

Analysis of Perfluorinated Chemicals and their Fluorinated Precursors in Sludge: Method Development and Initial Results

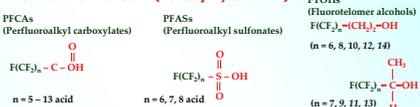
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ABSTRACT

A rigorous method was developed to maximize the extraction efficacy for perfluorinated chemicals (PFCs), fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAc), perfluorosulfonamides (FOSAs), and perfluorosulfonamidoethanols (FOSes) from wastewater-treatment sludge and quantitation using liquid-chromatography mass spectrometry (LC/MS/MS) and gas-chromatography (GC/MS). Of five solvents tested for their PFC extraction effectiveness, 50/50-ACN/MeOH(v/v) yielded the highest concentrations. Pretreatment of sludge with NaOH and HCl, prior to extraction, recovered additional PFCs, but KOH and K2S2O8 digestion were less effective than no pretreatment. Volatile fluorochlorinated in sludge were extracted with methyl tert-butyl ether (MTBE). NaOH-treated sludge resulted in recovery of more FTOHs, especially 8:2 FTOH. Presently we are investigating if this observation comes from the OH-facilitated hydrolysis of FTAc. With these efforts, we have been able to measure at least ten volatile fluorochlorinated from test sludge at the concentrations of sub-ng to tens ng/g, wet weight. The identification of a few suspected volatile fluorochlorinated, for which no standards exist, was evaluated with a derivatization technique.

MATERIALS AND METHODS

Chemicals of Concern (acronym, formula)



Selection of Appropriate Organic Extractant for PFCs

- Five candidate solvents were tested for 0.5g sludge: i) Acetonitrile (ACN), ii) Methanol (MeOH), iii) Isopropanol (IPA), iv) Tetrahydrofuran (THF), 50/50-ACN/MeOH (v/v)
- All sludge extracts were cleaned up with an ion-pairing method extraction
- Before a LC/MS/MS analysis, extract was filtered through a 0.22 um nylon filter

Testing of Sludge Pretreatment for PFCs

- Four pretreatments were evaluated for 0.5g sludge: i) 1M sodium hydroxide (NaOH), ii) 1M potassium hydroxide (KOH), iii) 1M hydrochloric acid (HCl), and iv) 0.2M potassium persulfate (K₂S₂O₈)
- About 0.5g wet sludge was spiked with each 5ng of ¹³C₁-PFOA and ¹³C₁-PFOS, and pretreated with 1 mL of each chemical for 30 min in a hot-bath.

Testing of Extract-Cleanup Methods for PFCs

- Three extract-cleanup techniques were compared: i) ion-pairing, ii) weak-anion exchange (WAX) cartridge, iii) hydrophilic-lipophilic (HLB) cartridge

Selection of Appropriate Pretreatment for FTOHs

- Four pretreatments were evaluated for 1g sludge: i) 2.5mL of H₂O, ii) 2.5mL of 8M Urea, iii) 2.5mL of Formic Acid, and iv) 2.5mL of NaOH (later neutralized)
- All treatments were sonicated in a hot bath for 30 min
- 5 mL of MTBE was added as an extractant for overnight extraction
- One milliliter extract was spiked with 1 ng of mass-labeled 10:2FTOH (an internal matrix standard)

LC/MS/MS Analysis

- The Waters Acquity ultra-performance liquid chromatograph (UPLC) was operated using ACN and polished water eluent, both containing 0.075% (v/v) glacial acetic acid. Pumping at a constant total flow rate of 0.5 mL/min, we started runs with an eluent of 35/65 (v/v) ACN/water, then linearly ramping to 90/10 at 5 min, holding composition constant until 11 min and back to 65/35 at 11.1 min
- Sludge extracts were analyzed on a Waters Quattro Premier XE tandem mass spectrometer interfaced with the UPLC. Twenty microliters of extract were withdrawn and introduced into a Waters BEH C18 guard followed by a Waters BEH C18 analytical column. The MS/MS was operated in ESI (-) and analytes were monitored using MRM mode. Detailed instrumental conditions are found in Ref. 1

GC/MS Analysis

- Soil extracts were analyzed on an Agilent Technologies 6890 GC system equipped with a 5975N mass selective detector (MSD). The MSD was operated in the positive chemical ionization (PCI) mode with methane reagent gas. Compound separation and quantification were performed on a Restek Rtx-1701 capillary column (30m x 0.25mm I.D. x 0.25µm film thickness) with a 10m deactivated Integra-Guard™ guard column as the inlet. Sample volumes of 1 µL were injected. A selected-ion monitoring (SIM) program was constructed. Detailed instrumental conditions are found in Ref. 2

RESULTS & DISCUSSION

Chromatographic Separation (Fig. 1)

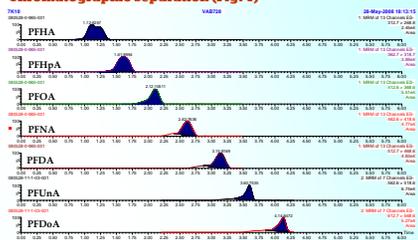


Figure 1. Typical LC/MS/MS chromatogram of selected PFCs from sludge extract.

Extraction Strength of Test Solvent for PFCs

- Among the test extractants, 50/50-ACN/MeOH(v/v) and THF extracted the greatest concentrations of PFCs from test sludge (Fig. 2)
- Due to special handling requirement for THF and its strong ability to draw more non-organic compounds, we selected a 50/50-ACN/MeOH as an extractant for PFCs
- Recoveries of fortified mass-labeled PFOA and PFOS before extraction were ranged from 91% to 99% and from 82% to 99%, respectively

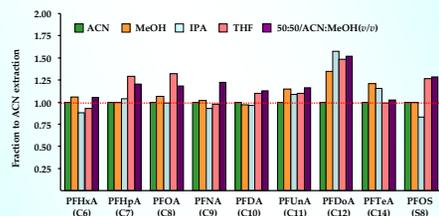


Figure 2. Extractability of different organic solvents. Extractable PFC concentrations were normalized to those from ACN extraction. MPFOA and MPFOS were used as extraction internal standards.

Efficacy of Chemical Pretreatments on PFCs Analysis

- Pretreatment with sonication in 1M NaOH before solvent extraction yielded the most PFCs from sludge, followed by 1M HCl (Table 1)
- Extracting efficacy of 1M KOH and 0.2M K₂S₂O₈ was comparable each other, and equal to an elemental extraction
- % recoveries (n=4, (s.d.)) of a mass-labeled PFOA used as recovery internal standard for each pretreatment were: an elemental ACN/MeOH = 94 (6), NaOH = 92 (5), KOH = 45 (14), HCl = 101 (12), and K₂S₂O₈ = 51 (9). The % recoveries of a mass-labeled PFOS were: elemental ACN/MeOH = 90 (12), NaOH = 86 (5), KOH = 93 (16), HCl = 106 (11), and K₂S₂O₈ = 102 (12).
- Organic-rich Cowart soil was included as a reference matrix to evaluate overall extraction efficiency. The % recoveries of fortified PFCs into soil were 85% to 117%

Table 1. Total extractable concentrations (n=9) of PFCs in test sludge with pretreatment (ng/g dw)

| Pretreatment | PFHA | PFHpA | PFOA | PFNA | PFDA | PFUnA | PFDoA | PFTEA | PFOS |
|---|-----------|-----------|------------|----------|-----------|-----------|----------|----------|-------------|
| Elemental | 5.1 (0.7) | 3.1 (0.7) | 43.1 (2.3) | 3.4(0.4) | 18.4(1.8) | 20.9(3.5) | 1.9(1.0) | 5.8(1.3) | 289.1(10.4) |
| 1M NaOH | 7.7(0.4) | 4.2(0.5) | 50.3(4.7) | 4.7(1.0) | 20.7(0.8) | 20.0(2.7) | 2.5(0.5) | 4.6(0.9) | 346.3(44.4) |
| 1M KOH | 1.3 (0.6) | 1.5(0.7) | 27.9(6.4) | 2.3(0.8) | 13.1(1.5) | 13.4(0.5) | 1.7(0.2) | 3.9(0.6) | 350.7(62.8) |
| 1M HCl | 5.6(0.5) | 3.9(0.6) | 49.0(4.6) | 4.5(1.1) | 20.3(2.4) | 19.8(3.3) | 2.5(0.3) | 5.4(1.0) | 343.6(33.7) |
| 0.2M K ₂ S ₂ O ₈ | 4.4(1.2) | 3.1(0.5) | 30.8(4.4) | 2.7(0.5) | 12.9(2.4) | 12.4(3.6) | 1.8(0.5) | 3.2(2.1) | 309.3(11.0) |
| LOQ | 1.8 | 1.8 | 6.8 | 1.8 | 1.8 | 1.8 | 1.8 | 1.8 | 5.8 |

*Elemental represents a 50/50-ACN:H₂O extraction without any pretreatment

Testing of Extract-Cleanup Method for PFCs

- All cleanup methods without sludge extracts showed 85-97% (ion pairing), 82-104% (HLB), and 85-98% (WAX) of recoveries (1ng PFCs spike in 100 mL H₂O)
- In general, a HLB cleanup approach retained and yielded PFCs in sludge extracts (Table 2); also peak separation were better with HLB cleanup (chromatograms not shown)
- The final analytical method for PFCs analysis from sludge or biosolid samples were established using current efforts (Fig. 3)

Table 2. Recoverable PFC concentrations (n=4) in test sludge extract (ng/g ww)

| Method | PFHA | PFHpA | PFOA | PFNA | PFDA | PFUnA | PFDoA | PFTEA | PFOS |
|-------------|-----------|-----------|------------|-----------|-----------|-----------|-----------|-----------|------------|
| WAX | 1.3 (0.1) | 0.9 (0.1) | 8.9 (1.1) | 0.8 (0.1) | 4.1 (0.2) | 3.9 (0.6) | 0.9 (0.2) | 2.3 (0.8) | 86.2 (3.2) |
| HLB | 1.7 (0.1) | 1.2 (0.1) | 12.0 (0.9) | 1.1 (0.1) | 4.9 (0.1) | 4.1 (0.1) | 0.8 (0.3) | 1.1 (0.2) | 78.6 (1.8) |
| Ion Pairing | 1.2 (0.2) | 1.2 (0.1) | 13.0 (0.8) | 1.0 (0.1) | 4.6 (0.2) | 4.2 (0.2) | 0.5 (0.1) | 1.0 (0.1) | 81.6 (3.6) |

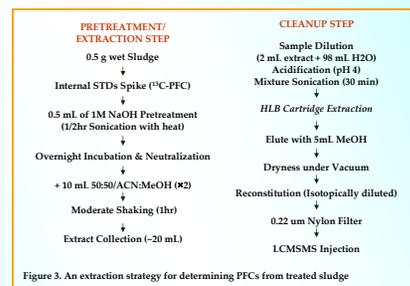


Figure 3. An extraction strategy for determining PFCs from treated sludge

Isotopic Dilution Method for Quantifying PFCs with LC/MS/MS

- The compound-specific mass-labeled PFC (¹³C-PFC) was used as a matrix internal standard for quantitation purpose in the current study. For example, ¹³C₁-PFOA was used for PFOA quantitation, ¹³C₁-PFOA for PFNA and so on.
- Adequacy of isotopically-diluted calibration against solvent-based calibration on PFC quantitation was explored using standard-addition method. Four fortifications (<0, >0.5, <1.0, and >2.0) were prepared triplicates to define 'true' concentrations
- Quantitation results using compound-matched ¹³C-PFC (internal calibration) were more accurate (see slopes in Fig. 4 below) than using solvent-based calibration (external CBT)
- While ¹³C-PFC appear to improve accuracy relative to an external calibration, quantitation is not dependably accurate if not with its native PFC or ¹³C-PFC having closed retention time (Ref 3)

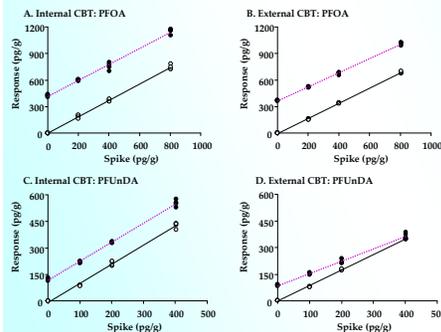


Figure 4. Plots of standard additions in diluted-sludge extract (dashed line) or solvent (straight line) for PFOA and PFDA. CBT represents calibration.

Selected Extraction Method for FTOHs in Sludge using GC/MS

- Among extraction conditions tested for FTOHs in sludge, the pretreatment sonicated in 1M NaOH in sonication and subsequent overnight extraction with MTBE was determined to be the best in terms of FTOHs extractability (Fig. 5)
- All target peaks were identified using 1) retention time of sample extract vs. genuine calibration standard, 2) derivatization technique (Fig. 6), and 3) qualifier ions

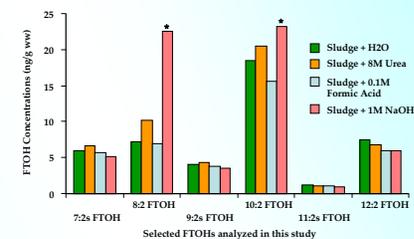


Figure 5. Comparison of extracting condition for FTOHs in test sludge. Asterisk symbolizes significant yields of NaOH method against other methods, except Urea method for 10:2FTOH

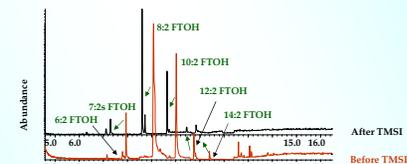


Figure 6. TMSI-peak confirmation using a TMSI-derivatization (shifted forward in time)

Concentrations of FTOHs in Sludge/Biosolid Samples

- Total ten semi-volatile fluorochlorinated were identified and quantified (Table 3)
- 8:2 FTOH and 10:2 FTOH were the predominant FTOHs in studied sludge/biosolids
- Me-FOSA and Et-FOSA were detected, but Me-FOSE and Et-FOSE were not detected (FOSA standards not in house at time of writing)
- 8-2 fluorotelomer acrylate was greater than LOD (100 pg/g), but less than LOQ (200 pg/g)

Table 3. Concentrations (s.d) of selected FTOHs in sludge/biosolids analyzed (ng/g ww)

| Source | 7:2sFTOH | 8:2FTOH | 9:2sFTOH | 10:2FTOH | 11:2sFTOH | 12:2FTOH |
|-------------|-------------|----------------|-------------|--------------|-------------|-------------|
| Decatur, AL | 4.63 (0.29) | 59.93 (12.90) | 3.28 (0.30) | 49.20 (6.79) | 0.99 (0.08) | 8.13 (1.08) |
| NY City A | 3.51 (0.28) | 23.79 (1.42) | 0.92 (0.04) | 19.61 (0.72) | 0.30 (0.03) | 3.38 (0.28) |
| NY City B | 1.80 (0.19) | 37.04 (7.40) | 0.75 (0.11) | 22.77 (6.79) | 0.25 (0.03) | 4.17 (1.67) |
| NY City C | 2.08 (0.13) | 159.24 (13.40) | 0.73 (0.08) | 60.16 (6.14) | 0.24 (0.01) | 8.05 (0.74) |
| LOQ | 0.20 | 0.45 | 0.10 | 0.40 | 0.25 | 0.15 |

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ACS Fall 2009 National Meeting

August 16th - 20th, 2009, Washington D.C., USA