



## Comparison of two extraction methods for the analysis of per- and polyfluorinated chemicals in digested sewage sludge

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### ABSTRACT

A rapid and reliable analytical method, based on ion-pair extraction, clean-up on Envicarb cartridge and detection by liquid chromatography–tandem mass spectrometry (LC–MS/MS), was developed for determination of 17 per- and polyfluorinated chemicals (PFCs) in digested sewage sludge. Envicarb cartridge and six labeled internal standards were selected for the elimination/reduction and correction of matrix effects, respectively. As a result, the matrix effect for perfluorooctane sulfonamides (FOSAs) and perfluorocarboxylic acids (PFCAs) with carbon chain length from C6 to C14 was lowered to a range of –14% to +28%. However, the matrix effect for other analytes was still great mainly due to the absence of appropriate internal standard. Mean recoveries of the target analytes based on matrix spikes, at different spike levels (10–300 ng/g), ranged from 70% to 169%. Relative standard deviations (RSDs) were in the range of 2–20% at different spike levels. The limit of quantification (LOQ) ranged between 0.6 and 30 ng/g. The method was successfully applied to several sewage sludge samples from wastewater treatment plants nearby Zürich, Switzerland. In addition, by comparing the accuracy and precision of ion-pair extraction method and methanol extraction method, we further demonstrated that the ion-pair extraction method can be used for the analysis of PFCs in sludge samples. To our knowledge, this is the first study to extract the PFCs in sewage sludge with ion-pair method and to find unsaturated fluorotelomer carboxylic acids (FTUCAs) in sewage sludge.

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### 1. Introduction

Per- and polyfluorinated chemicals (PFCs) comprise a family of man-made chemicals that have been used in a wide variety of industrial, commercial, and consumer applications, including coatings for textiles and paper packaging products [1], fire fighting foams [2], insecticides [3], and as polymerization aids in the manufacture of fluoropolymers. The PFCs include perfluorocarboxylic acids (PFCAs), perfluoroalkyl sulfonic acids (PFSAs), fluorotelomer alcohols (FTOHs), saturated fluorotelomer carboxylic

acids (FTCAs) and unsaturated fluorotelomer carboxylic acids (FTUCAs), perfluorooctane sulfonamido alcohols (FOSEs), perfluorooctane sulfonamides (FOSAs), and perfluorooctane sulfonamido acetic acids (FOSAAs). Recently, it has been shown that PFCs are global contaminants as evidenced by their extensive detection in wildlife [4–6], humans [7–9], surface waters [10–12] and wastewater treatment plants (WWTPs) [13–15]. The PFCs are persistent, bioaccumulative and potentially toxic [16–18]. Despite a voluntary phase-out of one perfluorooctane sulfonyl-based product, some PFCs such as perfluorooctanoic acid (PFOA) and FTOHs are still in production and use. Degradation of FTOHs may be an additional source of PFCAs in the environment [19–21].

WWTPs have been well documented to be a major source of PFCs to natural waters [13,14]. It has been reported that *n*-ethyl perfluorooctane sulfonamidoethanol (*n*-EtFOSE) and 8:2 fluorotelomer alcohol (8:2 FTOH) can be degraded to perfluorooctane sulfonate (PFOS) and PFOA, respectively, through biotransformation in activated sludge process [20–22]. An important elimination process of pollutants in WWTPs is sorption to suspended solids and sub-

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sequent removal by sedimentation as sewage sludge. The role of solid waste generated from WWTP in the environmental fate of hydrophobic organic pollutants has long been recognized [23]. But polar compounds like fluoroquinolone antibiotics could also sorb onto the suspended solids to a high degree likely due to electrostatic interactions between the positively charged amino group and the negatively charged surface of microorganisms [24]. Furthermore, the sorption of linear alkylbenzene sulfonate surfactants, which exhibit both hydrophobic and hydrophilic functionalities, has been reported for sediments [25,26]. Therefore, sewage sludge is considered as a sink for many pollutants in WWTPs.

Until now, very few studies have measured PFCs in solid matrices, such as sewage sludge, soil and sediment [27–33]. A “matrix effect-free” method for the analysis of various PFCAs in sludge, soil and sediment was developed by Powley et al. [27], and that method involves solid–liquid extraction (SLE) with methanol, dispersive clean-up on Envicarb and liquid chromatography–tandem mass spectrometry (LC–MS/MS) analysis. While this “matrix effect-free” method was widely used for environmental samples thereafter due to its reliable results (recovery value: 70–120%, limit of quantifications (LOQs) <1 ng/g) [27], it does not cover a wide range of PFCs. Measurement of PFCs such as PFSA and their precursors are needed for the assessment of mass loadings of PFCs in rivers and lakes downstreams of WWTPs. Higgins et al. [28] developed a method for a broader range of PFCs, namely PFCAs, PFSA and FOSAA in sediment and sewage sludge, and recovery value are in the range of 37–98% with LODs of 0.04–2.2 ng/g. The method employed three sequential cycles of washing of sediment by acetic acid solution and extraction by acidified methanol under sonication, and clean-up with a solid phase extraction cartridge (SPE, C<sub>18</sub>). The laborious extraction procedure is the main disadvantage of this method, and at least 6 h are needed for preparation of one sample. Moreover, short chain (C<sub>4</sub> and C<sub>5</sub>) analogs of PFCAs and PFSA were not included due to low recovery, and the recovery for PFHxS is only 37%. Schröder [29] tested three different extraction techniques, Soxhlet extraction, hot vapor and pressurized liquid extraction. The latter techniques with sequential use of methanol: phosphoric acid (99:1) and ethyl acetate dimethylformamide (8:2) provided the best extraction efficiency with recoveries between 105% and 120%. However, the overall extraction methods were not sensitive enough to be successfully applied for a range of environmental samples. More recently, Washington et al. [31] compared different combined extraction and clean-up methods for soil samples, and found that applying ion-pairing as a separate clean-up step is effective in minimizing instrumental noise, however, the analytical procedure includes eight steps, and is time consuming. Solvent evaporation was employed twice, which is unfavorable for recovering of volatile analogs.

Matrix effect is still a challenge in the analysis of PFCs in solid matrix. As reported previously [28,30], the analysis of complex environmental samples such as sludge by electrospray LC–MS/MS can be hampered by ionization effects induced by co-eluting components present in the extract. Ion suppression and enhancement can occur during the analysis by LC–MS/MS due to the matrix effects. Therefore, it is necessary to employ an appropriate clean-up method to remove salts and potential matrix components that interfere with the ionization of target analytes, and confirm that the internal standards used in the analysis were effective.

We developed a rapid and robust analytical method for the determination of 17 PFCs in sewage sludge. The elimination of matrix effects was accomplished by careful evaluation of the clean-up procedure, and the matrix effects were further corrected by addition of labeled internal standards for the target analytes. This is the first report using ion-pair method for extraction of PFCs in sewage sludge, and this is the first study to find FTUCAs in sewage sludge. The PFCs analyzed include seven PFCAs with carbon chain

length from C<sub>5</sub> to C<sub>14</sub>, PFSA with carbon chain length of C<sub>4</sub>, C<sub>6</sub> and C<sub>8</sub>, and 7 precursor compounds: 6:2 fluorotelomer unsaturated carboxylic acid (6:2 FTUCA), 8:2 fluorotelomer unsaturated carboxylic acid (8:2 FTUCA), perfluorooctane sulfonamide (FOSA), *n*-methyl perfluorooctane sulfonamide (*n*-MeFOSA), *n*-ethyl perfluorooctane sulfonamide (*n*-EtFOSA), *n*-methyl perfluorooctane sulfonamido acetic acid (*n*-MeFOSAA) and *n*-ethyl perfluorooctane sulfonamido acetic acid (*n*-EtFOSAA).

## 2. Experimental

### 2.1. Chemicals and materials

The purity of native standards and labeled internal standards was higher than 95%. Two micrograms per millilitre standard solution mixture in methanol of 11 PFCAs with carbon number from 4 to 14; 50 µg/ml standards of sodium perfluorobutane sulfonate (PFBS), sodium perfluorohexane sulfonate (PFHxS), PFOS, FOSA, *n*-MeFOSA, *n*-EtFOSA, *n*-MeFOSAA, *n*-EtFOSAA, 8:2 FTUCA and 6:2 FTUCA in methanol were purchased from Wellington Laboratories (Guelph, ON, Canada). Labeled internal standards (50 ng/mL in methanol), perfluoro-*n*-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]butanoic acid (MPFBA), perfluoro-*n*-[1,2-<sup>13</sup>C<sub>2</sub>]hexanoic acid (MPFHxA), perfluoro-*n*-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]octanoic acid (MPFOA), sodium perfluoro-1-[1,2,3,4-<sup>13</sup>C<sub>4</sub>] octanesulfonate (MPFOS), and *n*-methyl-*d*<sub>3</sub>-perfluoro-1-octane-sulfonamide (*d*-*n*-MeFOSA), 2-perfluorohexyl-[1,2-<sup>13</sup>C<sub>2</sub>]ethanoic acid (MFHUEA, e.g., <sup>13</sup>C-labeled 6:2 FTUCA) were from Wellington Laboratories. Tetrabutyl ammonium hydrogen sulfate (TABS; 95%) used as ion-pair reagent was obtained from Sigma–Aldrich Chemical (Buchs, Switzerland). All solvents were of HPLC grade. Methyl-*t*-butyl ether (MTBE), methanol and reagent water were purchased from Scharlau (Barcelona, Spain). Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and ammonium hydroxide (NH<sub>4</sub>OH) were from Sigma–Aldrich Chemical. Envicarb cartridge with 300 µm particle size was obtained from J.T. Baker (Amsterdam, Holland).

### 2.2. Sampling procedure

In August 2008, sewage sludge samples (*n*=3) were collected from WWTPs near Zürich, Switzerland in Dübendorf, Horgen and Wädenswil. The sewage sludge had a water content of approximately 95%. Prior to extraction, all samples were dried at 40 °C for 3–4 days, finely ground (<0.5 mm), and stored in polypropylene bottles at room temperature. The concentrations of the target analytes in sample were calculated and expressed as ng/g dry weight.

### 2.3. Extraction and clean-up procedure

#### 2.3.1. Ion-pair extraction method

All samples were extracted by ion-pair extraction method (IPM) similar to that previously reported by Hansen et al. [34]. Briefly, 0.5 mL of 0.5 M TBAS solution and 4 mL of 0.25 M sodium carbonate buffer (pH 10) were added into a 15-mL polypropylene tube containing 0.5 g of dried sludge. After a thorough mixing, 5 mL of MTBE was added to the solution, and the mixture was vigorously shaken for 20 min. The organic and aqueous layers were separated by centrifugation at 3500 rpm for 8 min, and a 4.5 mL of MTBE extract was removed from the solution. The aqueous mixture was extracted with another 5 mL of MTBE for second time and the two organic extracts were combined in a second polypropylene tube. The solvent was allowed to evaporate under a gentle stream of N<sub>2</sub> to almost dryness and then reconstituted with 5.0 mL of methanol.

For the evaluation of the clean-up method using Envicarb cartridge, target analytes were spiked into sludge at 100 ng/g for PFCAs

**Table 1**  
Optimized LC–MS/MS parameters for the determination of target fluorochemical analytes in sludge samples.

Analytes	Transition monitored ( <i>m/z</i> )	Collision energy (eV)	Cone voltage (V)	LOD (pg)	LOQ (ng/g)	Elution time (min)
PFCAs						
PFPeA	<b>263</b> → <b>219</b> <sup>a</sup>	7	–30	0.4	1.2	5.4
PFHxA	<b>313</b> → <b>269</b>	7.5	–30	0.2	0.6	7.5
	313 → 119	19				
PFHpA	<b>363</b> → <b>319</b>	7.5	–30	0.2	0.6	8.7
	363 → 169	15.5				
PFOA	<b>413</b> → <b>369</b>	7.5	–32	0.2	0.6	9.9
	413 → 169	16.5				
PFNA	<b>463</b> → <b>419</b>	7.5	–32	0.2	0.6	10.9
	463 → 219	15				
PFDoA	<b>613</b> → <b>569</b>	7.5	–36	1	3	11.6
PFTeA	<b>713</b> → <b>669</b>	7.5	–40	1	3	12.9
6:2 FTUCA	<b>357</b> → <b>293</b>	8	–35	0.3	1	8.9
8:2 FTUCA	<b>457</b> → <b>393</b>	8	–40	0.3	1	11.1
PFSAs						
PFBS	<b>299</b> → <b>99</b>	26.5	–76	2	6	3.8
	299 → 80	26.5				
PFHxS	<b>399</b> → <b>99</b>	30	–92	2	6	4.6
	399 → 80	40				
PFOS	<b>499</b> → <b>99</b>	19	–104	2	5	7.8
	499 → 80	45				
FOSA	<b>498</b> → <b>78</b>	24	–70	1	3	10.3
<i>n</i> -MeFOSA	<b>512</b> → <b>169</b>	24	–70	1.5	5	11.1
	512 → 219	20				
<i>n</i> -EtFOSA	<b>526</b> → <b>169</b>	23	–70	1.5	5	11.3
	526 → 219	20				
<i>n</i> -MeFOSAA	<b>570</b> → <b>419</b>	16	–81	8	25	8.7
	570 → 483	12.5				
<i>n</i> -EtFOSAA	<b>584</b> → <b>419</b>	16	–81	10	30	8.9
	584 → 483	12.5				
Internal standard <sup>b</sup>						
MPFBA	<b>217</b> → <b>172</b>	6.5	–30	N/A <sup>c</sup>	N/A	0.9
MPFHxA	<b>315</b> → <b>270</b>	7.5	–30	N/A	N/A	7.5
MPFOA	<b>417</b> → <b>372</b>	7.5	–32	N/A	N/A	9.9
MPFOS	<b>503</b> → <b>80</b>	19	–104	N/A	N/A	7.8
<i>d</i> - <i>n</i> -MeFOSA	<b>515</b> → <b>169</b>	24	–70	N/A	N/A	11.1
MFHUEA	<b>359</b> → <b>294</b>	8	–35	N/A	N/A	8.9

<sup>a</sup> Bold transition monitored was used for quantification.

<sup>b</sup> Internal standards selected for this study and these were analyte-dependent: MPFBA was selected for PFPeA, MPFHxA was selected for PFHxA and PFHpA, MPFOA was selected for PFCAs with carbon chain length from C8 to C14, MPFOS was selected for PFBS, PFHxS and PFOS, *d*-*n*-MeFOSA was selected for FOSA, *n*-MeFOSA, *n*-EtFOSA, *n*-MeFOSAA and *n*-EtFOSAA, and MFHUEA was selected for 6:2 FTUCA and 8:2 FTUCA.

<sup>c</sup> N/A, not available.

and FTUCAs, and 200 ng/g for PFSAs, FOSAs and FOSAA. The cartridge was conditioned by 5 mL of 0.1% NH<sub>4</sub>OH in methanol, 5 mL of water and 5 mL of methanol. Then, 5 mL of extracts was passed through the preconditioned cartridge at a rate of 1 drop/s, and the cartridge was eluted with 5 mL of methanol. Both the extracts and the elutes were collected and combined after passing through cartridge.

To further reduce matrix interferences, and improve the shape of analyte peak (especially of PFCAs), 430 μL of 0.01% NH<sub>4</sub>OH in water was added to 1000 μL of sample extracts in methanol to obtain methanol/0.01% NH<sub>4</sub>OH aqueous solution ratio of 70/30 (v/v) [25]. Ten nanogram internal standards (10 μL, 1 ng/μL) were added to the final sample before injection to correct for matrix interferences.

### 2.3.2. Methanol extraction method

For comparison with the IPM, we also tested a methanol extraction method (MEM), adapted from Powley et al. [27]. Briefly, 0.5 g of dried sludge sample was extracted three times with 2.5, 1.5, and 1.0 mL aliquots of methanol, in sequence. Each extraction was performed by shaking the slurry for 10 min, sonication for 10 min at 40 °C and centrifugation at 3500 rpm for 8 min. The extracts were combined to a total volume of 5 mL and the extract was cleaned up by the Envicarb method.

### 2.4. Liquid chromatography–tandem mass spectrometry

Analysis of the target analytes was performed by a Varian 1200 LC–MS/MS system. Separation of the target analytes was achieved by a 70 mm × 2 mm × 3 μm Nucleodur C<sub>18</sub> gravity column (Macherey–Nagel, Germany). Injection volume was 20 μL. Mobile phases of 2.5 mM NH<sub>4</sub>Ac in methanol/water 95:5 (A) and 2.5 mM NH<sub>4</sub>Ac in water/methanol 95:5 (B) were used. Target analytes were separated at a flow rate of 0.25 mL/min with two different mobile phase gradients: (i) Gradient for PFCAs and FTUCAs was as follows: the mobile phase was ramped from 20% to 50% A in 4 min, then to 75% A in 10 min, then maintained at 75% A for 1 min, then ramped to 20% A in 1 min, and then held for 9 min for equilibration; (ii) Gradient for PFSAs, FOSAs and FOSAA was as below: ramped from 5% to 60% A in 0.8 min, then to 100% A at 12.5 min, then maintained at 100% A for 1 min, then ramped to 5% A in 1 min, and then held for 10 min for equilibration. The MS–MS was operated in electrospray negative ionization mode. The parameters were: ion spray voltage at –3500 V, source temperature at 200 °C for PFCAs and FTUCAs at –4500 V and 350 °C for PFSAs, FOSAs and FOSAA; nebulizer gas 75 psi, housing temperature 50 °C, shield voltage –600 V, detection voltage 1650 V, and collision gas 3.50 Torr. Multiple reaction monitoring mode (MRM) abundant ions generated by collision induced fragmentation. The transitions are shown in Table 1.

## 2.5. Quantification and confirmation

For all target analytes, quantification was performed using an inverse weighted ( $1/X$ ) internal standard calibration curve (ICC) with calibration standards (containing 10 ng of each internal standard) prepared in 70:30 methanol/0.01%  $\text{NH}_4\text{OH}$  aqueous solution. A seven point calibration curve, spanning from 0.1 to 20 ng/mL for PFCAs and FTUCAs, and 0.25 to 50 ng/mL for PFSAs, FOSAs and FOSAs, was performed at the beginning and at the end of every sample batch. Solvent blanks were used to monitor instrument background. Calibration verification standards were used to monitor the validity of the calibration during the sample run and injected between every five samples. For each analyte, all points in the calibration curve were calculated to be within 20% of the actual values and the correlation coefficients ( $r^2$ ) were greater than 0.99. The internal standards selected for this study were MPFBA, MPFHxA, MPFOA, MPFOS, and d-*n*-MeFOSA and MFHUEA and these were analyte-dependent: MPFBA was selected for perfluoropentanoic acid (PFPeA), MPFHxA was selected for perfluorohexanoic acid (PFHxA) and perfluoroheptanoic acid (PFHpA), MPFOA was selected for PFCAs with carbon chain length from C8 to C14, MPFOS was selected for PFBS, PFHxS and PFOS, d-*n*-MeFOSA was selected for FOSA, *n*-MeFOSA, *n*-EtFOSA, *n*-MeFOSAA and *n*-EtFOSAA, and MFHUEA was selected for 6:2 FTUCA and 8:2 FTUCA. The identity of the target analytes was confirmed by quantification and the ratios of two MRM transitions for each analyte (Table 1).

## 2.6. Determination of method accuracy and precision

The accuracy and precision of both IPM and MEM were evaluated using sequential extraction experiments, standard addition, and matrix spike experiments. First, to evaluate whether the IPM's extraction procedure was capable of completely removing the analyte from the sewage sludge, sequential extraction experiments were conducted. Twenty nanogram per gram of each internal standard, and 80 ng/g of each native standard were spiked into sludge sample ( $n = 5$ , aged for 24 h). All spiked samples and corresponding un-spiked samples were conducted by extracting for three times (with 5 mL of MTBE for each time), and analyzing each extraction step separately. The sequential extraction profiles generated were then used to determine whether the concentrations of PFCs present in the extract accurately reflected the concentrations present on the environmental sample.

Standard addition was performed for a subset of the cleaned sludge extracts to evaluate matrix effects occurring in LC-MS/MS analysis procedure. Standard addition was carried out by adding 100  $\mu\text{L}$  of standard solutions with increasing concentrations of each analyte into 900- $\mu\text{L}$  aliquots of final sample extraction solution. Native standards were spiked at 0.1, 0.5, 1.25, 2.5, 5.0, 20 ng/mL for PFCAs and FTUCAs, and at 0.25, 1, 2.5, 5.0, 10, 50 ng/mL for PFSAs, FOSAs and FOSAs. Prior to LC-MS/MS analysis, 10  $\mu\text{L}$  internal standards (1 ng/ $\mu\text{L}$ ) and 430  $\mu\text{L}$  aqueous  $\text{NH}_4\text{OH}$  (0.01%) were added to each sample aliquot. All spiked extracts and the corresponding un-spiked extracts were analyzed using the same protocol. Matrix-matched-calibration curve (MCC) containing all spiked standards was calculated by inverse weighted ( $1/X$ ) internal standard method. By comparing the slope of MCC to the slope of ICC (internal standard calibration curve), the magnitude of matrix effect was evaluated. The formula for the calculation of ion suppression (or enhancement) was as follows: matrix effect (%) =  $(100 \times \text{slope}_{\text{MCC}} / \text{slope}_{\text{ICC}}) - 100$ , a negative value represents ion suppression, and a positive value represents ion enhancement.

To evaluate the accuracy of the method as a whole, matrix spike experiments were performed by spiking low, medium and high levels of PFCs into sludge sample, with the range of 10–300 ng/g. The spiked samples were extracted and analyzed. Recoveries of the

**Table 2**

Matrix effects<sup>a</sup> of internal standards in extracts cleaned by Envicarb cartridge while using ion-pair extraction method.

Internal standard	Peak area		Matrix effect (%)
	Extracts ( $n = 3$ )	Standard ( $n = 7$ )	
MPFBA	2.73E+07	3.31E+07	-18
MPFHxA	3.59E+08	3.12E+08	+15
MPFOA	4.06E+08	3.35E+08	+24
MFHUEA	2.82E+08	2.45E+08	+15
MPFOS	6.27E+06	7.23E+06	-13
d- <i>n</i> -MeFOSA	3.46E+07	4.39E+07	-20

<sup>a</sup> Matrix effect =  $(100 \times \text{the peak area of internal standard in extracts} / \text{the peak area of internal standard in standard solution}) - 100$ , positive value represents ion enhancement, negative value represents ion suppression. In this study, the same concentration of internal standard (10 ng/mL) was spiked in extracts and standard solution. Therefore, the ratio of peak area of internal standard in extracts and standard solution could be selected to reflect matrix effect.

spiked analytes were calculated by comparison of the concentration calculated by ICC and the spiked concentration. All extraction recoveries determined for sludges accounted for the presence of PFCs detected in the un-spiked sludge. The precision of the entire method was determined by calculating the relative standard deviation (RSD).

## 2.7. Contamination test

All the tubings in the LC-MS/MS system were changed to polyether ether ketone (PEEK) when possible. The PFC contamination in solvents was checked by concentrating the solvents and injecting them into the LC-MS/MS. Experimental vessels used in the extraction procedure were also analyzed for contamination by soaking them with methanol.

## 2.8. Determination of limits of detection and quantification

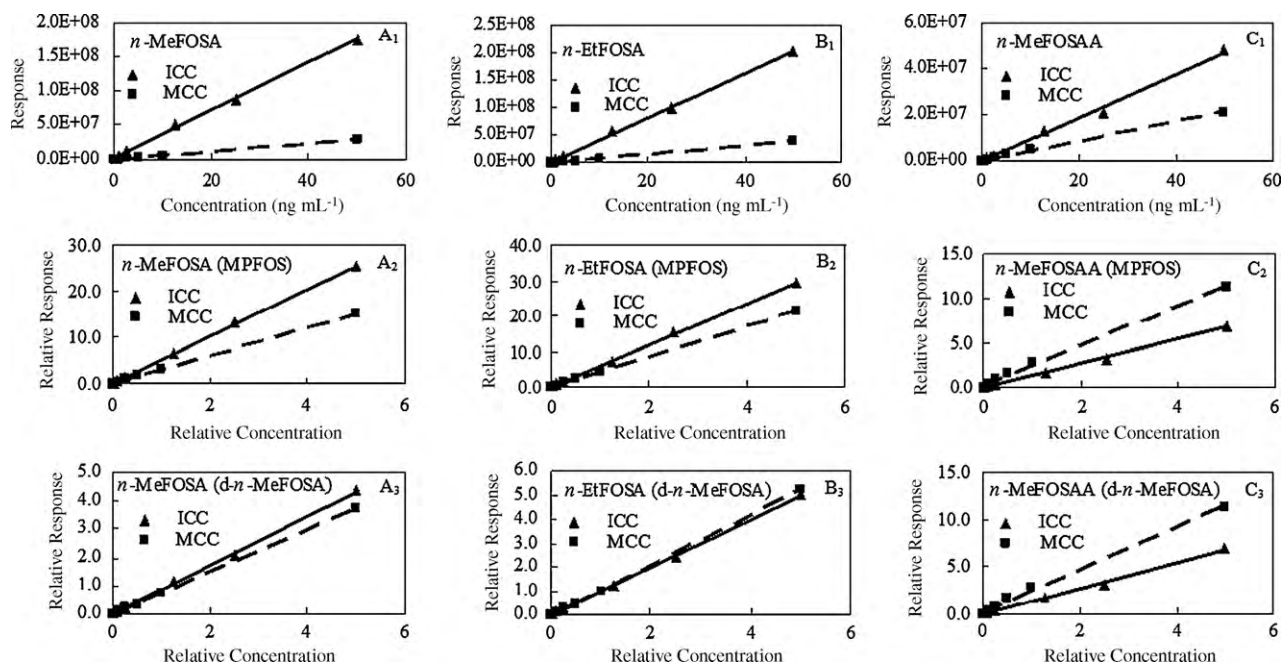
The LOD was defined as those concentrations of target analytes that were needed to produce a signal-to-noise (S/N) ratio of 3:1. The LOD was 0.2–1.0 pg for PFCAs and FTUCAs, 1–10 pg for PFSAs, FOSAs and FOSAs (Table 1). The LOQ was defined as those concentrations of target analytes that were needed to produce  $S/N \geq 10$ . The sample based LOQ for a 500 mg sludge sample was 0.5–3 ng/g for PFCAs and FTUCAs, and 3–30 ng/g for PFSAs, FOSAs and FOSAs, respectively.

## 3. Results and discussion

### 3.1.1. Clean-up method using Envicarb cartridge for ion-pair extraction

The selection of an optimized clean-up method was aimed to eliminate or reduce the matrix-induced ion suppression or enhancement. In the present study, our results showed that Envicarb cartridge reduced the color of the extracts efficiently, indicating efficient removal of colored substances. Repeated injections of colored extracts (non-treated with Envicarb) required frequent cleaning of the interface to maintain sensitivity and should be avoided [27]. Furthermore, the matrix effect using Envicarb clean-up method was low at the range of -13% to +24% (Table 2).

Envicarb adsorbs compounds via dispersive interaction with  $\pi$  electrons. As the perfluoroalkyl chain of the target PFCs contains no  $\pi$  electrons, there is no possibility for specific  $\pi$ - $\pi$  interactions between Envicarb and PFCs. Therefore, PFCs would not interact effectively with the sorbent, even in the presence of a weak eluting solvent like methanol. However, organic compounds with any degree of aromaticity will be strongly associated with the Envicarb,



**Fig. 1.** Matrix effects of selected target analytes with and without calibration by different internal standards using ion-pair extraction method. *Note:* Relative response (ordinate) means the relative peak area of target analytes as compared to the peak area of internal standard, relative concentration (abscissa) means the relative spiked concentration of target analytes as compared to that of internal standard; ICC means internal standard calibration curve, MCC means matrix-matched-calibration curve, more detailed information of ICC and MCC are given in Sections 2.5 and 2.6; plots A<sub>1</sub>, B<sub>1</sub> and C<sub>1</sub> did not have internal standard correction, MPFOS was used as internal standard for plots A<sub>2</sub>, B<sub>2</sub> and C<sub>2</sub>, and d-*n*-MeFOSA was used as internal standard for plot A<sub>3</sub>, B<sub>3</sub> and C<sub>3</sub>.

resulting in a very effective purification [27]. Therefore, Envicarb cartridge was selected for the clean-up of sludge extracts.

### 3.2. Selection of internal standards for ion-pair extraction

Stable isotope labeled target analytes can be used to compensate for matrix effects [8]. In this study, to evaluate signal suppression (or enhancement), the slope of MCC was compared with the slope of ICC, as illustrated in Fig. 1. Ion suppression (or enhancement) resulted in a lowered (or elevated) slope for MCC, as compared to that of ICC. Fig. 1 (A<sub>1</sub>, B<sub>1</sub> and C<sub>1</sub>; Table 3) shows matrix effects of *n*-MeFOSA, *n*-EtFOSA and *n*-MeFOSAA, respectively, when calibration by the internal standard was not performed. Prominent ion suppression was observed for *n*-MeFOSA (−78%), *n*-EtFOSA (−75%) and *n*-MeFOSAA (−55%) (Table 3), while the ion suppression of *n*-MeFOSA and *n*-EtFOSA could be corrected by selecting an appropriate internal standard. The ion suppression was corrected to −40% and −14% for *n*-MeFOSA (Fig. 1 A<sub>2</sub> and A<sub>3</sub>; Table 3), and to −30% and −5% for *n*-EtFOSA (Fig. 1 B<sub>2</sub> and B<sub>3</sub>; Table 3), when calibrated by internal standards of MPFOS and d-*n*-MeFOSA, respectively. The slope of MCC was closer to the slope of ICC when d-*n*-MeFOSA was used as the internal standard as compared to MPFOS, because d-*n*-MeFOSA has similar physical and chemical properties to *n*-MeFOSA and *n*-EtFOSA, suggesting that physical and chemical similarities are important when selecting internal standard [28]. Therefore, d-*n*-MeFOSA is more suitable internal standard for *n*-MeFOSA and *n*-EtFOSA than MPFOS. Furthermore, as shown in Fig. 1 (C<sub>1</sub>, C<sub>2</sub> and

C<sub>3</sub>), neither d-*n*-MeFOSA nor MPFOS could function well as an internal standard for *n*-MeFOSAA. The ion enhancement for *n*-MeFOSAA was still +35% and +30% when d-*n*-MeFOSA and MPFOS were used as internal standards, respectively (Table 3).

Overall, most of the internal standards selected in this study can correct matrix effects of the corresponding analytes to low levels. For FOSAs and PFCAs with carbon chain length from C<sub>6</sub> to C<sub>14</sub>, matrix effects ranged from −14% to +28%, as shown in Table 4. These results indicate that an appropriate internal standard corrects for ion suppression (or enhancement) induced by co-eluting matrix components present in sample extracts, and that similar physical and chemical properties to the target compound are an important criterion when selecting an internal standard.

### 3.3. Accuracy and precision of ion-pair extraction method

The results of sequential extraction experiments clearly indicate that two extractions (5 mL of MTBE for each time) were enough to extract the target compounds from sludge. Recoveries of first time extraction for all target analytes were generally good with the range of 85–153%, except for PFBS (52%) (Fig. 2); for PFCAs, recoveries of first extraction were higher than 100%, due to ion enhancement occurring in LC-MS/MS analysis procedure. In this experiment, clean-up procedure was not used. Although most of the total mass of the analytes was extracted by first time extraction, 0–25% of recoveries for analytes were obtained after second extraction (Fig. 2). The recoveries of third extraction were 0% for most of analytes (Fig. 2).

The matrix effect was eliminated and corrected by optimizing the clean-up method and by selecting appropriate internal standards (Table 4). For FOSAs and PFCAs (C<sub>6</sub>–C<sub>14</sub>), matrix effects were eliminated and corrected to be within −14% to +28% and −1% to +10%, respectively. However, large matrix effects remained for 6:2 FTUCA (+39%), 8:2 FTUCA (+114%), PFBS (−45%), PFHxS (−56%), *n*-MeFOSAA (+35%), and *n*-EtFOSAA (+43%). The addition of isotope labeled analogues to samples could correct for these effects,

**Table 3**  
Calculated matrix effect (%) of selected target analytes while using different internal standard.

Internal standard	<i>n</i> -MeFOSA	<i>n</i> -EtFOSA	<i>n</i> -MeFOSAA
– <sup>a</sup>	−78	−75	−55
MPFOS	−40	−30	+30
d- <i>n</i> -MeFOSA	−14	+5	+35

<sup>a</sup> (–) means no internal standard was used.

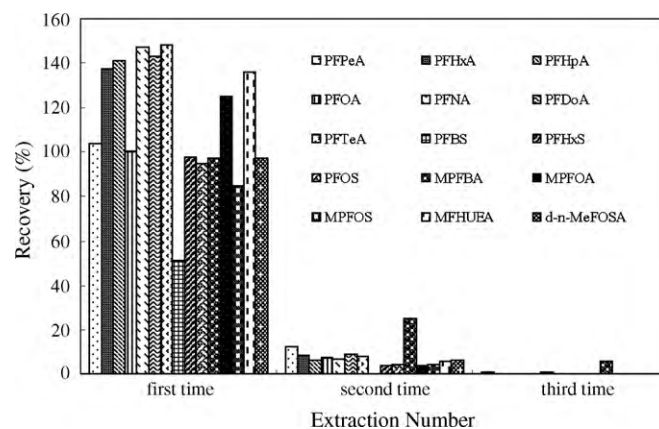
**Table 4**  
Matrix effects (%) of ion-pair extraction and methanol extraction during LC-MS/MS analysis procedure.

Target analytes	PFPeA	PFHpA	PFOA	PFNA	PFDoA	PFTeA	6:2 FTUCA	8:2 FTUCA	FTUCA	PFBS	PFHxS	PFOS <sup>c</sup>	FOSA	n-MeFOSA	n-Et FOSA	n-Me FOSAA	n-Et FOSAA
IPM <sup>a</sup>	+62	-2	+10	+8	+6	-1	+39	+114	-1	-45	-56		+28	-14	+5	+35	+43
MEM <sup>b</sup>	-4	+63	+5	+70	+81	+20	-3	-1	-1	-1	-10		-2	-2	+2	-26	-56

<sup>a</sup> IPM means ion-pair extraction method.

<sup>b</sup> MEM means methanol extraction method.

<sup>c</sup> The value of PFOS was not calculated due to the high background level (around 500 ng/g) in un-spiked sludge sample; all the values were calculated in the way that is shown in Section 2.6, positive and negative values of matrix effect were ion enhancement and suppression, respectively.



**Fig. 2.** Recoveries of sequential extraction of sludge for target analytes. *Note:* Five sludge samples were spiked to 80 ng/g of native standards, and 20 ng/g of internal standards, and aged for 24 h prior to extraction; 0% of recoveries for target analytes (second time extraction: PFBS; third time extraction: PFHxA, PFHpA, PFOA, PFNA, PFTeA, PFBS, PFHxS, PFOS, MPFOA, MPFOS, MFHUEA, d-n-MeFOSA) indicates that the concentration of these target analytes was less than LOQ; MPFHxA was not spiked due to this standard was unavailable.

enabling an accurate determination of their native analogues [35]. However, obvious matrix effects were found for FTUCAs although an appropriate internal standard, MFHUEA, has been used for FTUCAs analysis in this study, the reason for great matrix effect for 6:2 FTUCA and 8:2 FTUCA is unknown. For PFBS, PFHxS, n-MeFOSAA and n-EtFOSAA, no <sup>13</sup>C-labeled analogues were available at the time of the study and therefore correction for matrix effects by selecting an appropriate internal standard could not be accomplished.

Mean recoveries of the analytes by IPM as a whole were generally good, with the range of 70–131% for most analytes from dry sludge spiked at different levels (Table 5). Nevertheless, the recoveries of FOSA (low level), perfluorododecanoic acid (PFDoA, medium level) and n-EtFOSAA (high level) were low, being 47%, 64% and 53%, respectively. The low recovery for FOSA might be due to the neutral and hydrophobic nature of this compound [36]. The reason for the low recoveries for PFDoA may be the lowered ion-pair formation because long-chain PFCAs appear to bind strongly to particles [37]. Besides, we ascribed the low recovery of n-EtFOSAA to the fact that no suitable internal standard could be used. The recoveries of PFHpA and PFNA were high at low spiking level, being 169% and 156%, respectively. The low level spiked (10 ng/g) and background concentration, and possible laboratory contamination in sludge are the possible reasons for these high recoveries. The RSDs for all target analytes ranged from 2% to 10% when spiking at high level, generally lower than the RSDs at medium level (2–20%) and low level (5–36%) (Table 5), suggesting that the extraction method gave better precision for high concentration of PFCs in sludge, this result agrees with a previous report [28]. The RSD values of all spike levels are acceptable considering the matrix complexity [29] and are comparable to those reported in literatures [27–30]. Therefore, the precision of IPM for PFCs in sludge is considered satisfactory.

### 3.4. Contamination test

Methanol was concentrated from 50 to 1 mL to test for PFCs contamination. The concentrated methanol contained 0.13 ng/mL PFOA and 0.06 ng/mL perfluorononanoic acid (PFNA), which corresponded to 0.05 ng/g PFOA and 0.02 ng/g PFNA in sludge, respectively. No other target analytes were found in methanol. The contamination in methanol may arise from the Teflon lined cap. The washings of pipette tips and HPLC vials contained trace levels of target PFCAs. So, all the items were washed with methanol before use. Finally, the contamination level of the whole analyti-

**Table 5**  
PFCs matrix recovery of two extraction methods.

Target analytes	Low level spike				Medium level spike				High level spike			
	IPM <sup>a</sup> (n = 3)		MEM <sup>b</sup> (n = 3)		IPM (n = 3)		MEM (n = 1)		IPM (n = 5)		MEM (n = 5)	
	Spike level (ng/g)	Recovery (mean ± RSD, %)	Spike level (ng/g)	Recovery (mean ± RSD, %)	Spike level (ng/g)	Recovery (mean ± RSD, %)	Spike level (ng/g)	Recovery (mean ± RSD, %)	Spike level (ng/g)	Recovery (mean ± RSD, %)	Spike level (ng/g)	Recovery (mean ± RSD, %)
PFPeA	0	– <sup>c</sup>	–	–	80	115 ± 13	50	116	150	99 ± 5	150	121 ± 4
PFHxA	0	–	–	–	80	94 ± 11	50	122	150	119 ± 3	150	130 ± 4
PFHpA	10	169 ± 36	10	165 ± 17	80	95 ± 11	50	159	150	93 ± 6	150	120 ± 4
PFOA	10	120 ± 5	10	107 ± 1	80	93 ± 15	50	116	150	124 ± 3	150	129 ± 4
PFNA	10	156 ± 13	10	125 ± 15	80	81 ± 13	50	152	150	112 ± 5	150	139 ± 3
PFDoA	10	84 ± 11	10	63 ± 6	80	64 ± 19	50	137	150	81 ± 4	150	116 ± 1
PFTeA	0	–	–	–	0	–	0	–	0	–	0	–
6:2 FTUCA	0	–	–	–	80	105 ± 5	50	93	150	104 ± 2	150	105 ± 2
8:2 FTUCA	0	–	–	–	80	123 ± 3	50	88	150	109 ± 5	150	100 ± 2
PFBS	10	105 ± 19	10	85 ± 9	150	90 ± 20	100	93	300	144 ± 5	300	117 ± 4
PFHxS	10	78 ± 6	10	75 ± 4	150	103 ± 11	100	131	300	131 ± 5	300	104 ± 7
PFOS	10	84 ± 11	10	75 ± 1	150	82 ± 13	100	78	786 <sup>d</sup>	92 ± 8	786	80 ± 12
FOSA	10	47 ± 16	10	59 ± 21	150	103 ± 18	100	93	300	116 ± 8	300	135 ± 6
n-MeFOSA	0	–	–	–	150	96 ± 10	100	89	300	93 ± 7	300	105 ± 2
n-EtFOSA	0	–	–	–	150	100 ± 15	100	86	300	73 ± 7	300	92 ± 6
n-MeFOSAA	0	–	–	–	150	73 ± 2	100	57	300	70 ± 6	300	59 ± 13
n-EtFOSAA	0	–	–	–	150	80 ± 14	100	61	300	53 ± 10	300	53 ± 17

<sup>a</sup> IPM means ion-pair extraction method.

<sup>b</sup> MEM means methanol extraction method.

<sup>c</sup> Represents analytes were not analyzed.

<sup>d</sup> 786 ng/g of PFOS was spiked due to high background in un-spiked sample.

**Table 6**  
Concentrations (ng/g) of target analytes in sludge samples by both ion-pair extraction and methanol extraction method.

Sample ID	PFHxA	PFHpA	PFOA	PFNA	PFDoA	$\sum$ PFCa	PFOS	6:2 FTUCA	8:2 FTUCA	FOSA
Concentrations (by ion-pair extraction)										
Sludge 1	4.3	1.3	9.1	3.1	3.8	21.6	670	3.4	6.1	3.7
Sludge 2	3.4	2.4	5	2.1	4	16.9	117	2.1	5.4	4.2
Sludge 3	3.9	1.1	7.2	1.8	4.7	18.7	213	2.7	14.8	2.7
Concentrations (by methanol extraction)										
Sludge 1	5	1.7	11.6	<0.6	5.5	23.8	1121	2.8	5.8	4.5
Sludge 2	2.4	<0.6	4.3	<0.6	6.9	14.6	176	<1.0	4.6	3.5
Sludge 3	1.8	1.5	5.6	3.1	5.9	17.9	383	2.6	11.4	2.3
Relative standard deviations (%) of concentration value by both of methods										
Sludge 1	8	13	12	N/A <sup>a</sup>	18	5	25	9	3	10
Sludge 2	17	N/A	8	N/A	27	7	20	N/A	8	9
Sludge 3	37	15	13	27	11	2	29	2	13	8

<sup>a</sup> N/A, not available. Sludge 1, sludge 2 and sludge 3 were sludge samples collected from Dübendorf, Horgen and Wädenswil, respectively; concentrations of PFPeA, PFTeA, PFBS, PFHxS, *n*-MeFOSA, *n*-EtFOSA, *n*-MeFOSAA and *n*-EtFOSAA were not shown as their values were less than LOQ.

cal procedure was checked by passing quartz through the entire analytical procedure. The procedural blank extract contained 1.41 and 0.33 ng/g level of PFOA and PFNA, while the other target PFCAs were not detected. No contamination was found for PFSAs and all precursor compounds.

### 3.5. Limit of detection and quantification

The instrument responses (sensitivity) to PFCAs, FTUCAs and FOSAs were three to five times higher than those for PFSAs and FOSAs. Therefore, the LODs were low (0.2–1.5 pg) for PFCAs, FTUCAs and FOSAs, and the corresponding LOQs (for 500 mg sludge sample) were from 0.6 to 5 ng/g. The LOQs of PFSAs and FOSAs ranged from 5 to 30 ng/g. These LOQs are generally lower than the concentrations found in the sludge samples.

### 3.6. Comparisons of ion-pair method (IPM) and methanol extraction method (MEM)

The analytical protocol of MEM is straightforward and robust, including methanol extraction followed by Envicarb clean-up [27]. This method was adapted for many applications due to its simple handling and reliable results. Herein, we evaluated the feasibility of IPM and compared the accuracy and precision of IPM and MEM. The matrix effects of IPM and MEM are given in Table 4.

In general, matrix effects from IPM for PFCAs (C6 to C14) ranged from –1% to +10%, much lower than MEM (+5% to +81%), but more obvious matrix effects were prominent in the IPM (–45% to +114%) for FTUCAs, PFBS and PFHxS. For FOSAs, IPM enhanced ionization by +35% to +43%, but MEM suppressed ionization by –56% to –26% (Table 4). Clean-up using SPE cartridges and spiking of stable isotope labeled analogues of the target analytes as internal standards were two approaches for elimination/reduction or correction for matrix effects. In this study, however, the same clean-up procedure and internal standards were used for IPM and MEM. Therefore, selection of clean-up and internal standard are not the reason for the different matrix effects observed with two extraction methods. One possible explanation is the influence of the extraction procedure, such as different solvent and pH value of the solvent.

The recoveries for target analytes by the two extraction methods are summarized in Table 5. With MEM, mean recoveries were in the range of 70–165% for most analytes at different spike levels. These values are generally comparable to those of IPM. Higher recoveries were found for PFCAs for medium and high spike levels using MEM. Ionization enhancement (Table 4) for PFCAs (e.g., PFHpA, PFNA, PFDoA and perfluorotetradecanoic acid (PFTeA)) was the reason for the high recoveries [38]. Furthermore, RSDs of the two extraction methods (Table 5) were similar, at  $\leq$ 20% (except

PFHpA and FOSA). Overall, compared to MEM, the accuracy and precision of IPM were optimal for application to sludge samples.

### 3.7. Analysis of environmental samples

The ion-pair extraction was applied for the analysis of sewage sludge collected in WWTPs nearby Zürich, Switzerland. Determination of PFCs in the sludge samples revealed concentrations of  $\sum$ PFCAs and PFOS ranging from 16.9 to 21.6 ng/g and 117 to 670 ng/g, respectively (Table 6). Among PFCAs, PFOA (5.0 to 9.1 ng/g) was the most predominant compound, followed by PFDoA, PFHxA, PFNA and PFHpA. Concentrations of PFTeA and PFPeA were below the LOQ. Compared to the data reported in the literatures [27–30] for sludge from other countries, this study shows that the contamination level of PFCAs in the sludges from the region of Zürich is on the same order of magnitude. PFOS was the major compound in sludge, much higher than the concentrations of other PFCs.

6:2 FTUCA and 8:2 FTUCA were detected in all samples, ranging from 2.1 to 3.4 ng/g and 5.4 to 14.8 ng/g, respectively, these concentrations are compared to, and in several cases exceed, the level of their potential breakdown products, such as PFHxA and PFOA (Table 6). Moreover, the concentrations of even-chain PFCAs (e.g., PFHxA, PFOA and PFDoA) were higher than odd-chain PFCAs (PFHpA and PFNA) in sludge samples (Table 6). The pilot study indicate that degradation of FTOH and other related precursors were a possible source of even-chain PFCAs in sewage sludge [19], but this conclusion is tentative. FOSAs and FOSAs were not detected in any of the samples, except for FOSA which was found at 2–5 ng/g, much lower than the concentration of PFOS. This was different from the previous report which showed the presence of FOSAs in sludge at levels often exceeding PFOS [28]. The finding in this study suggests that transformation of precursors within wastewater treatment is not an important source of PFOS.

The measured concentrations of each target compound in tested sludges (Table 6, sludges 1, 2, and 3) were similar by using IPM and MEM. The RSDs between concentrations measured by IPM and MEM, were less than 30% for most of target compounds, except that RSD was 37% for PFHxA in sludge 3. These results suggest that the extraction method developed in the present study is robust and reliable for environmental samples.

## 4. Conclusions

We present a new, simple and robust method based on ion-pair extraction and Envicarb cartridge clean-up, followed by LC–MS/MS for the analysis of PFCs in sewage sludge. The method is important to study occurrence, behaviour, and fate of PFCs in environment,

as it covers 7 PFCAs, 3 PFSAAs and seven relative precursors. In this study, we focused on the reduction of matrix effect for the determination of PFCs in sewage sludge. The clean-up using Envi-carb cartridge and addition of six labeled internal standards was effective for elimination/reduction and correction of matrix effects. Similar physical and chemical properties to target compounds are an important criterion for the selection of an internal standard. The accuracy and precision of IPM demonstrated in this study suggest that it can be used for the analysis of PFCs in solid matrices. The IPM was successfully applied to several sewage sludge samples, and the validity of IPM was further confirmed by comparing IPM to MEM.

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