

# Extraction and analysis of poly- and perfluoroalkyl substances (PFAS) from soil

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## Introduction

Recent studies suggest that toxic and highly persistent poly- and perfluorinated alkyl substances (PFAS) are much more prevalent in tissue and soil than in water. The increasing length of perfluoroalkyl chain in PFAS is correlated strongly to lower water solubility/higher adsorption behavior of a particular PFAS molecule in the environment (i.e., migration of PFAS at soil/water/air interfaces) and in remediation/filtration (i.e., choice of filtration media or sorbents). There are over 6,000 PFAS commercially available, many of which have high environmental persistence and have been found in water and soils globally. This poses a significant challenge to developing analytical methods, especially for the extraction of a variety of PFAS from solid matrices such as soil. Previously, we reported unsatisfactory (0–50%) recovery of long-chain PFAS from soil using vortex/sonication.<sup>1</sup>

In the present study, soil was spiked with 24 PFAS (C4-C14 acids, C4-C10 sulfonates, 4:2, 6:2 and 8:2 fluorotelomers, C8 sulfonamide) at 1 ng/g, which were allowed to absorb overnight into the soil samples.



The soil samples were extracted using the Thermo Scientific™ Dionex™ ASE™ 350 Accelerated Solvent Extractor, which produced 70–130% recovery of all PFAS target compounds. Accelerated solvent extraction has outperformed commonly used, manual “shaking” extraction methods under the same conditions.

After ASE extraction, the solution from the ASE sample collection vials underwent clean-up using solid-phase extraction (SPE) and were analyzed on an LC/MS/MS in a 15-min run. Blanks contained no significant amounts of PFAS. Accelerated solvent extraction is demonstrated to be acceptable for the extraction of short- and long-chain PFAS, with a variety of polarities and head-groups, from soil in the range of 1 ng/g to 400 ng/g.

## Experimental

### Sample information

A 10 g soil sample was in 250 mL polypropylene or polyethylene bottles with no PTFE or other fluorinated polymers. Two grams were taken for analysis.

### Spiking

Sample preparation: Weigh out 2 g of soil sample in a 250 mL glass beaker.

- Add 10 g diatomaceous earth to the beaker and mix with the soil sample.
- Transfer the sample mixture into a 100 mL stainless steel ASE cell with cellulose filter at the bottom of the cell.
- Top up the cell with diatomaceous earth.
  - Spike extraction surrogate and native standard.
  - Place a 250 mL bottle with septa cap in the bottle tray of the Dionex ASE 350 system.

### Accelerated solvent extraction (Dionex ASE 350 setup)

#### Rinse settings

|         |              |
|---------|--------------|
| Solvent | 100% acetone |
| Volume  | 13 mL        |
| Cycles  | 3            |

#### Extraction settings

|                  |                 |                                 |
|------------------|-----------------|---------------------------------|
| Cell type        | Stainless steel |                                 |
| Oven temperature | 100 °C          |                                 |
| Static cycle     | Time            | 300 s                           |
|                  | Solvent         | 80:20 methanol/<br>acetonitrile |
|                  | Volume          | 50 mL                           |
| Cycles           | 3               |                                 |
| Purge time       | 120 s           |                                 |

### Clean-up

Sample clean-up used a styrene-divinylbenzene (SDVB) polymer SPE cartridge (500 mg, 6 mL), on a vacuum-controlled manifold, under the following sequential conditions:

- Condition cartridges with 15 mL methanol.
- Run 20 mL of reagent water through the cartridge.
- Transfer the extracted sample solution from the Dionex ASE 350 system to the SPE cartridge using a large-volume sampler.
- Rinse the sample bottle with 10 mL reagent water and transfer to the cartridge.
- Vacuum dry the SPE cartridge.

### Elution phase

- Rinse the sample bottle with 10 mL methanol and transfer to the SPE cartridge.
- Elute all methanol extracts into a polypropylene centrifuge tube.

### LC parameters

A Thermo Scientific™ Vanquish™ LC, with all Teflon™ lines replaced by PEEK tubing, coupled to a Thermo Scientific™ TSQ Quantis™ triple quadrupole mass spectrometer, was used for sample analysis.

|                    |   |
|--------------------|---|
| Solvent B          | 10 mM ammonium acetate<br>in 19% v/v acetonitrile/81%<br>methanol   |
| Solvent A          | 10 mM ammonium acetate<br>in 19% v/v acetonitrile in<br>water       |
| Column temperature | 25 °C   |
| Gradient           | Solvent ramps from 40%<br>Solvent B to 90% Solvent B<br>over 15 min |
| LC flow rate       | 0.300 mL/min  |

## MS parameters

The H-ESI source was used in the negative ionization mode and the optimized MS parameters were as follows:

|                      |         |
|----------------------|---------|
| Q1 resolution        | 0.7 Da  |
| Q3 resolution        | 1.2 Da  |
| Use cycle time       | True    |
| Cycle time           | 0.5 s   |
| CID gas              | 2 mTorr |
| Source fragmentation | 0 V     |

|                               |          |
|-------------------------------|----------|
| Chromatographic peak width    | 6 s      |
| ESI negative voltage          | 1,500 V  |
| Sheath gas                    | 57.6 arb |
| Aux gas                       | 2.4 arb  |
| Sweep gas                     | 0.4 arb  |
| Ion transfer tube temperature | 325 °C   |
| Vaporizer temperature         | 350 °C   |

Table 1. Monitored SRM transitions

| Compound                              | Retention time (min) | Precursor (m/z) | Product (m/z) | Collision energy (V) | RF lens (V) |
|---------------------------------------|----------------------|-----------------|---------------|----------------------|-------------|
| PFBA                                  | 1.38                 | 212.979         | 168.97        | 10.23                | 56          |
| <sup>13</sup> C <sub>4</sub> -PFBA    | 1.38                 | 216.979         | 171.97        | 12.81                | 71          |
| PFPeA                                 | 1.89                 | 262.976         | 219.042       | 10.23                | 79          |
| <sup>13</sup> C <sub>5</sub> -PFPeA   | 1.89                 | 268             | 223           | 10.23                | 64          |
| PFHxA                                 | 3.00                 | 312.9           | 268.8         | 10.23                | 73          |
| <sup>13</sup> C <sub>5</sub> -PFHxA   | 3.00                 | 318             | 273           | 10.23                | 76          |
| 4:2 FTS                               | 2.70                 | 326.974         | 307.042       | 19                   | 129         |
| <sup>13</sup> C <sub>2</sub> -4:2 FTS | 2.70                 | 328.974         | 81.040        | 19                   | 147         |
| PFPeS                                 | 3.76                 | 307.042         | 80.042        | 35                   | 151         |
| PFBS                                  | 2.33                 | 298.912         | 79.946        | 32                   | 152         |
| <sup>13</sup> C <sub>2</sub> -PFBS    | 2.33                 | 302             | 79.946        | 32                   | 152         |
| PFHpA                                 | 4.74                 | 362.97          | 319           | 10.23                | 81          |
| <sup>13</sup> C <sub>4</sub> -PFHpA   | 4.74                 | 367             | 322           | 10.23                | 82          |
| PFHxS                                 | 5.56                 | 398.912         | 79.929        | 37.2                 | 154         |
| <sup>13</sup> C <sub>3</sub> -PFHxS   | 5.56                 | 401.947         | 79.957        | 37.3                 | 171         |
| PFOA                                  | 6.75                 | 412.966         | 369           | 10.23                | 91          |
| <sup>13</sup> C <sub>8</sub> -PFOA    | 6.75                 | 421             | 376           | 10.23                | 92          |
| 6:2 FTS                               | 6.36                 | 426.968         | 406.988       | 22.43                | 164         |
| <sup>13</sup> C <sub>2</sub> -6:2 FTS | 6.36                 | 428.968         | 81.040        | 23.6                 | 164         |
| PFHpS                                 | 7.43                 | 448.933         | 80.012        | 39.67                | 184         |
| PFNA                                  | 8.68                 | 462.963         | 418.946       | 10.23                | 99          |
| <sup>13</sup> C <sub>9</sub> -PFNA    | 8.68                 | 472             | 427           | 10.23                | 97          |
| PFOS                                  | 9.19                 | 498.862         | 79.946        | 40.78                | 164         |
| <sup>13</sup> C <sub>8</sub> -PFOS    | 9.19                 | 507             | 79.917        | 40.63                | 169         |
| PFDA                                  | 10.39                | 512.96          | 469           | 10.23                | 108         |
| <sup>13</sup> C <sub>6</sub> -PFDA    | 10.39                | 519             | 474           | 10.23                | 109         |
| 8:2 FTS                               | 10.17                | 526.962         | 506.97        | 25.73                | 190         |
| <sup>13</sup> C <sub>2</sub> -8:2FTS  | 10.17                | 528.962         | 81.010        | 25.27                | 190         |
| PFNS                                  | 10.73                | 548.927         | 80.071        | 44.4                 | 177         |
| PFUdA                                 | 11.87                | 562.957         | 519           | 10.23                | 117         |
| <sup>13</sup> C <sub>7</sub> -PFUdA   | 11.87                | 570             | 525           | 10.23                | 117         |
| NMeFOSAA                              | 11.13                | 569.925         | 418.926       | 19.36                | 200         |

Table 1. Monitored SRM transitions (cont.)

| Compound  | Retention time (min) | Precursor (m/z) | Product (m/z) | Collision energy (V) | RF lens (V) |
|---|----------------------|-----------------|---------------|----------------------|-------------|
| d3-N-MeFOSAA                                      | 11.13                | 572.912         | 418.958       | 20.39                | 167         |
| PFOSA   | 9.47                 | 497.946         | 78.071        | 30.24                | 175         |
| <sup>13</sup> C <sub>8</sub> -PFOSA               | 9.47                 | 505.946         | 78.071        | 31.57                | 186         |
| NEtFOSAA  | 11.89                | 583.983         | 526           | 19.02                | 187         |
| d5-N-EtFOSAA                                      | 11.89                | 588.962         | 530.97        | 18.96                | 144         |
| PFDS  | 12.06                | 598.924         | 80.042        | 44.92                | 192         |
| PFD <sub>o</sub> A                                | 13.11                | 612.9           | 569           | 10.23                | 126         |
| <sup>13</sup> C <sub>2</sub> -PFD <sub>o</sub> A  | 13.11                | 615             | 570           | 10.23                | 122         |
| PFT <sub>r</sub> DA                               | 14.16                | 662.95          | 619           | 10.23                | 134         |
| PFT <sub>e</sub> DA                               | 15.06                | 712.95          | 668.97        | 11.782               | 143         |
| <sup>13</sup> C <sub>2</sub> -PFT <sub>e</sub> DA | 15.06                | 714.95          | 670           | 10.23                | 142         |
| <b>PFOA and PFOS Alternatives</b>                 |                      |                 |               |                      |             |
| HFPO-DA   | 3.52                 | 284.96          | 168.887       | 17.35                | 68          |
| <sup>13</sup> C <sub>3</sub> -HFPO-DA             | 3.52                 | 286.912         | 168.833       | 10.23                | 67          |
| ADONA   | 5.09                 | 376.912         | 250.988       | 10.23                | 91          |
| <sup>9</sup> Cl-PF <sub>3</sub> ONS               | 10.21                | 530.825         | 350.917       | 24.67                | 167         |
| <sup>11</sup> Cl-PF <sub>3</sub> OUdS             | 12.80                | 630.825         | 450.887       | 27.17                | 254         |

All PFAS compounds analyzed in this method are shown in Figure 1.

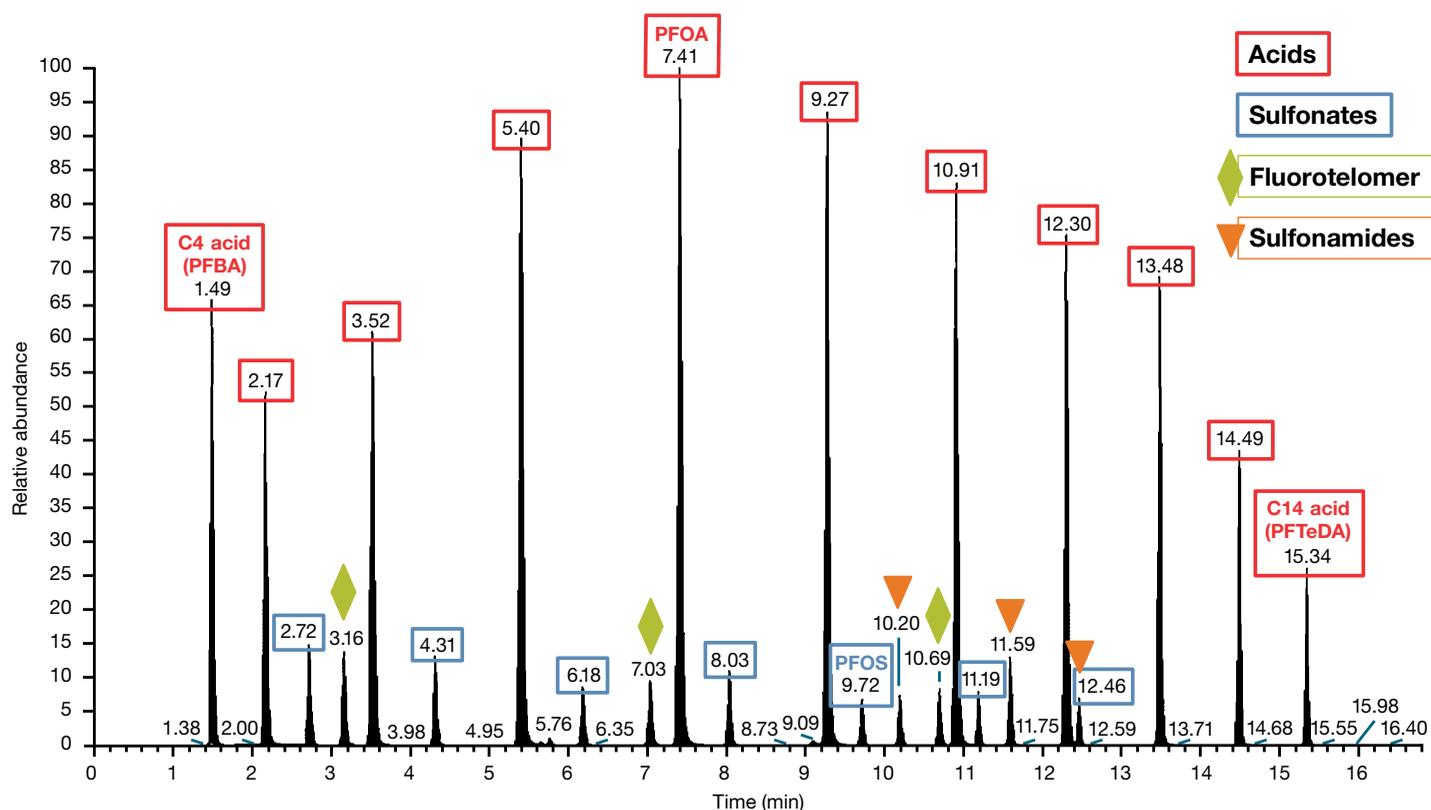


Figure 1. Chromatogram of PFAS compounds analyzed

## Chromatogram of a soil sample

Only native analytes found at appreciable levels in the soil sample are shown in Figure 2. These levels are between 1 and 5 ng/g, with the exception of PFOS at 50 ng/g. From top to bottom, the analytes are PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFHxS, and PFOS. The other 21 PFAS analytes were at or below detection limit.

## PFAS background levels

The Dionex ASE 350 system, which was used to develop this method, contains Teflon lines. Due to the lines being exposed to a variety of solvents over several years, the PFAS background is at a minimum. Table 3 shows the levels of PFAS measured in the blanks processed within different spike batches (i.e., in a batch of soil samples spiked with PFAS, these are the PFAS levels in the blanks processed with that batch). These blanks contain diatomaceous earth and isotopically labeled PFAS internal standards (surrogates), but no spiked native PFAS and no soil. Table 4 shows the linearity for PFAS in soil.

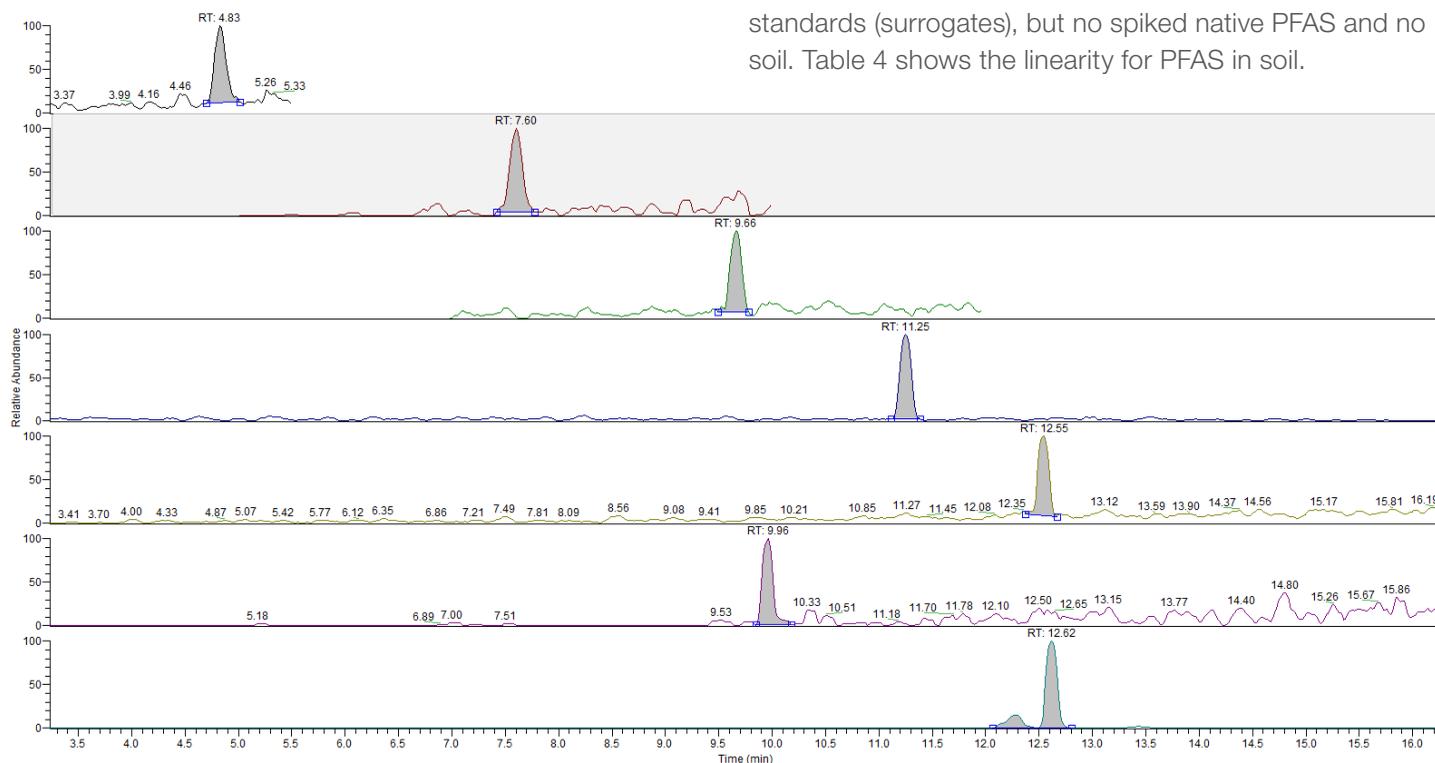


Figure 2. Native analytes found at appreciable levels in a soil sample

Internal standard recoveries (spiked in at 10 ng/g or 5 ng/g) are as listed in Table 2.

Table 2. Recovery of the isotopically labeled PFAS compounds

| Compound                  | Recovery (%) | Compound                  | Recovery (%) |
|---------------------------|--------------|---------------------------|--------------|
| $^{13}\text{C}_4$ -PFBA   | 71           | $^{13}\text{C}_3$ -PFBS   | 98           |
| $^{13}\text{C}_5$ -PFPeA  | 93           | $^{13}\text{C}_3$ -PFHxS  | 95           |
| $^{13}\text{C}_5$ -PFHxA  | 97           | $^{13}\text{C}_8$ -PFOS   | 91           |
| $^{13}\text{C}_4$ -PFHpA  | 96           | $^{13}\text{C}_3$ -HFPODA | 56           |
| $^{13}\text{C}_8$ -PFOA   | 94           | $^2\text{H}_3$ -NMEFOSAA  | 93           |
| $^{13}\text{C}_9$ -PFNA   | 104          | $^2\text{H}_3$ -NETFOSAA  | 90           |
| $^{13}\text{C}_6$ -PFDA   | 99           | $^{13}\text{C}_9$ -FOSA   | 92           |
| $^{13}\text{C}_7$ -PFUdA  | 95           | $^{13}\text{C}_2$ -4:2FTS | 110          |
| $^{13}\text{C}_2$ -PFDaA  | 97           | $^{13}\text{C}_2$ -6:2FTS | 93           |
| $^{13}\text{C}_2$ -PFTeDA | 108          | $^{13}\text{C}_2$ -8:2FTS | 98           |

**Table 3. Measured PFAS levels in blanks**

| Spike level batch | 1 ng/g spike |      | 20 ng/g spike | 400 ng/g spike |
|-------------------|--------------|------|---------------|----------------|
|                   | ng/g         | ng/g | ng/g          | ng/g           |
| PFBA              | 0.01         | 0.01 | 0.05          | 0.05           |
| PFPeA             | n.d.         | n.d. | n.d.          | n.d.           |
| PFHxA             | 0.01         | 0.01 | 0.03          | 0.04           |
| PFHpA             | n.d.         | n.d. | 0.02          | 0.01           |
| PFOA              | 0.01         | 0.01 | 0.04          | 0.04           |
| PFNA              | n.d.         | n.d. | n.d.          | n.d.           |
| PFDA              | n.d.         | n.d. | n.d.          | n.d.           |
| PFUdA             | n.d.         | n.d. | n.d.          | n.d.           |
| PFDoA             | n.d.         | n.d. | n.d.          | n.d.           |
| PFTRDA            | n.d.         | n.d. | n.d.          | n.d.           |
| PFTEDA            | n.d.         | n.d. | n.d.          | n.d.           |
| NMEFOSAA          | n.d.         | n.d. | n.d.          | n.d.           |

| Spike level batch | 1 ng/g spike |      | 20 ng/g spike | 400 ng/g spike |
|-------------------|--------------|------|---------------|----------------|
|                   | ng/g         | ng/g | ng/g          | ng/g           |
| NETFOSAA          | n.d.         | n.d. | n.d.          | n.d.           |
| FOSA              | n.d.         | n.d. | n.d.          | n.d.           |
| PFBS              | n.d.         | n.d. | 0.01          | n.d.           |
| PFPeS             | n.d.         | n.d. | n.d.          | n.d.           |
| PFHxS             | n.d.         | n.d. | n.d.          | n.d.           |
| PFHpS             | n.d.         | n.d. | n.d.          | n.d.           |
| PFOS              | n.d.         | n.d. | n.d.          | n.d.           |
| PFNS              | n.d.         | n.d. | n.d.          | n.d.           |
| PFDS              | n.d.         | n.d. | n.d.          | n.d.           |
| 4:2FTS            | n.d.         | n.d. | n.d.          | n.d.           |
| 6:2FTS            | n.d.         | n.d. | n.d.          | n.d.           |
| 8:2FTS            | n.d.         | n.d. | n.d.          | n.d.           |

**Table 4. PFAS in soil linearity**

| Spike level | 1 ng/g | 5 ng/g | 20 ng/g | 100 ng/g | 400 ng/g | Slope | r <sup>2</sup> |
|-------------|--------|--------|---------|----------|----------|-------|----------------|
| PFBA        | 0.979  | 5.05   | 21.7    | 101.0    | 408      | 1.020 | 1.000          |
| PFPeA       | 1.035  | 5.22   | 22.0    | 101.4    | 423      | 1.058 | 1.000          |
| PFHxA       | 1.024  | 5.15   | 22.1    | 102.4    | 429      | 1.073 | 1.000          |
| PFHpA       | 0.985  | 5.28   | 22.4    | 99.2     | 423      | 1.056 | 1.000          |
| PFOA        | 1.02   | 5.02   | 22.1    | 100.7    | 425      | 1.062 | 1.000          |
| PFNA        | 1.032  | 5.21   | 21.8    | 102.6    | 426      | 1.064 | 1.000          |
| PFDA        | 1.000  | 5.06   | 21.5    | 100.5    | 428      | 1.071 | 1.000          |
| PFUdA       | 0.982  | 5.01   | 22.6    | 96.8     | 418      | 1.044 | 1.000          |
| PFDoA       | 1.05   | 5.43   | 23.5    | 77.3     | 339      | 0.841 | 0.999          |
| PFTRDA      | 0.567  | 3.65   | 15.5    | 45.4     | 200      | 0.496 | 0.998          |
| PFTEDA      | 1.076  | 5.57   | 23.9    | 76.6     | 317      | 0.786 | 0.999          |
| NMEFOSAA    | 1.13   | 4.86   | 22.8    | 97.2     | 368      | 0.915 | 1.000          |
| NETFOSAA    | 1.097  | 5.18   | 19.5    | 117.0    | 424      | 1.061 | 0.999          |
| FOSA        | 0.991  | 5.16   | 21.7    | 93.0     | 438      | 1.097 | 0.998          |
| PFBS        | 0.966  | 5.14   | 22.4    | 104.6    | 453      | 1.133 | 1.000          |
| PFPeS       | 0.915  | 4.93   | 21.1    | 99.6     | 433      | 1.084 | 1.000          |
| PFHxS       | 0.945  | 4.98   | 21.6    | 110.6    | 451      | 1.129 | 1.000          |
| PFHpS       | 0.976  | 4.55   | 22.8    | 111.4    | 467      | 1.169 | 1.000          |
| PFOS        | 1.076  | 6.14   | 20.3    | 108.2    | 468      | 1.172 | 1.000          |
| PFNS        | 0.893  | 5.51   | 21.4    | 107.1    | 462      | 1.156 | 1.000          |
| PFDS        | 0.999  | 5.54   | 20.8    | 104.4    | 447      | 1.119 | 1.000          |
| 4:2FTS      | 1.129  | 5.89   | 22.2    | 57.8     | 272      | 0.672 | 0.997          |
| 6:2FTS      | 1.128  | 6.19   | 21.8    | 89.2     | 430      | 1.074 | 0.998          |
| 8:2FTS      | 1.149  | 5.43   | 21.0    | 79.8     | 384      | 0.958 | 0.998          |

## Conclusion

Accelerated solvent extraction can extract a variety of PFAS from soil including acids, sulfonates, fluorotelomer sulfonates, and sulfonamide compounds. Although the Dionex ASE 350 system utilized in this method contained Teflon lines, the lines had been used under a variety of different solvent conditions, effectively reducing the PFAS background contamination to a minimum. Isotopic dilution quantification was utilized for most analytes and demonstrated linearity for all PFAS studied in soil over the range of 1 ppb to 400 ppb. PFTrDA linearity is biased low which is partially due to PFTrDA being quantified via the internal standard method against  $^{13}\text{C}_2$ -PFTeDA and not an isotopically labeled analog of PFTrDA, but more strongly due to the effects of naturally abundant  $^{13}\text{C}_2$ -PFTeDA (from the native spiked levels) artificially increasing the recoveries of internal standard, thus underestimating the native levels of PFTrDA.

Previously experienced difficulties recovering long-chain PFAS from soil using sonication/vortex methods were surmounted by using ASE, demonstrating that the absence of long-chain PFAS is a true absence and not simply low recovery. The approach described here was applied to a soil sample and it was found to contain between 1 and 50 ng/g of several PFAS. Accelerated solvent extraction is an acceptable method for extracting a wide selection of PFAS, from 4-carbon to 14-carbon fluoroalkyl chain lengths and five different polar head-groups, from soil over a wide range of concentrations. Accelerated solvent extraction shows high potential for effective extraction of the growing list of PFAS from solid samples.

## Reference

1. MacLennan, Matthew S.; Ng, Daniel; Hope, David (2019): Extraction of poly-and perfluorinatedalkyl substances (PFAS) from solid matrices. Society of Ecotoxicology and Chemistry (SETAC) North America, 40th Annual Meeting, Toronto, Poster. <https://doi.org/10.6084/m9.figshare.13557185.v1>

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