in

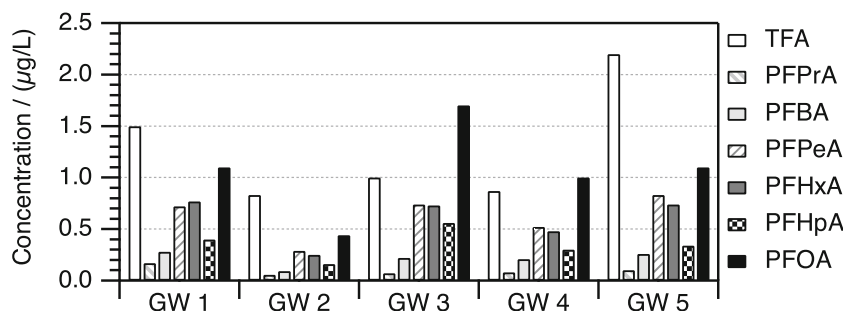
Table 3 Repeatability and intermediate reproducibility expressed as mean recovery and RSD for three different matrices: tap water (TW), groundwater (GW) and surface water (SW); *n* = 5

Analyte	TW (Recovery ± RSD)/%	GW	SW
Repeatability			
TFA	97 ± 0.7	99 ± 4.4	101 ± 1.4
PFPrA	95 ± 2.3	83 ± 2.1	104 ± 4.5
PFBA	92 ± 1.2	93 ± 1.0	100 ± 3.5
PFPeA	93 ± 1.7	102 ± 2.7	85 ± 3.9
PFHxA	93 ± 2.4	96 ± 3.6	98 ± 3.6
PFHpA	93 ± 6.2	92 ± 3.2	99 ± 4.7
PFOA	91 ± 3.6	94 ± 3.8	99 ± 2.5
Intermediate reproducibility			
TFA	98 ± 2.9	99 ± 4.9	97 ± 10
PFPrA	98 ± 5.9	95 ± 8.8	107 ± 15
PFBA	93 ± 1.2	93 ± 1.2	94 ± 2.5
PFPeA	87 ± 9.6	92 ± 8.2	96 ± 5.8
PFHxA	94 ± 2.8	91 ± 3.9	94 ± 4.7
PFHpA	92 ± 4.1	92 ± 4.5	92 ± 10
PFOA	93 ± 4.0	92 ± 2.5	89 ± 2.9

spring water (data not shown) to estimate the measurement uncertainty across all investigated matrices. The resulting measurement uncertainties for the individual analytes, expressed as relative expanded uncertainties (U_{rel}) calculated with a coverage factor of $k=2$, are as follows: 21% (TFA), 36% (PFPrA), 17% (PFBA), 28% (PFPeA), 26% (PFHxA), 28% (PFHpA) and 20% (PFOA).

Procedural blanks were prepared from spring water with each series of environmental samples in order to monitor for blank contamination. For PFPrA and other analytes, this measure was qualitative. For TFA, however, there was a systematically occurring signal (below LOQ) in each blank due to the spring water matrix and the internal standard. This signal was integrated and monitored but no actions due to blank contamination were required during the period in which the analyses were carried out. The overall method performance was found suitable for the analysis of environmental samples.

Fig. 3 Concentrations of PFCAs in five contaminated groundwater samples



Analyses of aqueous samples

Groundwater samples were taken at five polluted sampling sites in the state of Baden-Württemberg, Germany. All seven PFCAs have been found in these samples and range from 0.056 µg/L (PFPrA in GW 2) to 2.2 µg/L (TFA in GW 1), with TFA and PFOA being the predominant analytes (Fig. 3). Samples with analyte concentrations above the indicated working ranges were reanalysed in dilution.

Interestingly, the distribution patterns of the seven PFCAs in the samples are similar, which is an argument for similar input sources. The contamination sources at the sampled sites are not entirely elucidated, but further investigations have revealed that paper chemicals play a major role (data not shown). The concentration levels are generally higher than reported for background contamination due to diffuse sources (e.g. 0.18 µg/L of TFA or < 50 ng/L Σ PFAS in groundwater (Scott and Mehran 1998; Eschauzier et al. 2012)) and therefore point sources have to be taken into consideration. The distribution patterns of the PFCAs with C_4 to C_8 shown in Fig. 3 are similar to patterns found in groundwater samples, which were presumably contaminated with FT-based surfactants from AFFF (Backe et al. 2013). The decomposition of FT compounds ultimately leads to formation of PFCAs in a way, that an $x:2$ FT precursor with x being the number of perfluorinated C-atoms can yield PFCAs with C_{x+1} , C_x , C_{x-1} and C_{x-2} (Lee and Mabury 2014). Assuming that the contamination of our investigated groundwater samples is also related to the degradation of FT compounds, the distribution patterns shown in Fig. 3 have possibly been caused by a mixture of precursors with 8:2 FT, 6:2 FT and—due to the presence of PFPrA—4:2 FT substructures. With respect to the transformation pathways, TFA can be derived from 4:2 FT precursors, though, considering the present PFPrA levels, TFA concentrations resulting from the degradation of PFASs would be expected to be lower than the measured concentrations. Mean values of the PFCAs concentrations normalised to PFOA and the corresponding standard deviations were calculated, as is depicted in Fig. 4.

The considerably higher spread of TFA concentrations (53% RSD) compared to PFBA and its higher homologues ($\leq 24\%$) may indicate another TFA source like from

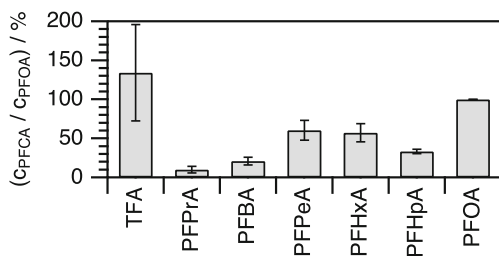


Fig. 4 Mean values and standard deviations of PFOA-normalised concentrations of the contaminated groundwater samples

atmospheric deposition. Thus, a contribution to the measured TFA levels resulting from the degradation of PFASs can neither be concluded nor excluded, yet.

Regarding the concentrations of organically bound fluorine corresponding to the analysed PFCAs in the individual groundwater samples, the sums of the organofluorine fractions of TFA and PFPrA account for 17 to 35% compared to the sums of the organofluorine of all seven PFCAs. Thus, analysis of TFA and PFPrA (in addition to other PFASs) may partially fill the gap uncovered by analyses of ‘extractable organic fluorine’ (EOF) in water samples (Miyake et al. 2007).

Due to the surprisingly high levels of TFA in the PFAS-impacted groundwater, further water samples (tap water, groundwater, surface water) with no known PFAS contamination were analysed. In these samples, PFCAs other than TFA were typically below LOQ with a few exceptions—maximum concentrations of these analytes were 0.011 $\mu\text{g/L}$ of PFPrA in tap water, 0.023 $\mu\text{g/L}$ of PFOA in groundwater, and 0.012 $\mu\text{g/L}$ of PFPeA in surface water. The measured TFA levels are displayed in Fig. 5. Since the results (arranged in groups according to water types) were not normally distributed, outliers were identified applying the Hampel test.

Fifty percent of the investigated surface waters—mostly rivers—contained TFA between 0.48 and 1.2 $\mu\text{g/L}$, which is in the same order of magnitude, as recently reported for

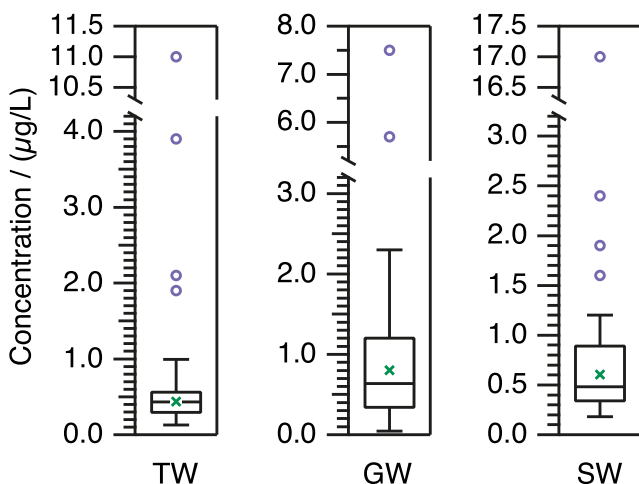


Fig. 5 TFA concentrations in tap- (TW, $n=21$), ground- (GW, $n=42$) and surface water (SW, $n=43$) samples. Outliers are marked as circles

Chinese surface water samples (Zhai et al. 2015). In contrast, the upper 50% of concentrations in tap water (0.43–0.99 $\mu\text{g/L}$) and groundwater (0.64–2.3 $\mu\text{g/L}$) were considerably higher than the concentrations reported earlier (Jordan and Frank 1999, Scott and Mehran 1998; Zhai et al. 2015). Individual samples exhibited even higher microgram per litre levels e.g. 11 $\mu\text{g/L}$ in tap water, 7.5 $\mu\text{g/L}$ in groundwater and 17 $\mu\text{g/L}$ in surface water, which is remarkable and initiated investigations beyond this study, in which industrial discharges of TFA into the Neckar river have been identified as the cause for the unusually high concentrations (Scheurer et al. 2017).

Conclusions

An LC-MS/MS method for the simultaneous determination of seven short to median chain-length PFCAs, including TFA and PFPrA, in water samples is presented. Method development involved evaluation of two SPE sorbents and two stationary phases for liquid chromatography. A robust method was achieved using Oasis WAX material and a sample pH of 3.9 ± 0.1 for SPE, one-step elution-filtration and a core shell C_{18} -column with an acidified eluent for LC separation. Quantification of environmental samples was based on matrix-matched calibration and isotopically labelled standards, since ion-suppression effects were apparent. Particularly in the case of TFA, the use of an isotopically labelled standard was indispensable for reliable quantification. Method validation provided satisfactory working ranges as well as precision and recovery values in the environmental water types in scope of this study. Groundwater analyses with samples from PFAS-contaminated sites have revealed that TFA and PFPrA were present in addition to the commonly investigated PFCAs and can account for a large proportion of the organically bound fluorine in an aqueous sample. Additional analyses of samples from sites, where PFASs were found to have only subordinate impact—if any—resulted in $\mu\text{g/L}$ concentrations of TFA in tap water, groundwater and surface water. TFA and PFPrA are relevant contaminants of the hydrosphere and should not be neglected in analyses of PFCAs. Still, the contribution of degradation of PFCA precursors in the environment to the presence of PFPrA and TFA needs to be investigated. Further studies should clarify if the increase of TFA in environmental waters compared to earlier analyses can be attributed solely to the use of HFCs/HCFs or if other sources have to be taken into account e.g. waste incineration or the use of pesticides and pharmaceuticals with trifluoromethyl-containing active substances. Regarding the $\mu\text{g/L}$ levels of TFA in drinking water, toxicological effects of this polar substance as well as removal options from raw water are topics which need to be addressed.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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