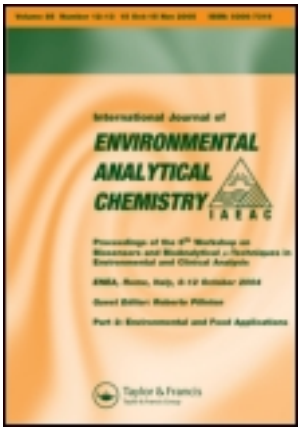


International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

# Method development for analysis of short- and long-chain perfluorinated acids in solid matrices

Fei Li [a], Chaojie Zhang [a], Yan Qu [a], Jing Chen [a], Xiang Hu [a] & Qi Zhou [a]

[a] State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai, China

Available online: 14 Sep 2011

To cite this article: Fei Li, Chaojie Zhang, Yan Qu, Jing Chen, Xiang Hu & Qi Zhou (2011): Method development for analysis of short- and long-chain perfluorinated acids in solid matrices, International Journal of Environmental Analytical Chemistry, 91:12, 1117-1134

To link to this article: http://dx.doi.org/10.1080/03067310903191721

*Intern. J. Environ. Anal. Chem.*
Vol. 91, No. 12, October 2011, 1117–1134

Taylor & Francis
Taylor & Francis Group

# Method development for analysis of short- and long-chain perfluorinated acids in solid matrices

Fei Li, Chaojie Zhang, Yan Qu, Jing Chen, Xiang Hu and Qi Zhou*

*State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai, China*

(*Received 5 March 2009; final version received 22 June 2009*)



In order to help to elucidate the transport and fate of perfluorinated acids (PFAs) in the environment, a reliable and sensitive analytical method has been developed in present study for determination of short- and long-chain PFAs in various solid matrices. The method consisted of solvent extraction of PFAs from solid matrices using sonication, solid phase extraction (SPE) using weak anion exchange (WAX) cartridges, clean-up of SPE eluent with dispersive carbon sorbent and quantitation by high performance liquid chromatography-negative electrospray-tandem mass spectrometry (HPLC-negative ESI-MS/MS). The method detection limits (MDL) and quantitation limits (MQL), which were analyte- and sample-dependent, ranged from 0.02 to 0.06 ng $g^{-1}$ and 0.10 to 0.90 ng $g^{-1}$, respectively. The recoveries of all PFAs were generally good enough for quantitative analysis of these chemicals (57–115%), especially for short-chain (<C8, 80–115%) PFAs excluded in previous studies because methods were not available. The precisions of this method, represented by the percent relative standard deviation (RSD) of spiked measurements, were in a range of 1–19%. In addition, matrix effect did not affect analyte quantification in solid matrices in most cases, and the validated method was successfully applied to analyses of short- and long-chain PFAs in various solid matrices.

**Keywords:** perfluorinated acids; LC-MS/MS; solid matrix; matrix effect

## 1. Introduction

Perfluorinated acids (PFAs) such as perfluorocarboxylates (PFCAs) and perfluoroalkanesulfonates (PFSAs) are a class of compounds with unique physical-chemical properties that have been manufactured for over 50 years. Because the perfluorinated alkyl chain is both hydrophobic and oleophobic [1], PFAs are used in a wide range of industrial, commercial and consumer applications [2]. Meanwhile, PFAs are extremely resistant to hydrolytic, thermal, biological, chemical and photolytic degradation [3]; as a result, PFAs have been widely detected in the environment, even in the Arctic, Antarctic, and other remote areas [4]. Some PFAs exhibit bioaccumulative effects in some organisms and aquatic food webs [5–10] and toxicological effects in laboratory animals [3,11–14]. Due to their widespread occurrence, environmental persistence, and bioaccumulative and toxicological capacity, there is growing concern in the sources, transport and fate of PFAs in the environment [15,16].

*Corresponding author. Email: zhouqi@mail.tongji.edu.cn

ISSN 0306–7319 print/ISSN 1029–0397 online

http://dx.doi.org/10.1080/03067310903191721
http://www.tandfonline.com

Given the important role of solid matrices in the environmental fate of hydrophobic organic contaminants [17], a detailed understanding of the transport and fate of PFAs in the environment must include the elucidation of the sorption of these compounds onto the solid matrices [18] and determination of their pollution levels in the solid matrices. Unfortunately, these studies have been disturbed to a certain degree by lack of analytical methods for determination of PFAs in environmental solid matrices, especially for short-chain PFAs. Therefore, robust analytical methodology for determination of short- and long-chain PFAs in complex and heterogeneous solid matrices is important to better understand their environmental behaviours.

Recently, a reliable and sensitive analytical method for PFAs in solid samples has been developed, but this method is not valid for short-chain PFAs (<C8 PFCAs and <C6 PFSAs, respectively) because of their poor recoveries [19]. The analytical methods for PFCAs reported by other researchers also exclude the PFCAs with carbon chain length less than six [20]. Previous study indicates that the most commonly measured PFAs, including PFOA and PFOS, etc. with longer perfluorocarbon chains, together account only for a small fraction of the extractable organofluorines present in surface water [21] while the concentrations of trifluoroacetic acid (TFA) and several short-chain PFAs are as high as or even much higher than long-chain PFAs in rainwater [22–24]. It is unknown yet whether the same phenomena will happen on the environmental solid matrices because the currently available methods are not valid for short-chain PFAs. TFA has been identified to be mildly phytotoxic [25], and other short-chain PFAs might also have reverse effects on ecosystems although there is no toxicological data revealing their toxicity. In view of their high stability, harmful levels could be reached by continual accumulation over time in ecosystems [25–27]. Therefore, a method for determination of PFAs with a wide range of perfluorocarbon chain length is inherently necessary for describing the PFAs profiles in solid matrices and understanding the relative importance of solid matrices in the environment as to the transport and fate of PFAs.

Since the homologous series of PFAs have a wide range of physical properties, the simultaneous extraction and determination of all PFAs with carbon chain lengths from 2 to 14 is a challenging task, especially for measuring these chemicals in complex matrices [22,28]. The main problems of the currently available methods for analysis of short-chain PFAs in solid samples are that the reverse phase or polymeric sorbent cartridges (e.g. C18 and HLB etc.) used for solid phase extraction (SPE) have insufficient retention for short-chain PFAs, and consequently lead to poor recoveries [28,29]. The piperazine weak anion exchange (WAX) sorbent possesses both reverse-phase and ion-exchange retention capacities and therefore provides relative better retention for both short- (mainly ion-exchange retention) and long-chain (both reverse-phase and ion-exchange retention) PFAs. Recently, WAX cartridges have been used for analysis of PFAs in environmental water and biota samples [22,29]. However, the use of ion-exchange cartridges requires some special attention because the ion-exchange capacity of the sorbent may be quickly overloaded by other ions presented in environmental samples [30].

The objective of this study was to develop and demonstrate a simple yet sensitive quantitative method for determination of short- and long-chain PFAs (C2–C14 PFCAs and C4, C6, and C8 PFSAs; hereafter referred as C2–C14 PFAs) in solid matrices. The method consists of solvent extraction of PFAs from solid samples using sonication, solid phase extraction (SPE) using Oasis® WAX cartridges, clean-up with dispersive carbon sorbent and quantitative determination by high performance liquid chromatography-

negative electrospray tandem mass spectrometer (HPLC-MS/MS). This is the first method to report concentrations of short-chain PFAs (<C6) in solid matrices.

## 2. Experimental

### 2.1 *Chemicals and materials*

Trifluoroacetic acid (TFA, 99%) and perfluoroundecanoic acid (PFUnA, 95%) were purchased from Sigma-Aldrich (St. Louris, MO). Pentafluoropropionic acid (PFPrA, 97%), perfluorobutyric acid (PFBA, 99%), perfluoroheptanoic acid (PFHpA, 99%), perfluorodecanoic acid (PFDA, 98%), perfluorododecanoic acid (PFDoA, 95%), perfluoro-1-butanesulfonic acid potassium salt (PFBS, 98%) and perfluorooctanesulfonic acid (PFOS, ~40% in water) were obtained from Aldrich Chemical Co. (Milwaukee, WI). Perfluoropentanoic acid (PFPeA, ≥94%), perfluorohexanoic acid (PFHxA, ≥97.0%), perfluorooctanoic acid (PFOA, ≥90%), perfluorononanoic acid (PFNA, ≥95.0%) and perfluorohexanesulfonic acid potassium salt (PFHxS, ≥98.0%) were purchased from Fluka (Buchs, Switzerland). Perfluorotetradecanoic acid (PFTA, 96%) was provided by Alfa Aesar (Ward Hill, MA). Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid (MPFOA, ≥98%, ≥99% $^{13}C$) and sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate (MPFOS, ≥98%, ≥99% $^{13}C$) were acquired from Wellington Laboratories Inc. (Guelph, ON, Canada). The internal standard MPFOA was used for the quantification of the PFCAs, while MPFOS was used for the quantification of the PFSAs.

Oasis® WAX (6 cc, 150 mg, 30 μm) SPE cartridges were acquired from Waters (Milford, MA). Bulk Envi-Carb sorbent (100 $m^2 g^{-1}$, 120/400 mesh) and C18 SPE cartridges were purchased from Supelco (Bellefonate, PA). HPLC grade formic acid (96%), glacial acetic acid (99.7%) and ammonium acetate (97.0%) were purchased from TEDIA (Fairfield, OH). Ammonium hydroxide solution (25%), HPLC grade sodium acetate (≥99.0%) and 2-propanol were obtained from Fluka, and HPLC grade methanol (≥99.9%) was acquired from Sigma-Aldrich. Milli-Q water was used throughout the whole experiment.

### 2.2 *Sample collection and preparation*

New 1-L polypropylene containers with wide-mouth bottles and screw tops were used for collection of sediment and sludge samples, while PE self-locked packages were used for collection of soil samples.

In October 2006, surficial sediments were collected from Huangpu River in Shanghai, China in triplicate using a stainless steel grab dredge. Huangpu River, the largest river in Shanghai area, originates from Dianshan Lake and flows into Yangtze Estuary at Wusong and its overall length is about 114.5 km. The sediments were transported to laboratory in 1-L polypropylene bottles on ice.

In October 2007, surficial soils were collected in triplicate in PE self-locked packages from a forest park in an agricultural area of Shanghai, China. In the same sampling period, waste activated sludge was collected from a municipal wastewater treatment plants in triplicate in 1-L polypropylene bottles.

Upon arrival at the laboratory, all samples were stored at −20°C until analysis. Prior to extraction, all samples were thawed to room temperature and $\gamma$-irradiated to reduce biological activity. Then, the samples were transferred to aluminum salvers for air-drying. To avoid the pollution of solid samples, the aluminum salvers were placed on a shelf in an

incubator, which has been disinfected by UV. The air-dried samples were ground and homogenized with a mortar and pestle and subsequently passed through a 60-mesh sieve to remove pebbles, debris, glass, and weed etc. Then, the organic matter contents were determined in triplicate by Shimadzu TOC-$V_{cpn}$ analyser with solid sample module (SSM-5000A) and their values were $12.9 \pm 0.1$, $16.0 \pm 0.1$, and $292.9 \pm 3.8\,mg\,g^{-1}$ in sediment, soil and sludge matrices, respectively.

### 2.3 *Extraction and clean-up*

The samples were treated by the following 3 steps, i.e. (1) sonication solvent (i.e. 90:10 methanol/1% acetic acid) extraction was used for extracting PFAs; (2) SPE was performed to concentrate the PFAs using WAX cartridges; and (3) the SPE eluents were cleaned up using dispersive carbon sorbent to remove the co-eluted interfering compounds.



#### 2.3.1 *Sonication solvent extraction*

All solid samples were extracted according to a method reported recently by Higgins *et al.* [19], with some modification in order to improve the recoveries of PFAs and to reduce matrix interferences. Briefly, proper amount of air-dried solid matrices (e.g. 1 g sludge and 2 g soil and sediment) were transferred to 50-mL polypropylene tubes and sonicated at 60°C for 15 min in 30 mL of 1% acetic acid. The supernatant was removed by centrifugation at $2450 \times g$ for 5 min. The remaining pellet was re-suspended in 7.5 mL methanol/1% acetic acid (90:10) using a vortex stirrer (Lab dancer, IKA, Staufen, Germany), and was sonicated at 60°C for 15 min before centrifuging at $2450 \times g$ for 5min and subsequently decanting the extract. The two extracts were combined, and the procedure of 1% acetic acid washing followed by methanol/1% acetic acid extraction was repeated twice to produce 112.5 mL of extract. A further 30 mL 1% acetic acid wash was performed and the supernatant was decanted and added to extract to a final volume of 142.5 mL (hereafter referred as aqueous extract). To reduce SPE cartridges clogging, the vials containing aqueous extracts of sludge samples were centrifuged at $23{,}665 \times g$ for 15 min (Jouan KR25i, ThermoFisher, Waltham, MA).

#### 2.3.2 *SPE and clean-up of SPE cartridges*

To concentrate the extracts and to remove some potential matrix interferences, each aqueous extract was passed through an Oasis® WAX or C18 cartridge. The flow rate was controlled at $1\,drop\,s^{-1}$ in all steps of SPE including preconditioning, sample loading, washing and elution.

The SPE procedures of WAX cartridges were similar to that described earlier [29], and the modifications were aimed at encompassing more target analytes, especially for short-chain PFAs such as TFA and PFPrA. Briefly, the cartridges were preconditioned by passage of 10 mL of 1% ammonium hydroxide in methanol (V/V, 25% ammonium hydroxide solution/methanol; hereafter referred as 1% $NH_4OH/CH_3OH$), and then 10 mL of methanol and 10 mL of 1% acetic acid. The aqueous extracts of samples were then loaded onto SPE cartridges that were mounted on a vacuum manifold (GL Sciences, Tokyo, Japan). The cartridges were rinsed with 10 mL of washing solvent, which was used for clean-up of SPE cartridges after loading, and then the cartridges were dried completely under vacuum to remove water. The target analytes were eluted using a total of 2 mL

methanol and 3 mL 1% $NH_4OH/CH_3OH$ in sequence, which were loaded on one by one milliliter. The two fractions of elution were combined completely on the vortex stirrer.

The SPE procedures of C18 cartridges (LC-18, 500 mg, Supelco, Bellefonte, PA) were similar to that described earlier [19]. Cartridges were conditioned with 10 mL methanol followed by 10 mL 1% acetic acid. The aqueous extracts of solid matrices were then loaded onto C18 cartridges. After loading, the cartridges were rinsed with 10 mL Milli-Q water before being allowed to dry completely. Finally, PFAs were eluted from the C18 cartridges with 5 mL methanol.

#### 2.3.3 *Clean-up of SPE eluents*

The SPE eluents were cleaned up using a dispersive carbon sorbent as described by Powley *et al* [20]. Briefly, a small amount (~25 mg) of Envi-Carb graphitised carbon sorbent (Supelco, Belledonate, PA) was added to a 15-mL polypropylene centrifuge tube along with 100 μL glacial acetic acid and a 1 mL aliquot of SPE eluents. The centrifuge tube was capped, vortexed for 30 s and then filtered using 0.2-μm nylon syringe filters (Shanghai Anpel Instrument Co., LTD, Shanghai, China). Immediately prior to HPLC-MS/MS analysis, a 400-μL aliquot of this purified SPE eluent was exactly transferred into a 1-mL polypropylene snap top autosampler vial with a polypropylene snap top cap (Agilent, Santa Clara, CA), and 100 μL of 20ng $mL^{-1}$ mass-labelled PFOA and PFOS, i.e. MPFOA and MPFOS, was added as internal standard.

### 2.4 *Instrumental analysis*

Separation of PFAs was performed using a Finnigan Surveyor Plus LC System (HPLC; Thermo Electron, San Jose, CA, USA) consisting of a Surveryor Autosampler and a Surveryor LC Pump. Aliquots of 10-μL of SPE eluents were injected onto a 150 mm × 2.1 mm Hypersil Gold C18 column (3-μm pore size, Thermo Hypersil-Keystone, Bellefonte, PA) by the Surveyor autosampler, and a gradient mobile phase of methanol and 2 mM ammonium acetate aquatic solution was delivered at a flow rate of 25 μL $min^{-1}$ by the Surveryor LC Pump. Initial eluent conditions were 10% methanol and kept for 2 min, and the percent methanol was increased to 40% at 3 min, ramped to 100% at 12 min, held at 100% for 3 min, and then reverted to 10% at 15.5 min. The column and tray temperature were maintained at 30°C and 4°C, respectively. The HPLC tubing and internal fluoropolymer parts were identified as the instrumental blanks in the earlier study [31], therefore, the HPLC tubing made up of polytetrafluoroethylene (PTFE) were replaced with polyetheretherketone (PEEK) tubing and degasser with fluoropolymer coatings was by-passed in HPLC. In order to stabilise the retention times of analytes, helium gas was used for degasification of the mobile phase solvents. In addition, in order to avoid the contamination among different samples, the needle of the autosampler was washed and flushed using an appropriate volume (e.g. 100 μL and 1500 μL, respectively) of 50% 2-propanol in methanol (V/V) after every injection.

For quantitative determination, the HPLC was interfaced to a Finnigan TSQ™ Quantum Access™ (Thermo Electron, San Jose, CA, USA) triple quadrupole mass spectrometer equipped with electrospray ionisation (ESI) source. Electrospray negative ionisation was used in the tandem mass spectrometer (MS/MS) ion source. The spray voltage, for all analytes, was set at negative 3200 V. Sheath gas pressure, ion sweep gas pressure and auxiliary gas pressure were 35 arbitrary units (au), 0 au and 5 au, respectively.

Capillary temperature was 320°C. Transitions for all ions were observed using selected reaction monitoring (SRM) mode, and analyte-specific mass spectrometer parameters such as parent ions, product ions and collision energies were optimised for each compound (Table 1).

### 2.5 *Quantitation and confirmation*

Two inverse weighted ($1/X$) linear internal standard calibration curves covered the range of 0.01–100 ng mL$^{-1}$ were prepared daily in the same solvent as cleaned-up SPE eluents and run before and after each set of samples. The low one generally spanned the range of 0.01 to 1 ng mL$^{-1}$, while the high one ranged from 1 to 100 ng mL$^{-1}$. A coefficient of determination ($R^2$), for each target analyte, greater than 0.99 was deemed acceptable for the linear calibration curve, which was not forced through zero. Each calibration curve contained at least 5 active points and all active points were required to be within ±30% of their actual values. If the lowest point of the low calibration curve for some individual analytes did not meet stated criteria, its upper limit was increased from 1 to 5 or even to 10 ng mL$^{-1}$. Meanwhile, calibration verification standards, used to monitor the drift of instrument, were consistently within ±30% of its theoretical value during the sample runs. If calibration verification standards did not meet the stated criteria, new calibration curves were also performed again during a sequence of samples. When the levels of TFA in native and spiked sludge were out of the upper limit of the calibration curves, the SPE eluent were diluted two to four times and then another injection was required for TFA analysis.

Confirmation was performed by quantitating on both transitions for every analyte except for TFA (Table 1). For samples where both transitions were above the limits of quantitation, the calculated values from the two transitions were in very good agreement (average ratio of 0.97 to 1.02 for all analytes monitored two transitions).

### 2.6 *Quality control*

To avoid contamination during sample collection and preparation, Teflon bottles and Teflon materials were avoided throughout the experiments as interferences may be introduced to the samples. Glass materials were also avoided as the target analytes may bind to the glass. Prior to use, the containers and PE self-locked packages as well as other materials were rinsed with methanol and Milli-Q water and then air-dried.

To monitor potential contamination during sample extraction and clean-up, method blanks without solid matrices were prepared along with the samples using the same procedures. Solvent blanks, prepared in the same solvent as purified SPE eluents but without internal standards, were used to monitor instrumental background after every 10th sample. When the background contamination reduced the signal-to-noise ratio (S/N) of the lowest calibration standard to <10:1 or increased the S/N of the solvent blank to >3:1, a solvent mixture consisting of 10% formic acid in 2-propanol (V/V) was run overnight through the system [32]. In order to monitor the validity of the calibration curves and the drift of instrument, calibration verification standards (0.25 and 10 ng mL$^{-1}$ for the low and high calibration curve, respectively) were also performed after every 10th sample.

To evaluate the accuracy of the method as a whole, spike/recovery experiments were performed for sediment, soil and sludge, respectively. Except for some individual analytes

Table 1. Analyte-specific mass spectrometer parameters of perfluorinated acids (PFAs).

| Compound | Abbr. | Parent ion | Product ion and Collision energy (CE) | | | |
|---|---|---|---|---|---|---|
| | | | Quantitation | CE/eV | Confirmation | CE/eV |
| *Perfluorocarboxylates* (*PFCAs*) | | | | | | |
| Trifluoroacetic acid | TFA | 112.95 | 69.078 | 12 | 59.078 | 19 |
| Pentafluoropropionic acid | PFPrA | 162.97 | 118.945 | 13 | 68.993 | 41 |
| Perfluorobutyric acid | PFBA | 212.99 | 168.980 | 11 | 119.091 | 44 |
| Perfluoropentanoic acid | PFPeA | 262.94 | 218.971 | 10 | 118.980 | 25 |
| Perfluorohexanoic acid | PFHxA | 312.96 | 268.740 | 10 | 118.913 | 23 |
| Perfluoroheptanoic acid | PFHpA | 362.95 | 318.673 | 12 | 169.006 | 18 |
| Perfluorooctanoic acid | PFOA | 412.93 | 368.861 | 11 | 168.896 | 19 |
| Perfluorononanoic acid | PFNA | 462.94 | 419.232 | 13 | 218.795 | 16 |
| Perfluorodecanoic acid | PFDA | 512.96 | 468.920 | 13 | 268.752 | 18 |
| Perfluoroundecanoic acid | PFUnA | 562.93 | 518.947 | 13 | 268.900 | 18 |
| Perfluorododecanoic acid | PFDoA | 612.95 | 568.770 | 14 | 318.915 | 19 |
| Perfluorotetradecanoic acid | PFTA | 712.90 | 668.858 | 15 | 318.850 | 19 |
| *Perfluoroalkanesulfonates* (*PFSAs*) | | | | | | |
| Perfluoro-1-butanesulfonic acid potassium salt | PFBS | 298.89 | 79.982 | 42 | 98.919 | 28 |
| Perfluorohexanesulfonic acid potassium salt | PFHxS | 398.88 | 98.913 | 33 | 79.947 | 38 |
| Perfluorooctanesulfonic acid | PFOS | 498.91 | 98.988 | 41 | 80.054 | 62 |
| Internal standards | | | | | | |
| Perfluoro-n-[1,2,3,4-$^{13}C_4$] octanoic acid | MPFOA | 416.99 | 371.929 | 12 | – | – |
| Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$] octanesulfonate | MPFOS | 502.93 | 98.887 | 44 | – | – |

such as TFA, PFOA and PFOS, the spiked levels were 1 ng $g^{-1}$ in sediment and soil, while sludge samples were spiked at 10 ng $g^{-1}$. For PFOA and PFOS, the spiked levels were 10 ng $g^{-1}$ in sediment and soil and 50 ng $g^{-1}$ in sludge, while TFA spiked levels were 100, 100, and 500 ng $g^{-1}$ in sediment, soil and sludge, respectively. The spiked solid matrices were air-dried again prior to analysis. Endogenous PFAs concentrations, previously determined in solid matrices using the same procedures as spiked samples, were subtracted from the calculated concentrations to determine the recoveries for each analyte. Finally, the precision of the entire method was determined by extracting and analyzing each spiked sediment, soil and sludge sample in 7 replicates, and calculating the relative standard deviation (RSD) of these spiked measurements.

### 2.7 *Statistical analysis*

Differences of PFAs recoveries in method development and PFAs concentrations among all solid matrices were determined using analysis of variation (ANOVA) and all analyses were performed using the software functions included in a conventional spreadsheet program (Excel, Microsoft Corporation, Redmond, WA).



## 3. Results and discussion

In order to obtain better recoveries of both short- and long-chain PFAs (C2-C14), the SPE method was optimised for the extraction of PFAs from different solid matrices. As the results and the trends were similar among all solid matrices included in the present study (data not shown), the sediment was used as a representation in the following discussions from Sections 3.1 to 3.5.

### 3.1 *Selection of SPE cartridges*

To concentrate the extracts, C18 or HLB cartridges have been used for SPE after solvent extraction of solid matrices in previous studies for PFAs analysis [19,33–35]. In the present study, the recoveries of short- and long-chain PFAs were compared when C18 and WAX cartridges were used for SPE, respectively. The results were listed in Figure 1.

As shown in Figure 1, although recoveries of longer chain PFAs (>C6) were generally >60% when C18 cartridges were used, the values of the short-chain, such as TFA, PFPrA, PFBA, PFPeA, PFHxA and PFBS, were nearly or even equal to zero. However, when the WAX cartridges were used, the recoveries of these short-chain PFAs ranged from 54 to 106%, which were much better than C18 cartridges ($p < 0.01$). Therefore, the WAX cartridges were employed for SPE in the present study.

### 3.2 *Influence of dilution of solvent extracts on PFAs recovery*

The effect of methanol in the solvent extracts on the recoveries of PFAs was examined in the present study (Figure 2). In view of the methanol presented in aqueous extracts (around 15%, V/V) might influence the sorbent retention for target analytes and lead to breakthrough, extracts were diluted to 250 mL using acid wash solvent (i.e. 1% acetic acid) before performing SPE. Meanwhile, the aqueous extracts (142.5 mL) were also directly loaded on SPE cartridges for comparison.

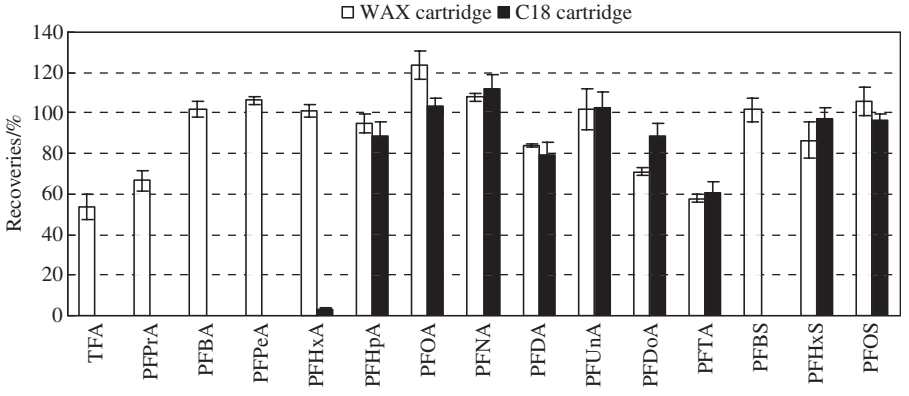


Figure 1. Recoveries of PFAs using C18 and WAX cartridges for SPE ($n = 4$).

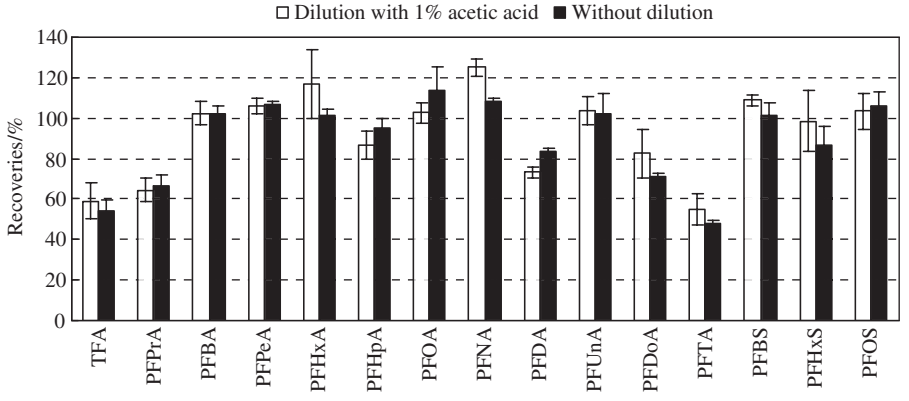


Figure 2. Influence of dilution of solvent extracts before loading on SPE Cartridges ($n = 5$).

As shown in Figure 2, recoveries of target PFAs did not vary considerably between dilution and non-dilution of aqueous extracts. The reasons for this phenomenon may be that the dominant interaction between the PFAs and the WAX cartridges is electrostatic, and the relatively low content of methanol (around 15%) did not affect the adsorption of PFAs onto WAX cartridges. Therefore, the aqueous extracts were directly loaded on SPE cartridges without dilution for all the solid samples in the further analysis.

### 3.3 *Effect of washing solution on PFAs recovery*

After loading the aqueous extracts of samples, different washing solutions, such as 25 mM sodium acetate/acetic acid buffer (pH = 4.0, hereafter referred as NaAc/HAc), 2% formic acid, and 20% methanol, were passed through the WAX cartridges to remove co-extracted interfering compounds. The effect of different washing solutions on the recoveries of PFAs was examined (Figure 3). In order to independently evaluate the effects of different washing solution, the SPE eluents were not cleaned up using dispersive carbon sorbent.

The results indicated that recoveries of PFCAs with medium perfluorocarbon length (C4–C11) and all PFSAs did not vary considerably for all of the washing solutions, but recoveries of some short- (mainly TFA and PFPrA) and long-chain (mainly PFTA) PFCAs were considerably reduced as NaAc/HAc and 20% methanol were used ($p < 0.01$).

For short-chain PFCAs such as TFA and PFPrA, the sorbent of WAX cartridges mainly adsorbed these chemicals via ion-exchange retention. However, in order to maintain the ion-exchange retention capacity of WAX cartridges 100% active, the pH values of aqueous extracts and washing solutions should be at least $\leq 3.5$ since the p$K_a$ of the sorbent is around 5.5. After loading of aqueous extracts (pH $< 4.0$) on WAX cartridges, the ion-exchange retention capacity was partly inactivated when NaAc/HAc and 20% methanol were used for clean-up of WAX cartridges because their pH values were generally $\geq 4.0$. Therefore, breakthrough of short-chain PFAs might not be avoided in clean-up steps of SPE and consequently resulted in poor recoveries of these chemicals.

For medium-chain PFCAs and all PFSAs, since the sorbent of WAX cartridges adsorbed these chemicals via both reverse phase and ion-exchange retention, although the high pH values of NaAc/HAc and 20% methanol could partly deactivate the ion-exchange retention capacity, the adsorption of medium-chain PFAs were not influenced because of the compensation of reverse phase retention. Therefore, unlike short-chain PFAs, breakthrough did not occur during clean-up steps of SPE cartridges and the recoveries did not vary considerably for all of the washing solutions.

For long-chain PFAs (PFTA), since they were retained via both reverse phase and ion-exchange retention capacities similar to medium-chain PFAs, breakthrough was not the reason for their poor recoveries; the lack of removal interfering compounds, which resulted heavy ionisation suppression during HPLC-ESI-MS/MS analysis, might be responsible for the relatively lower recoveries for NaAc/HAc and 20% methanol given that the SPE eluents were not cleaned up with dispersive carbon sorbent.

As shown in Figure 3, recoveries of all target PFAs were $\geq 90\%$ except for PFDoA (77%) and PFTA (65%) when 2% formic acid was used as washing solution. Therefore, 2% formic acid was selected for further studies.

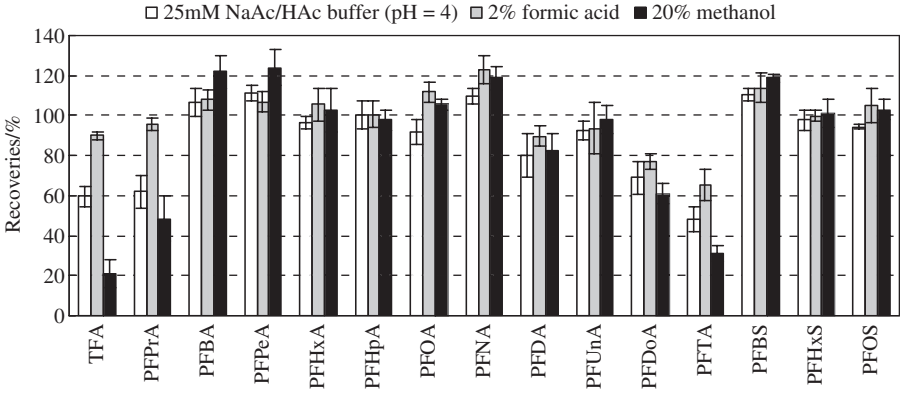


Figure 3. Effect of different washing solutions on the recoveries of target PFAs ($n = 5$).

### 3.4 *Influence of ammonium hydroxide concentration in methanol*

The effect of $NH_4OH/CH_3OH$ concentrations used for SPE elution on the recoveries of target PFAs was examined over a range from 0.05 to 5% (V/V). The results indicated that variation of the $NH_4OH/CH_3OH$ concentrations did not obviously affect recoveries of target PFAs except for 0.05% because of lack of elution of analytes from the sorbent (data not shown). This was consistent with the results of an earlier study in which WAX cartridges was used for analysis of short- and long-chain PFAs in water samples [29]. Given the tolerant pH range of the HPLC column and the elution ability, 1% $NH_4OH/CH_3OH$ was selected for further studies.



### 3.5 *Matrix effect and its elimination*

Matrix effects have been observed in HPLC-MS/MS analysis of perfluoroalkyl surfactants in environmental matrices and may impair the accuracy of the results [19,20,33]. To assess this possibility, single-point standard additions were performed by removing 350-μL aliquot of each SPE eluent and adding 50 μL of standards (100 ng $mL^{-1}$) and 100 μL of internal standards (20 ng $mL^{-1}$) to each aliquot immediately prior to HPLC-MS/MS analysis. The matrix effects were then determined according to Equation 1:

$$\text{Matrix effect} = \frac{\text{Peak area ratio}_{\text{standard addition}} - \text{Peak area ratio}_{\text{unspiked}}}{\text{Peak area ratio}_{\text{solvent standard}}} \times 100\% \quad (1)$$

where: peak area ration = target analyte peak area/internal standard area; Standard addition concentrations were equal to solvent standard concentration, i.e. the standards were spiked in the same solvent as cleaned-up extracts; Ionisation enhancement = >100% matrix effect, Ionisation suppression = <100% matrix effect, No matrix effect =100%.

Standard additions were performed on sediments with or without cleanup of SPE eluent using dispersive carbon sorbent, respectively, and the results were summarised in Figure 4. Generally, matrix effect were not considered significant if on average the peak area ratio of target analyte was enhanced or suppressed by less than ±30% of the solvent

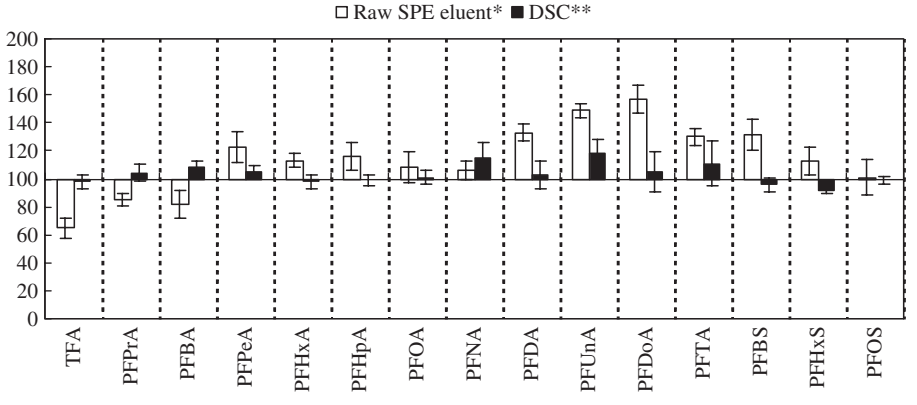


Figure 4. Determination and elimination of matrix effects ($n = 5$).
Notes: *SPE eluent without cleanup before determining matrix effect.
**SPE eluent cleaned up using dispersive carbon sorbent (DCS) before determining matrix effect.

standard peak area ratio at equivalent concentrations. Therefore, as shown in Figure 4, some ultra-short chain PFCAs, such as TFA and PFPrA, suffered ionisation suppression in ESI, while PFBS and longer chain PFCAs (>C9) suffered ionisation enhancement. However, the medium chain PFAs (C4–C9) were not significantly affected by matrix effect in most cases. The possible reasons for these phenomena were that internal standards, MPFOA an MPFOS, could effectively offset the matrix effects of medium chain PFAs, but they were not suitable for some short- (<C4 PFCAs and PFBS) and long-chain PFAs (>C10 PFCAs), which were eluted significantly earlier or later than the retention times of internal standards. Therefore, similarities of the chemicals and the retention times are important in choosing internal standards for this particular class of compounds.

In order to negate the matrix effects for all the analytes, dispersive graphitised carbon sorbent was used for the clean-up of the SPE eluent. As shown in Figure 4, the results indicated that matrix effects of all analytes were effectively eliminated by dispersive carbon sorbent. Given that the main causes of ionisation suppression are the changes of the droplet solution properties by non-volatile solutes in samples [36], the possible reasons for these eliminations are that most co-eluting interference compounds with any degree of aromaticity would be strongly adsorbed onto the graphitised carbon sorbent via dispersive interaction with $\pi$ electrons, resulting in a very effective purification of SPE eluents without affecting of PFAs [20]. Meanwhile, the usage of Envi-Carb for clean-up of SPE eluents not only eliminated the matrix effect, but also avoided the frequent clean of the ESI in order to maintain instrumental sensitivity.



### 3.6 *Method detection limit (MDL) and quantitation limit (MQL)*

The instrumental detection limit (IDL) was defined as the mass of analyte needed to yield a S/N ≥ 3:1 added to the same solvent as purified SPE eluents of solid matrices, while the instrumental quantitation limit (IQL) was defined as the analyte concentration yielding a S/N ≥ 10:1 or as the lowest calibration curve point calculated to be within 30% of its actual value, whichever is greater. Then, the method detection limit (MDL) and quatitation limit (MQL) were calculated from their corresponding IDL an IQL based on the mass of sample and the volume of SPE eluent except for PFOA and PFOS according to Equations 2 and 3, respectively:

$$\mathrm{MDL} = \frac{\mathrm{IDL} \times V_{\mathrm{SPE}}}{M_{\mathrm{solid}}} \tag{2}$$

$$\mathrm{MQL} = \frac{\mathrm{IQL} \times V_{\mathrm{SPE}}}{M_{\mathrm{solid}}} \tag{3}$$

where $V_{\mathrm{SPE}}$ = SPE eluent volume of solid matrices; $M_{\mathrm{solid}}$ = mass of solid matrices, g.

The usage of internal standards introduced native PFOA and PFOS into purified SPE eluents because internal standards contained <1% non-labelled PFOA and PFOS. Introduction of native PFOA and PFOS by internal standards disturbed the determination of their MDL and MQL using the method stated above. Therefore, the PFOA and PFOS MDL of sediment and soil were determined according to Equation 4 [37]:

$$\mathrm{MDL} = t^{p=0.99}_{\mathrm{df}=n-1} s/\sqrt{n} \tag{4}$$

where $t$ is Student's $t$-statistic for $n-1$ degrees of freedom and encompassing 99% of the population in a one-sided statistical test, and $s$ is the standard diviation of $n=7$ analytical readings of a low concentration of the analyte. Since MDL should be <MQL, only PFOA MDL of soil could be determined from 7 replicate measurements using the soil samples included in present study, which contained $3.32 \pm 0.23\,ng\,g^{-1}$ PFOA from 7 replicate measurement and $16.0 \pm 0.1\,mg\,g^{-1}$ organic matters. For PFOS, its levels in the sediment and soil included in present study were relatively too high to determine its MDL; therefore, other sediment collected from Dianshan Lake, the source of Huangpu River, were used instead. The sediment collected from Diansh Lake contained $2.52 \pm 0.25\,ng\,g^{-1}$ PFOS from 7 replicate measurements and $14.8 \pm 0.2\,mg\,g^{-1}$ organic matters. The PFOA and PFOS MDL of sediment and soil were arbitrarily considered to be equal. For sludge samples, PFOA and PFOS MDL were arbitrarily given a value of two times MDL of sediment and soil because no sludge samples were acquired to contain low pollution levels of PFOA and PFOS.

For PFOA and PFOS, the IQL were required to produce a signal with at least twice the area of the highest blanks, which were prepared by adding 100-μL internal standards mixture ($20\,ng\,mL^{-1}$) into 400-μL solvent that was same as the purified SPE eluent of solid matrices. Then, the MQL were calculated according Equation 3.

The MDL and MQL for sediment, soil and sludge are summarised in Table 2. As shown in Table 2, the MDL and MQL were analyte and sample dependent. The MDL ranged from 0.02 to $0.30\,ng\,g^{-1}$ for sediment and soil and 0.04 to $0.60\,ng\,g^{-1}$ for sludge, while the MQL were in a range of 0.10 to $0.45\,ng\,g^{-1}$ for sediment and soil and 0.25 to $0.90\,ng\,g^{-1}$ for sludge. For calculation of total concentrations, all non-detections were treated as zero, and all concentrations greater than MDL but less than MQL were arbitrarily given a value of MDL or one-half MQL, whichever was greater.

Table 2. Method detection limits (MDL) and quantitation limits (MQL) of PFAs.

| | Sludge | | Sediment and soil | |
|---|---|---|---|---|
| Compound | MDL (ng/g) | MQL (ng/g) | MDL (ng/g) | MQL (ng/g) |
| *Perfluorocarboxylates* (*PFCAs*) | | | | |
| TFA | 0.30 | 0.50 | 0.15 | 0.25 |
| PFPrA | 0.30 | 0.50 | 0.15 | 0.25 |
| PFBA | 0.06 | 0.25 | 0.03 | 0.10 |
| PFPeA | 0.20 | 0.30 | 0.10 | 0.15 |
| PFHxA | 0.04 | 0.25 | 0.02 | 0.10 |
| PFHpA | 0.06 | 0.25 | 0.03 | 0.10 |
| PFOA | 0.54 | 0.90 | 0.27 | 0.45 |
| PFNA | 0.06 | 0.25 | 0.03 | 0.10 |
| PFDA | 0.06 | 0.25 | 0.03 | 0.10 |
| PFUnA | 0.06 | 0.25 | 0.03 | 0.10 |
| PFDoA | 0.06 | 0.25 | 0.03 | 0.10 |
| PFTA | 0.15 | 0.25 | 0.06 | 0.10 |
| *Perfluoroalkanesulfonates* (*PFSAs*) | | | | |
| PFBS | 0.15 | 0.25 | 0.05 | 0.10 |
| PFHxS | 0.09 | 0.25 | 0.04 | 0.10 |
| PFOS | 0.60 | 0.90 | 0.30 | 0.45 |

Table 3. Method validation for all solid samples included in present study ($n = 7$).

| Compound | Sediment | | Soil | | Sludge | |
|---|---|---|---|---|---|---|
| | Recovery (%)[a] | Precision[b] | Recovery (%)[a] | Precision[b] | Recovery (%)[a] | Precision[b] |
| *Perfluorocarboxylates* (*PFCAs*) | | | | | | |
| TFA | 98 ± 1 | 1 | 91 ± 1 | 1 | 101 ± 3 | 3 |
| PFPrA | 111 ± 1 | 1 | 88 ± 5 | 6 | 115 ± 5 | 4 |
| PFBA | 80 ± 3 | 4 | 80 ± 3 | 4 | 99 ± 2 | 2 |
| PFPeA | 94 ± 2 | 2 | 90 ± 3 | 4 | 104 ± 7 | 6 |
| PFHxA | 96 ± 2 | 2 | 97 ± 6 | 6 | 91 ± 12 | 14 |
| PFHpA | 109 ± 9 | 9 | 112 ± 10 | 9 | 93 ± 2 | 2 |
| PFOA | 107 ± 2 | 2 | 112 ± 9 | 8 | 110 ± 4 | 3 |
| PFNA | 99 ± 2 | 2 | 108 ± 5 | 5 | 97 ± 3 | 3 |
| PFDA | 94 ± 3 | 3 | 108 ± 9 | 9 | 83 ± 5 | 6 |
| PFUnA | 91 ± 14 | 15 | 112 ± 3 | 2 | 65 ± 4 | 7 |
| PFDoA | 71 ± 3 | 5 | 81 ± 5 | 6 | 57 ± 6 | 10 |
| PFTA | 66 ± 8 | 13 | 73 ± 14 | 19 | 60 ± 11 | 18 |
| *Perfluoroalkylsulfonate* (*PFSAs*) | | | | | | |
| PFBS | 99 ± 2 | 2 | 90 ± 3 | 3 | 107 ± 11 | 10 |
| PFHxS | 96 ± 12 | 13 | 107 ± 2 | 1 | 103 ± 7 | 7 |
| PFOS | 94 ± 11 | 11 | 102 ± 9 | 9 | 105 ± 10 | 10 |

Notes: [a]Recovery ± standard deviation, the results were corrected for the endogenous concentrations.
[b]Expressed by per cent relative standard deviation (RSD).

### 3.7 *Method validation*

Method blanks, used to monitor contamination during sample extraction and clean-up, were consistently below the IDL except for PFOA and PFOS, which were introduced by internal standards. If method blanks were analysed without internal standards, PFOA and PFOS were also not detected. These results indicate that contamination did not occur during sample extraction and clean-up.

The method validation parameters are summarised in Table 3 and the typical chromatograms for all PFAs monitored in solid matrices (sludge) are provided in Figure 5. The mean recoveries of all analytes were in a range of 57–115%, which were generally good enough for quantitative analysis of these compounds in solid matrices, especially for the short-chain (<C8, 80–115%) excluded in previous studies. As to individual solid matrix, the PFAs recoveries were 66–111%, 73–112%, and 57–115% in sediment, soil, and sludge, respectively. The precisions of this method, represented by the percent relative standard deviation (RSD) of the spiked measurements, were in the range of 1–15%, 1–19%, and 2–18% for sediment, soil, and sludge, respectively (Table 3). These data strongly indicate that the method used in the present study is effective for analysis of both short- and long-chain PFAs in solid matrices.

### 3.8 *PFAs concentration in solid matrices*

The concentrations of all PFAs in different solid matrices were determined and listed in Table 4. The total PFAs concentrations in sediment, soil and sludge were 116.25, 141.20 and 652.35 $ng\,g^{-1}$, respectively. The dominant analyte in all solid matrices were TFA,

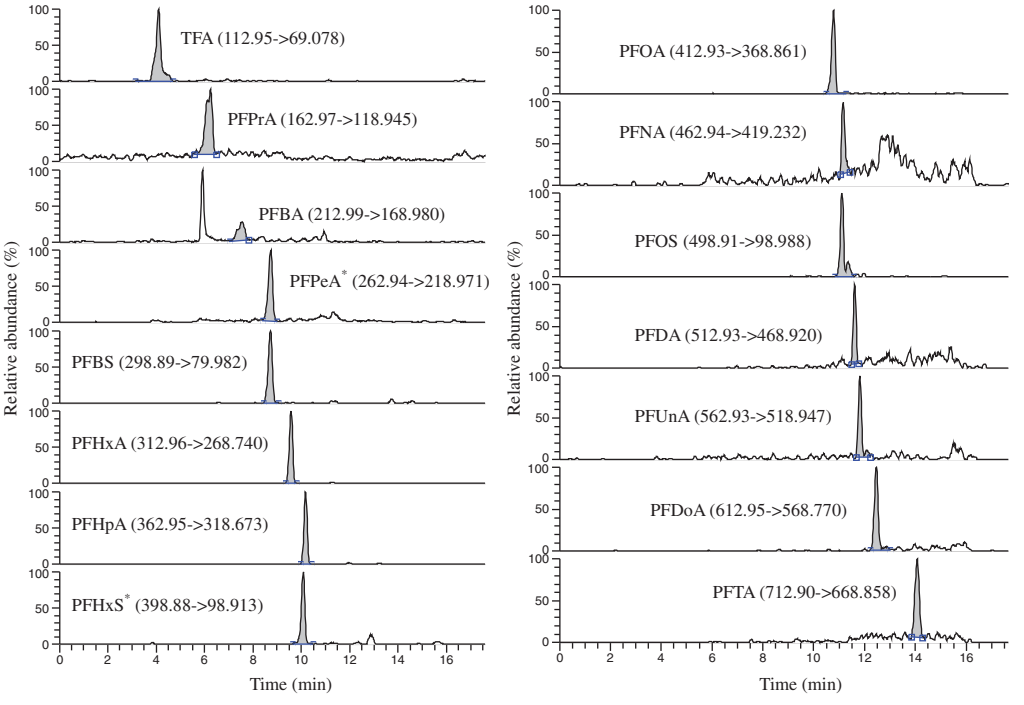


Figure 5. Typical chromatograms of PFAs in solid matrix (sludge).
Note: *PFPeA and PFHxS were spiked at 10 ng g$^{-1}$ because they were not detected in sludge.

especially in sludge, its concentrations was as high as 562.35 ng g$^{-1}$. Since previous studies have reported very high concentrations of TFA in water samples [24,26,27], the TFA concentrations in surface water and wastewater, from where the sediment and sludge were collected, were also determined by our research group and the results also indicated that the TFA levels were much higher than the other PFAs (data not shown). Given sorption potential of PFAs increasing with perfluorocarbon chain length [18], the high TFA concentrations determined in the sediment and sludge samples might mainly result from water phase in view of the high water contents (>80% and >99% in sediment and sludge, respectively) before air-dried. Therefore, the high concentrations might not represent the pollution levels of TFA in these matrices. For soil samples, although the water contents (<12%) were much lower than sediment and sludge before air-dried, TFA was still the dominant pollutant. Similar to the accumulation in seasonal wetlands [38], TFA was retained in soil because of evaporation when it sank down with precipitation. Meanwhile, dry deposition may be another source of TFA in soils in view of that dry deposition has been identified as the primary contributors of TFA to surface waters in arid and semiarid environments [26].

As shown in Table 4, PFOA and PFOS were still two major pollutants in solid matrices though their pollution levels were lower than TFA. Meanwhile, nearly all of the PFAs concentrations in sludge were almost always higher than the values determined in soil and sediment. Therefore, wastewater treatment plants may be one of the sources of these contaminants in environments, which receive effluent or/and sludge [33,39].

Table 4. PFAs concentrations various solid matrices ($n = 3$).

| PFAs | Sediment[a] | Soil[b] | Sludge[c] |
|---|---|---|---|
| *Perfluorocarboxylates* (*PFCAs*) | | | |
| TFA | $63.40 \pm 3.5$[d] | $126.47 \pm 7.88$ | $561.90 \pm 25.10$ |
| PFPrA | $2.76 \pm 0.19$ | $0.60 \pm 0.03$ | $4.39 \pm 0.05$ |
| PFBA | $0.21 \pm 0.01$ | $0.15 \pm 0.01$ | $1.11 \pm 0.28$ |
| PFPeA | $0.21 \pm 0.01$ | $0.37 \pm 0.02$ | N.D. |
| PFHxA | $0.15 \pm 0.01$ | $0.13 \pm 0.01$ | $0.84 \pm 0.09$ |
| PFHpA | <MQL[e] | $0.15 \pm 0.00$ | $0.52 \pm 0.07$ |
| PFOA | $34.59 \pm 4.63$ | $3.28 \pm 0.22$ | $25.28 \pm 2.84$ |
| PFNA | $0.70 \pm 0.03$ | $0.24 \pm 0.02$ | <MQL |
| PFDA | $0.22 \pm 0.02$ | $0.18 \pm 0.03$ | $2.44 \pm 0.31$ |
| PFUnA | $0.35 \pm 0.01$ | N.D. | $2.80 \pm 0.24$ |
| PFDoA | $0.43 \pm 0.02$ | N.D. | $0.93 \pm 0.21$ |
| PFTA | N.D.[f] | $0.11 \pm 0.02$ | <MQL |
| *Perfluoroalkylsulfonate* (*PFSAs*) | | | |
| PFBS | $0.48 \pm 0.07$ | <MQL | $12.14 \pm 2.63$ |
| PFHxS | N.D. | $0.28 \pm 0.04$ | N.D. |
| PFOS | $12.52 \pm 1.54$ | $9.20 \pm 0.87$ | $37.72 \pm 5.10$ |
| Total[g] | 116.25 | 141.20 | 652.35 |

Notes: [a]Sediment samples were collected from Huangpu River, the largest river in Shanghai aera.
[b]Soil samples were collected from a forest park in an agricultural area of Shanghai, China.
[c]Sludge samples were collected from a municipal WWTP in Shanghai, China
[d]Mean ± standard deviation.
[e]Detected but not above the MQL.
[f]Not detected, which is treated as zero when calculate total concentration.
[g]Total concentration of PFAs, which is calculated using MDL or one-half of MQL, whichever is greater, when the value is <MQL.



## 4. Conclusions

The proposed method allows the simple and sensitive determination of short- and long-chain PFAs (C2–C14) in various solid matrices. The MDL and MQL, which are analyte and sample dependent, are 0.02–0.30 ng $g^{-1}$ and 0.10–0.90 ng $g^{-1}$, respectively. The recoveries of all PFAs (57–115%) are generally good enough for quantitative analysis of these chemicals, especially for the short-chain PFAs (<C8, 80–115%) excluded in previous studies because of no available methods. The precisions of this method, represented by the percent relative standard deviation (RSD) of the spiked measurements, are in a range of 1–19%. Generally, matrix effect do not obviously affect analytes quantification from solvent-based internal standard calibration curves in various solid matrices because dispersive carbon sorbent could effectively adsorb interfering compounds presented in SPE eluent but not affect PFAs. Therefore, the proposed method in the present study is a reliable means to determine short- and long-chain PFAs in various solid matrices.

## Acknowledgements

This study has been supported by the National Science Foundation Committee of China (Project No. 20807032), the State Key Laboratory of Pollution Control and Resource Reuse

(Project No. PCRRF06007), the Provincial Key Laboratory of Environmental Science and Engineering, Jiangsu Province (Project No. ZD061203) and the Ministry of Science and Technology of China (Project No. 2007DFR90050).

## References

[1] B. Key, R. Howell, and C. Criddle, Environ. Sci. Technol. **31**, 2445 (1997).
[2] E. Kissa, *Fluorinated Surfactants and Repellants*, 2nd ed. (CRC Press, New York, 2001).
[3] J.P. Giesy and K. Kannan, Environ. Sci. Technol. **36**, 146A (2002).
[4] M. Houde, J.W. Martin, R.J. Letcher, K.R. Solomon, and D.C.G. Muir, Environ. Sci. Technol. **40**, 3463 (2006).
[5] M. Haukås, U. Berger, H. Hop, B. Gulliksen, and G.W. Gabrielsen, Environ. Pollut. **148**, 360 (2007).
[6] M. Houde, T.A.D. Bujas, J. Small, R.S. Wells, P.A. Fair, G.D. Bossart, K.R. Solomon, and D.C.G. Muir, Environ. Sci. Technol. **40**, 4138 (2006).
[7] K. Kannan, L. Tao, E. Sinclair, S.D. Pastva, D.J. Jude, and J.P. Giesy, Arch. Environ. Contam. Toxicol. **48**, 559 (2005).
[8] A. Morikawa, N. Kamei, K. Harada, K. Inoue, T. Yoshinaga, N. Saito, and A. Koizumi, Ecotox. Environ. Safe. **65**, 14 (2006).
[9] P.R. Dorneles, J. Lailson-Brito, A.F. Azevedo, J. Meyer, L.G. Vidal, A.B. Fragoso, J.P. Torres, O. Malm, R. Blust, and K. Das, Environ. Sci. Technol. **42**, 5368 (2008).
[10] M.G. de Vos, M.A.J. Huijbregts, M.J. van den Heuvel-Greve, A.D. Vethaak, K.I. van de Vijver, P.E.G. Leonards, S.P.J. van Leeuwen, P. de Voogt, and A.J. Hendriks, Chemosphere **70**, 1766 (2008).
[11] M.E. Austin, B.S. Kasturi, M. Barber, K. Kannan, P.S. MohanKumar, and S.M.J. MohanKumar, Environ. Health Perspect. **111**, 1485 (2003).
[12] D.J. Luebker, M.T. Case, R.G. York, J.A. Moore, K.J. Hansen, and J.L. Butenhoff, Toxicology **215**, 126 (2005).
[13] L.W.Y. Yeung, K.S. Guruge, N. Yamanaka, S. Miyazaki, and P.K.S. Lam, Toxicology **237**, 111 (2007).
[14] E. Mulkiewicz, B. Jastorff, A.C. Składanowski, K. Kleszczyński, and P. Stepnowski, Environ. Toxicol. Phar. **23**, 279 (2007).
[15] R. Renner, Environ. Sci. Technol. **35**, 154A (2001).
[16] K. Prevedouros, I.T. Cousins, R.C. Buck, and S.H. Korzeniowski, Environ. Sci. Technol. **40**, 32 (2006).
[17] R.G. Luthy, G.R. Aiken, M.L. Brusseau, S.D. Cunningham, P.M. Gschwend, J.J. Pignatello, M. Reinhard, S.J. Traina, W.J. Weber, and J.C. Westall, Environ. Sci. Technol. **31**, 3341 (1997).
[18] C.P. Higgins and R.G. Luthy, Environ. Sci. Technol. **40**, 7251 (2006).
[19] C.P. Higgins, J.A. Field, C.S. Criddle, and R.G. Luthy, Environ. Sci. Technol. **39**, 3946 (2005).
[20] C.R. Powley, S.W. George, T.W. Ryan, and R.C. Buck, Anal. Chem. **77**, 6353 (2005).
[21] Y. Miyake, N. Yamashita, P. Rostkowski, M.K. So, S. Taniyasu, P.K.S. Lam, and K. Kannan, J. Chromatogr. A **1143**, 98 (2007).
[22] S. Taniyasu, K. Kannan, L.W.Y. Yeung, K.Y. Kwok, P.K.S. Lam, and N. Yamashita, Anal. Chem. Acta **619**, 221 (2008).
[23] B.F. Scott, C.A. Moody, C. Spencer, J.M. Small, D.C.G. Muir, and S.A. Mabury, Environ. Sci. Technol. **40**, 6405 (2006).
[24] B.F. Scott, C. Spencer, S.A. Mabury, and D.C.G. Muir, Environ. Sci. Technol. **40**, 7167 (2006).
[25] M.F. Smit, P.D.R. van Heerden, J.J. Pienaar, L. Weissflog, R.J. Strasser, and G.H.J. Krüger, Plant Physiol. Biochem. (2009), doi:10.1016/j.plaphy.2009.02.003.
[26] C.E. Wujcik, T.M. Cahill, and J.N. Seiber, Environ. Sci. Technol. **33**, 1747 (1999).
[27] C.E. Wujcik, T.M. Cahill, and J.N. Seiber, Anal. Chem. **70**, 4074 (1998).

[28] S.P.J. van Leeuwen, A. Kärrman, B. van Bavel, J. de Boer, and G. Lindström, Environ. Sci. Technol. **40**, 7854 (2006).
[29] S. Taniyasu, K. Kannan, M.K. So, A. Gulkowska, E. Sinclair, T. Okazawa, and N. Yamashita, J. Chromatogr. A **1093**, 89 (2005).
[30] M. Hennion and V. Pichon, Environ. Sci. Technol. **28**, 576A (1994).
[31] N. Yamashita, K. Kannan, S. Taniyasu, Y. Horii, T. Okazawa, G. Petrick, and T. Gamo, Environ. Sci. Technol. **38**, 5522 (2004).
[32] M.M. Schultz, D.F. Barofsky, and J.A. Field, Environ. Sci. Technol. **40**, 289 (2006).
[33] E. Sinclair and K. Kannan, Environ. Sci. Technol. **40**, 1408 (2006).
[34] B.G. Loganathan, K.S. Sajwan, E. Sinclair, K.S. Kumar, and K. Kannan, Water Res. **41**, 4611 (2007).
[35] R. Bossi, J. Strand, O. Sortkjær, and M.M. Larsen, Environ. Int. **34**, 443 (2008).
[36] R. King, R. Bonfiglia, C. Fernandez-Metzler, C. Miller-Stein, and T. Olah, J. Am. Soc. Mass Spectrom. **11**, 942 (2000).
[37] J.W. Washington, J.J. Ellington, T.M. Jenkins, and J.J. Evans, J. Chromatogr. A **1154**, 111 (2007).
[38] T.M. Cahill, C.M. Thomas, S.E. Schwarzbach, and J.N. Seiber, Environ. Sci. Technol. **35**, 820 (2001).
[39] B. Boulanger, J.D. Vargo, J.L. Schnoor, and K.C. Hornbuckle, Environ. Sci. Technol. **39**, 5524 (2005).