**Supporting information for:**

The decomposition and emission factors of a wide range of PFAS in diverse, contaminated organic waste fractions undergoing dry pyrolysis

Erlend Sørmo1,2\*, Gabriela Castro3, Michel Hubert143, Viktória Licul-Kucera,5,6, Marjorie Quintanilla3, Alexandros G. Asimakopoulos3, Gerard Cornelissen1,2, Hans Peter H. Arp1,3

1) Geotechnics and Environment, Norwegian Geotechnical Institute (NGI), Oslo, Norway

2) Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences (NMBU), Ås, Norway

3) Department of Chemistry, Norwegian University of Science and Technology (NTNU), NO-7491, Trondheim, Norway

4) Faculty of Engineering, Norwegian University of Science and Technology (NTNU), NO-7491, Trondheim, Norway

5) Institute for Analytical Research, Hochschulen Fresenius gem. Trägesellschaft mbH, Idstein, Germany.

6) Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, Amsterdam, Netherlands

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1. Information about the PFAS target analytes for the different analytical methods applied.

**Method AA:**

41 congeners: 15 perfluorinated alkylcarboxylic acids (PFCA): perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), 7H-dodecafluoroheptanoic acid (7H-PFHpA), perfluorooctanoic acid (PFOA), perfluoro-3,7-dimethyloctanoic acid (P37DMOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTriDA), perfluorotetradecanoic acid (PFTDA), perfluorohexadecanoic acid (PFHxDA), and perfluorooctadecanoic acid (PFOcDA); 9 perfluorinated alkylsulphonic acids (PFSA): perfluorobutane sulphonic acid (PFBS), perfluoropentane sulphonic acid (PFPeS), perfluorohexane sulphonic acid (PFHxS), perfluoroheptane sulphonic acid (PFHpS), perfluorooctane sulphonic acids (PFOS), perfluorononane sulphonic acid (PFNS), perfluorodecane sulphonic acids (PFDS), perfluorododecane sulphonic acid (PFDoDS), and perfluoroethylcyclohexane sulphonic acid (PEECHS); 4 fluorotelomere sulphonates (FTS): 4:2 fluorotelomere sulphonic acid (4:2 FTS), 6:2 fluorotelomere sulphonic acid (6:2 FTS), 8:2 fluorotelomere sulphonic acid (8:2 FTS), and 10:2 fluorotelomere sulphonic acid (10:2 FTS); 8 fluorosulphonamides (FSA): perfluorooctane sulphonamide (PFOSA), N-methyl perfluorooctane sulphonamide (MeFOSA), N-ethyl perfluorooctane sulphonamide (EtFOSA), perfluorooctane sulphonamidoacetic acid (FOSAA), N-methyl perfluorooctane sulphonamidoacetic acid (MeFOSAA), N-ethyl perfluorooctane sulphonamidoacetic acid (EtFOSAA), N-methylperfluorooctane sulfonamido ethanol (MeFOSE), and N-methylperfluorooctane sulfonamido ethanol (EtFOSE); and 5 miscellaneous compounds: decasulfonic acid (DecaS), 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoic acid (GenX), sodium dodecafluoro-3H-4, 8-dioxanonanoate (NaDONA), 9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (F53 B), and perfluorooctane sulphonamido ethanol-based phosphate ester (diSAMPAP).

**Method BB:**

11 precursor compounds: 2H-perfluoro-2-alkanoic acids (6:2,8:2,10:2, FTUCA), 2H,3H,3H-perfluoroalkanoic acids (4:3,5:3,6:3,7:3-acid), 1H,1H,2H,2H-perfluoroalkoxy acetic acids (6:2, 8:2 FTEOC), and bis(1H,1H,2H,2H-perfluoroalkyl) phosphates (6:2,8:2 diPAP).

**Method BC:**

4 ultrashort chain PFAS: trifluoromethane sulphonic acid (TFMS), perfluoroethane sulphonic acid (PFEtS), perfluoropropane sulphonic acid (PFPrS), and perfluoropropanoic acid (PFPrA)

1. Development of method A.

Analysis methods for PFAS from other solid matrices typically includes methanol extraction at room temperature, e.g. standard DIN 38414-S14. This approach was tested, yielding poor recoveries and high matrix effects for PFAS spiked to sludge (Table S3) suggesting stronger extractions methods were needed. All the protocols tested, and results are described below.

The extraction efficiency of the proposed methodology was assessed through absolute recoveries (Abs%) and relative recoveries (Rel%) for each target analyte in pooled matrices (sludge and biochar) fortified at 3 different concentrations (2.5, 10 and 20 ng mL-1, d.w.) with 10 ng mL-1 of IS. Abs% were calculated by dividing the area of quantification peak of the analyte in a pre-extraction spiked sample by the respective area of the analyte obtained in a post-extraction spiked sample (Arvaniti et al., 2014). Rel % were estimated following the same formula as Abs% but considering the areas of the target analytes divided by the area of a specific IS (Table S2). Matrix effects (MEs%) were calculated for each target analyte as the ratio between the slope of the target analyte matrix matched (post-extraction calibration curve) and the slope of the target analyte calibration curve prepared in solvent, multiplied by 100. Values closer to 100%, indicate the absence of matrix effects during ionization, while values below and above 100% indicate signal suppression and enhancement, respectively (Raposo & Barceló, 2021). Obtained Abs%, Rel% and ME% are presented in Table S4. Quantification of the target analytes was accomplished based on the internal standard method and matrix-matched calibration standards (Raposo & Barceló, 2021).

1. **Arvaniti et al.** (2014)

0.1 g of sample fortified with 10 ng of a mixture of IS we introduced into a 15 mL PP tube and 7.5 mL of 1% acetic acid (v/v) and 1.5 mL of MeOH were added. The extraction of target analytes was carried out through ultrasound assisted extraction for 45 minutes, followed by 15 min of centrifugation (3500 rpm). The supernatant was collected and transferred into a clean PP tube. The extraction was repeated twice (3 x 7.5 mL of acetic acid). Supernatants were combined and diluted until 50 mL and pH was adjusted to 3. Clean-up and concentration were carried out through solid-phase extraction (SPE) in a Strata X cartridge (200 mg), previously conditioned with 6 mL of MeOH and 10 mL of Milli-Q water (pH 3). After loading the sample, the cartridge was washed with 2 mL of MeOH:Milli-Q water (pH3) and dried vacuum. Target analytes were eluted with 4 mL of MeOH and concentrated to almost dryness. Finally, the extracts were reconstituted in MeOH:Milli-Q water (50:50).

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| 1. **Liquid solid extraction + ultrasound assisted extraction**   0.1 g of sample was introduced in a 15 mL PP tube and spiked with 10 ng mL-1 of a mixture of ISs. Then, 300 µL of 1M ammonium acetate aqueous buffer was added to the sample to favour the salting-out. Ultrasound assisted extraction (UAE) was performed with 3 mL of EtOAc and ultrasonication (45 min, 40 °C) followed by centrifugation (10 min, 4000 rpm). The supernatant was collected and transferred into a clean PP tube. The UAE was repeated another two times to produce a final volume of ~9 mL (3 x 3mL). Clean-up was carried out with 2 mL Milli-Q water, the extract was shaken and centrifuged (10 min, 4000 rpm). The obtained extract was concentrated (N2, 35 ºC) to near dryness, before being reconstituted in MeOH:Milli-Q (1 mL, 50:50).   1. **Higher Temperature**   EtOAc or ACN  0.1 g of sample was introduced in a 15 mL PP tube and spiked with 10 ng mL-1 of a mixture of ISs. Then, 300 µL of 1M ammonium acetate aqueous buffer was added to the sample to favour the salting-out. Ultrasound assisted extraction (UAE) was performed with 3 mL of EtOAc (or ACN) and ultrasonication (15 min, 60 °C) followed by centrifugation (10 min, 4000 rpm). The supernatant was collected and transferred into a clean PP tube. The UAE was repeated another two times to produce a final volume of ~9 mL (3 x 3mL). Clean-up was carried out with 2 mL Milli-Q water, the extract was shaken and centrifuged (10 min, 4000 rpm). The obtained extract was concentrated (N2, 35 ºC) to near dryness, before being reconstituted in MeOH:Milli-Q (1 mL, 50:50).   1. **Clean-up**   EtOAc or ACN  0.1 g of sample was introduced in a 15 mL PP tube and spiked with 10 ng mL-1 of a mixture of ISs. Then, 300 µL of 1M ammonium acetate aqueous buffer was added to the sample to favour the salting-out. Ultrasound assisted extraction (UAE) was performed with 3 mL of EtOAc (or ACN) and ultrasonication (15 min, 60 °C) followed by centrifugation (10 min, 4000 rpm). The supernatant was collected and transferred into a clean PP tube. The UAE was repeated another two times to produce a final volume of ~9 mL (3 x 3mL). The obtained extract was concentrated (N2, 35 ºC) to 1 mL and submitted to clean-up in a 1.7 mL centrifuge tube with 25 mg Envi-Carb and 50 µL glacial acetic acid. The sample was vigorously shaken and centrifuged for 10 min, 10000 rpm. The obtained supernatant was transferred into a vial and concentrated to almost dryness. Finally, the extract was reconstituted in 1 mL MeOH:Milli-Q (50:50).   1. Detailed description of analytical method C   **Instrumental method C:** Ultrashort chain PFAS, 4 congeners, including 3 PFCA and 1 PFSA (see SI section A and Table S1) were analysed using hydrophilic interaction chromatography coupled to mass spectrometry (HILIC-MS), as previously described by Neuwald et al (2022). Namely, a Shimadzu Nexera X2 HPLC sytem (Shimadzu Germany GmbH, Duisburg, Germany) was coupled to a QTrap 5500 MS system (AB Sciex Germany GmbH, Darmstadt, Germany). Chromatographic separation was achieved on an Acquity BEH Amide column (1.7 μm, 2.1 x 100 mm) (Waters, Milford, MA, USA) which was heated to 30 °C. The eluents consisted of 95% water and 5% acetonitrile (v:v, eluent A) and 5% water and 95% acetonitrile (v:v, eluent B) with 5 mM ammonium formate, adjusted to pH 3. The gradient started at 100 % eluent B for 0-1 min, decreased to 75% from 1-5 min, reduced to 50% from 5-6 min and held 50% from 6-8 min, re-equilibrated to 100 % from 8-8.1 min and held it until 10 min. The total run time was 10 min, the injection volume was 5 μL and the flow rate was 500 μL min-1. |

1. Tables and figures

Table S1. List of PFAS analytes with molecular structures, CAS number, formulae, and supply information.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Abbreviation** | **Name** | **Structure** | **CAS** | **Formula** | **Supplier** |
| ***Ultrashort chain perfluoroalkyl sulphonic acids and carboxylic acid*** | | | | | |
| TFMS | Trifluoromethane sulfonic acid |  | 1493-13-6 | CHF3O3S | Sigma Aldrich (≥99%) |
| PFEtS | Perfluoroethane sulfonic acid |  | 354-88-1 | C2HF5O3S | Self-synthesized |
| PFPrS | Perfluoropropane sulfonic acid |  | 423-41-6 | C3HF7O3S | Self-synthesized |
| PFPrA | Perfluoropropanoic acid |  | 422-64-0 | C3HF5O2 | Self-synthesized |
| ***Perfluorocarboxylic Acids (PFCA)*** | | | | | |
| PFBA | Perfluorobutanoic acid |  | 375-22-4 | C4HF7O2 | Cambridge Isotope Laboratories (50 ug/mL, methanol) |
| PFPeA | Perfluoropentanoic acid |  | 2706-90-3 | C5HF9O2 | Sigma Aldrich (97%, neat) |
| PFHxA | Perfluorohexanoic acid |  | 307-24-4 | C6HF11O2 | Sigma Aldrich (97%, neat) |
| PFHpA | Perfluoroheptanoic acid |  | 375-85-9 | C7HF13O2 | Sigma Aldrich (99%, neat) |
| PFOA | Perfluorooctanoic acid |  | 335-67-1 | C8HF15O2 | Sigma Aldrich (96%, neat) |
| PFNA | Perfluorononanoic acid |  | 375-95-1 | C9HF17O2 | Sigma Aldrich (97%, neat) |
| PFDA | Perfluorodecanoic acid |  | 335-76-2 | C10HF19O2 | Sigma Aldrich (98%, neat) |
| PFUnA | Perfluoroundecanoic acid |  | 2058-94-8 | C11HF21O2 | Sigma Aldrich (95%, neat) |
| PFDoDA | Perfluorododecanoic acid |  | 307-55-1 | C12HF23O2 | Sigma Aldrich (97%, neat) |
| PFTriDA | Perfluorotridecanoic acid |  | 72629-94-8 | C13HF25O2 | Sigma Aldrich (97%, neat) |
| PFTDA | Perfluorotetradecanoic acid |  | 376-06-7 | C14HF27O2 | Sigma Aldrich (96%, neat) |
| PFHxDA | Perfluoro-n-hexadecanoic acid |  | 67905-19-5 | C16HF31O2 | Chiron (50 ug/mL, methanol) |
| PFOcDa | Perfluorooctadecanoic acid |  | 16517-11-6 | C18HF35O2 | Wellington Laboratories (2000 ng/mL, solution MIX methanol) PFCAMXC |
| P37DMOA | Perfluoro-3,7-dimethyloctanoic acid |  | 172155-07-6 | C10HF19O2 | Wellington Laboratories (50 ug/mL, methanol) |
| 7H-PFHpA | 7H-Dodecafluoroheptanoic Acid |  | 1546-95-8 | C7H2F12O2 | Sigma Aldrich (95%, neat) |
| ***Perfluoroalkyl Sulfonates (PFSAs)*** | | | | | |
| PFBS | Perfluorobutanoic acid sulfonate |  | 375-73-5 | C4F9SO3 | Cambridge Isotope Laboratories (50 ug/mL, methanol)\* |
| PFPeS | Perfluoropentane sulfonic acid |  | 2706-91-4 | C5H11O3S | Wellington Laboratories (2000 ng/mL, solution MIX methanol) PFCAMXC\* |
| PFHxS | Perfluorohexane sulfonic acid |  | 355-46-4 | C6HF13O3S | Sigma Aldrich (98%) |
| PFHpS | Perfluoroheptano sulfonic acid |  | 146689-46-5 | C7F15O3S | Cambridge Isotope Laboratories (50 ug/mL, methanol) |
| PFOS | Perfluorooctano sulfonic acid |  | 1763-23-1 | C8F17O3S | Cambridge Isotope Laboratories (50 ug/mL, methanol) |
| PFNS | Perfluorononane sulfonic acid |  | 68259-12-1 | C9H2F16O3S | Sigma Aldrich (98%) |
| PFDS | Perfluorodecane sulfonic acid |  | 335-77-3 | C10HF21O3S | Wellington Laboratories (2000 ng/mL, solution MIX methanol) PFCAMXC\* |
| PFDoDS | Perfluorododecane sulfonic acid |  | 79780-39-5 | C12H2F24O3S | Wellington Laboratories (2000 ng/mL, solution MIX methanol) PFCAMXC\* |
| PFECHS | Perfluoroethylcyclohexane sulfonic acid |  | 335-24-0 | C8HF15O3S | Wellington Laboratories (50 ug/mL, methanol)\* |
| ***Fluorotelomer Sulfonates (FTS)*** | | | | | |
| 4:2 FTS | 1H,2H-Perfluorohexan sulfonate (4:2) |  | 757124-72-4 | C6H5F9O3S | Cambridge Isotope Laboratories (50 ug/mL, methanol) |
| 6:2 FTS | 1H,2H-Perfluorooctane sulfonate (6:2) |  | 27619-97-2 | C8H5F13O3S | Cambridge Isotope Laboratories (50 ug/mL, methanol) |
| 8:2 FTS | 1H,2H-Perfluorodecan sulfonate (8:2) | |  | | --- | |  | | 39108-34-4 | C10H5F17O3S | Cambridge Isotope Laboratories (50 ug/mL, methanol) |
| 10:2 FTS | 1H,2H-Perfluorododecan sulfonate (10:2) |  | 120226-60-0 | C12H5F21O3S | Cambridge Isotope Laboratories (50 ug/mL, methanol) |
| ***Fluorosulfonamides (FSA)*** | | | | | |
| FOSAA | Perfluoro-1-octanesulfonamidoacetic acid |  | 2806-24-8 | C10H4F17NO4S | Chiron (50ug/mL, methanol) |
| MeFOSAA | 2-(N-methylPerfluoro-1-octansulfonamido)acetic acid |  | 2355-31-9 | C11H6F17NO4S | Chiron (50ug/mL, methanol) |
| EtFOSAA | N-ethylPerfluoro-1-octanesulfonamide acetic acid |  | 2991-50-6 | C12H8F17NO4S | Chiron (50ug/mL, methanol) |
| PFOSA | Perfluorooctane sulfonamide |  | 754-91-6 | C8H2F17NO2S | Sigma Aldrich (99%) |
| MeFOSA | N-methylperfluoro-1-octanesulfonamide |  | 31506-32-8 | C9H4F17NO2S | Chiron (50ug/mL, acetonitrile) |
| EtFOSA | N-ethylperfluoro-1-octanesulfonamide |  | 4151-50-2 | C10H6F17NO2S | Chiron (neat) |
| MeFOSE | N-(2-hydroxyethyl)-N-methylperfluorooctane sulfonamide | |  | | --- | |  | |  | | 24448-09-7 | C11H8F17NO3S | Chiron (50ug/mL, acetonitrile) |
| EtFOSE | N-ethyl-N-(2-hydroxyethyl)-N-methylperfluorooctane sulfonamide |  | 1691-99-2 | C12H10F17NO3S | Chiron (50ug/mL, acetonitrile) |
|  |
| ***Miscellaneous*** | | | | | |
| DecaS | Decasulfonic acid |  | 13419-61-9 | C10H21O3S | Sigma Aldrich (99%)\* |
| Gen X | 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoate |  | 62037-80-3 | C6H4F11NO3 | AccuStandard |
| NaDONA | dodecafluoro-3H-4,8-dioxanonanoate |  | 958445-44-8 | C7H5F12NO4 | Wellington Laboratories (50 ug/mL, methanol)\* |
| 9Cl-PF3ONS | 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate | |  | | --- | |  | | 73606-19-6 | C8ClF16KO4S | Wellington Laboratories (50 ug/mL, methanol)\* |
| ***Precursor compounds*** | | | | | |
| diSAMPAP | bis[2-(N-ethylperfluorooctane-1-sulfonamido)ethyl] phosphate | |  | | --- | |  | |  | | 30381-98-7 | C24H22F34N3O8PS2 | Wellington Laboratories (50 ug/mL, methanol)\* |
| 6:2 diPAP | 6:2 polyfluoroalkyl phosphate diesters |  | 57677-95-9 | C16H9F26O4P | Wellington Laboratories (50 ug/mL, methanol) |
| 8:2 diPAP | 8:2 polyfluoroalkyl phosphate diesters |  | 1578186-42-1 | C24H9F42O4P | Wellington Laboratories (50 ug/mL, methanol) |
| 6:2-FTEO1C | 2-Perfluorhexylethyl acetate |  | - | C10H7F13O2 | Self-synthesized |
| 8:2-FTEO1C | 2-Perfluorooctylethyl acetate |  | 37858-04-1 | C12H7F17O2 | Self-synthesized |
| 4:3-acid | 3-(Perfluorobutyl)propanoic acid |  | 80705-13-1 | C7H5F9O2 | DuPont |
| 5:3-acid | 2H,2H,3H,3H-Perfluorooctanoic acid |  | 914637-49-3 | C8H5F11O2 | DuPont |
| 6:3-acid | 2H,2H,3H,3H-Perfluorononanoic acid |  | 27854-30-4 | C9H5F13O2 | DuPont |
| 7:3-acid | 2H,2H,3H,3H-Perfluoroundecanoic acid |  | 34598-33-9 | C11H5F17O2 | DuPont |
| 6:2 FTUCA | 2H-Perfluoro-2-octenoic acid |  | 70887-88-6 | C8H2F12O2 | Wellington Laboratories (50 ug/mL, methanol) |
| 8:2 FTUCA | 2H-Perfluoro-2-decenoic acid |  | 70887-84-2 | C10H2F16O2 | Wellington Laboratories (50 ug/mL, methanol) |
| 10:2 FTUCA | 2H-Perfluoro-2-dodecenoic acid |  | 70887-94-4 | C12H2F20O2 | Wellington Laboratories (50 ug/mL, methanol) |

\*Standards were in salt form but assumed neat when calculating calibration curves. This yielded an error due to the wrong molar mass being used. However, the resulting error was smaller than the overall method error, so it was assumed insignificant.

Table S2. Determination parameters for the analysis of PFAS.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Category** | **Abbreviation** | **Extraction and determination method** | **Cone voltage (V)** | **Q1 → Q3(1) (CE)** | **Q1 → Q3(2) (CE)** | **IS** | **iLOQ**  **(ng mL-1)** | **mLOQ (ng g-1)** |
| Ultrashort chainPFSAs and PFCAs | TFMS | BC- Ahmadireskety et al. (2021) | - | - | - | None | 0.01 | 0.05 |
| PFEtS | BC- Ahmadireskety et al. (2021) | - | - | - | None | 0.01 | 0.05 |
| PFPrS | BC- Ahmadireskety et al. (2021) | - | - | - | None | 0.01 | 0.05 |
| PFPrA | BC- Ahmadireskety et al. (2021) | - | - | - | None | 0.05 | 0.25 |
| PFCAs | PFBA | AA | 28 | 213 → 169 (10) | - | PFOA 13C8 | 1.00 | 10.0 |
| PFPeA | AA | 20 | 263 → 219 (8) | - | PFOA 13C8 | 0.10 | 1.00 |
| PFHxA | AA | 10 | 313→ 269 (8) | 313 → 119 (18) | PFOA 13C8 | 0.10 | 1.00 |
| PFHpA | AA | 6 | 363 → 169 (18) | 363 → 119 (22) | PFOA 13C8 | 0.20 | 2.00 |
| PFOA | AA | 20 | 413 → 369 (8) | 413 → 169 (18) | PFOA 13C8 | 0.05 | 0.50 |
| PFNA | AA | 20 | 463 → 419 (10) | 463 → 219 (16) | PFOA 13C8 | 0.10 | 1.00 |
| PFDA | AA | 10 | 513 → 269 (16) | 513 → 219 (18) | PFOS 13C8 | 0.05 | 0.50 |
| PFUnA | AA | 12 | 563 → 519 (10) | 563 → 269 (18) | PFOA 13C8 | 0.10 | 1.00 |
| PFDoDA | AA | 26 | 613 → 569 (12) | 613 → 169 (26) | PFOS 13C8 | 0.05 | 0.50 |
| PFTriDA | AA | 6 | 663 → 619 (10) | 663 → 169 (24) | PFOA 13C8 | 0.10 | 1.00 |
| PFTDA | AA | 20 | 713 → 669 (14) | 713 → 169 (30) | PFOS 13C8 | 0.10 | 1.00 |
| PFHxDA | AA | 36 | 813 → 169 (34) | 813 → 219 (24) | PFOS 13C8 | 0.50 | 5.00 |
| PFOcDA | AA | 5 | 913 → 869 (15) | 913 → 169 (30) | 6:2 FTS 13C2 D4 | 5.00 | 50.00 |
| PFSAs | PFBS | AA | 42 | 299 → 99 (28) | 299→ 80 (26) | PFOS 13C8 | 0.05 | 0.5 |
| PFPeS | AA | 20 | 349 → 80 (30) | 349 → 99 (26) | PFOS 13C8 | 0.05 | 0.50 |
| PFHxS | AA | 5 | 399 → 80 (30) | 399 → 99 (30) | 6:2 FTS 13C2 D4 | 0.05 | 0.50 |
| PFHpS | AA | 2 | 449 → 80 (34) | 449 → 99 (34) | PFOS 13C8 | 0.05 | 0.50 |
| PFOS | AA | 20 | 499 → 99 (38) | 499 → 80 (20) | PFOS 13C8 | 0.01 | 0.10 |
| PFNS | AA | 10 | 549 → 80 (40) | 549 → 99 (10) | 6:2 FTS 13C2 D4 | 0.05 | 0.50 |
| PFDS | AA | 10 | 599 → 80 (40) | 599 → 99 (40) | 6:2 FTS 13C2 D4 | 0.10 | 1.00 |
| PFDoDS | AA | 15 | 699 → 99 (40) | 699 → 80 (10) | 6:2 FTS 13C2 D4 | 0.10 | 1.00 |
| FTS | 4:2 FTS | AA | 34 | 327 → 307 (18) | 327 → 81 (26) | 6:2 FTS 13C2 D4 | 0.01 | 0.10 |
| 6:2 FTS | AA | 24 | 427 → 407 (24) | 427 → 81 (26) | 6:2 FTS 13C2 D4 | 0.01 | 0.10 |
| 8:2 FTS | AA | 40 | 527 → 507 (26) | 527 → 81 (28) | 6:2 FTS 13C2 D4 | 0.05 | 0.50 |
| 10:2 FTS | AA | 8 | 627 → 607 (32) | 627 → 81 (32) | 6:2 FTS 13C2 D4 | 0.01 | 0.10 |
| FSA | PFOSA | AA | 12 | 498 → 78 (28) | 498 → 478 (26) | PFOS 13C8 | 0.01 | 0.10 |
| MeFOSA | AA | 42 | 512 → 219 (24) | 512 → 112 (26) | PFOS 13C8 | 0.05 | 0.50 |
| EtFOSA | AA | 44 | 526 → 169 (26) | 526 → 219 (26) | PFOS 13C8 | 0.10 | 1.00 |
| FOSAA | AA | 12 | 556 → 498 (28) | 556 → 419 (24) | PFOS 13C8 | 0.10 | 1.00 |
| MeFOSAA | AA | 6 | 570 → 419 (18) | 570 → 483 (16) | PFOS 13C8 | 0.05 | 0.50 |
| EtFOSAA | AA | 76 | 526 → 169 (24) | 526 → 219 (24) | PFOS 13C8 | 0.50 | 5.00 |
| MeFOSE | AA | 24 | 616 → 59 (14) | - | PFOS 13C8 | 0.20 | 2.00 |
| EtFOSE | AA | 28 | 630 → 59 (12) | - | PFOS 13C8 | 0.20 | 2.00 |
| Miscellaneous | DecaS | AA | 56 | 221 → 80 (24) | 221 → 65 (22) | PFOA 13C8 | 0.20 | 2.00 |
| 7H-PFHpA | AA | 8 | 345 → 281 (10) | 345 → 131 (24) | PFOS 13C8 | 0.05 | 0.50 |
| P37DMOA | AA | 44 | 469 →269 (24) | 469 →219 (24) | PFOS 13C8 | 0.01 | 0.10 |
| PFECHS | AA | 34 | 461 → 381 (26) | 461 → 99 (28) | 6:2 FTS 13C2 D4 | 0.05 | 0.50 |
| 9Cl-PF3ONS (F36 B) | AA | 66 | 531 → 351 (20) | 531 → 199 (22) | PFOS 13C8 | 0.05 | 0.50 |
| HFPO-DA (GenX) | AA | 36 | 285 → 119 (20) | 285 → 169 (10) | PFOA 13C8 | 1.00 | 10.0 |
| NaDONA | AA | 14 | 377 → 251 (8) | 377 → 85 (30) | PFOS 13C8 | 0.01 | 0.10 |
| Precursor compounds | diSAMPAP | AA | 92 | 1203 → 526 (40) | 1203 → 169 (66) | PFOS 13C8 | 0.50 | 5.00 |
| 6:2 diPAP | BB- Ahmadireskety et al. (2021) | 32 | 789 → 97 (132) | 789 → 79 (133) | M-8:2 diPAP | 0.10 | 0.50 |
| 8:2 diPAP | BB- Ahmadireskety et al. (2021) | 50 | 989 → 97 (120) | 989 → 97 (140) | M-8:2 diPAP | 0.50 | 2.50 |
| 6:2-FTEO1C | BB- Ahmadireskety et al. (2021) | 57 | 421 → 75 (39) | 421 → 255 (57) | MPFOA | 0.50 | 2.50 |
| 8:2-FTEO1C | BB- Ahmadireskety et al. (2021) | 57 | 521 → 75 (39) | 21 → 355 (57) | MPFDA | 0.50 | 2.50 |
| 4:3-acid | BB- Ahmadireskety et al. (2021) | 84 | 291 → 187 (22) | 291 → 167 (28) | MPFHxA | 0.50 | 2.50 |
| 5:3-acid | BB- Ahmadireskety et al. (2021) | 112 | 341 → 237 (14) | 341 → 217 (26) | MPFHpA | 0.50 | 2.50 |
| 6:3-acid | BB- Ahmadireskety et al. (2021) | 56 | 391 → 287 (18) | 391 → 267 (26) | MPFOA | 0.10 | 0.50 |
| 7:3-acid | BB- Ahmadireskety et al. (2021) | 84 | 441 → 337 (16) | 441 → 317 (32) | MPFNA | 0.05 | 0.25 |
| 6:2 FTUCA | BB- Ahmadireskety et al. (2021) | 41 | 357 → 293 (23) | - | M-6:2 FTUCA | 0.05 | 0.25 |
| 8:2 FTUCA | BB- Ahmadireskety et al. (2021) | 55 | 457 → 393 (22) | - | M-6:2 FTUCA | 0.05 | 0.25 |
| 10:2 FTUCA | BB- Ahmadireskety et al. (2021) | 51 | 557 → 493 (27) | - | M-6:2 FTUCA | 0.05 | 0.25 |

Table S3. Method comparison table

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **Absolute recoveries % (RSD)** | | | | | | **Matrix effects % (RSD)** | | | | | |
| **Compound** | **Arvaniti** | **LSE (EtOAc)** | **LSE Higher T** | | **LSE Clean-up** | | **Arvaniti** | **LSE (EtOAc)** | **LSE Higher T** | | **LSE Clean-up** | |
| *EtOAc* | *ACN* | *EtOAc* | *ACN* | *EtOAc* | *ACN* | *EtOAc* | *ACN* |
| *PFBA* | NA | 125 (107) | 93.3 (27.3) | 105.6 (16.5) | 76.8 (22.9) | 136 (19) | NA | 13.3 (77.2) | 360 (39.0) | 550 (41.5) | 357 (118) | 81.6 (645) |
| *PFPeA* | 127 (49.6) | 101 (17.8) | 64.7 (10.5) | 97.2 (4.46) | 81.9 (27.4) | 112 (4.48) | 10.3 (8.81) | 16.1 (31.7) | 107 (6.74) | 57.0 (27.5) | 37.5 (8.89) | 18.7 (49.4) |
| *PFHxA* | 64.1 (15.4) | 76.1 (23.1) | 63.3 (3.91) | 94.3 (10.3) | 97.1 (22.9) | 112 (13.7) | 48.8 (5.02) | 47.1 (5.75) | 78.2 (14.9) | 29.6 (35.5) | 48.7 (15.2) | 23.8 (62.1) |
| *PFHpA* | 61.5 (21.2) | 63.2 (23.2) | 53.1 (7.00) | 91.6 (8.27) | 117 (45.7) | 103 (17.9) | 34.9 (48.8) | 21.7 (12.1) | 45.7 (15.1) | 17.9 (56.0) | 20.4 (48.6) | 12.0 (43.8) |
| *PFOA* | 43.0 (36.1) | 54.3 (16.2) | 69.7 (8.12) | 79.5 (11.9) | 86.4 (6.91) | 86.8 (14.8) | 46.1 (16.83) | 12.8 (26.6) | 86.7 (8.44) | 12.5 (60.6) | 70.9 (22.0) | 10.2 (43.5) |
| *PFNA* | 29.6 (33.9) | 54.9 (17.3) | 71.2 (5.40) | 75.8 (6.05) | 126. (36.9) | 96.6 (17.2) | 37.6 (1.36) | 13.0 (14.7) | 38.5 (31.1) | 13.0 (68.1) | 11.6 (52.0) | 9.85 (43.4) |
| *PFDA* | 11.1 (41.7) | 57.1 (17.9) | 52.7 (13.0) | 70.1 (12.3) | 103 (33.4) | 90.4 (27.7) | 22.5 (4.51) | 10.0 (4.43) | 39.1 (37.6) | 12.7 (73.2) | 16.6 (41.7) | 10.3 (81.9) |
| *PFUnA* | 12.2 (18.7) | 51.6 (7.37) | 43.8 (20.3) | 41.3 (14.5) | 117 (11.0) | 137 (32.4) | 18.9 (12.0) | 12.7 (2.65) | 22.8 (33.9) | 6.81 (97.4) | 7.87 (68.4) | 3.70 (34.7) |
| *PFDoDA* | 13.3 (25.4) | 43.3 (15.8) | 44.0 (20.4) | 30.4 (35.5) | 125 (4.36) | 82.3 (39.0) | 10.1 (37.8) | 7.77 (14.4) | 23.1 (45.6) | 5.29 (115) | 3.18 (97.4) | 1.83 (51.0) |
| *PFTriDA* | 8.94 (109) | 37.8 (14.7) | 60.9 (7.7) | 32.4 (24.9) | 95.1 (1.21) | 91.5 (18.6) | 7.55 (8.61) | 5.93 (62.7) | 28.1 (58.6) | 6.71 (124) | 3.25 (49.9) | 1.70 (69.9) |
| *PFTDA* | 6.31 (45.4) | 44.2 (8.31) | 30.7 (18.0) | 35.8 (28.4) | 99.7 (1.48) | 83.0 (16.5) | 14.3 (35.9) | 15.8 (35.6) | 44.2 (29.2) | 12.5 (138) | 6.62 (65.4) | 4.70 (29.5) |
| *PFHxDA* | 4.19 (60.7) | 47.4 (18.6) | 9.26 (26.9) | 34.7 (28.7) | 86.1 (30.6) | 66.5 (20.6) | 55.1 (2.72) | 134 (6.98) | 46.8 (5.4) | 18.0 (137) | 21.0 (29.0) | 10.9 (0.81) |
| *PFOcDA* | NA | 42.5 (13.3) | 4.02 (51.0) | 38.7 (39.7) | 92.1 (25.3) | 67.0 (28.2) | NA | 272 (22.6) | 28.7 (10.1) | 15.5 (136) | 10.6 (8.44) | 4.91 (19.0) |
| *PFBS* | 99.0 (31.1) | 57.6 (23.2) | 66.0 (13.8) | 96.5 (7.89) | 88.9 (38.3) | 105 (14.4) | -1967 (-0.03) | 56.9 (3.41) | 65.9 (4.21) | 35.6 (36.4) | 52.0 (14.5) | 32.7 (53.9) |
| *PFPeS* | NA | 63.1 (19.2) | 73.6 (8.10) | 95.6 (6.41) | 87.4 (32.3) | 104 (14.1) | NA | 69.6 (5.97) | 79.7 (3.22) | 45.5 (44.2) | 66.7 (14.2) | 45.5 (55.3) |
| *PFHxS* | NA | 62.5 (24.4) | 77.5 (8.81) | 88.7 (1.83) | 86.1 (30.4) | 102 (13.9) | NA | 72.1 (5.27) | 75.4 (2.72) | 46.3 (51.5) | 73.6 (17.6) | 51.3 (53.5) |
| *PFHpS* | 36.0 (41.7) | 59.9 (26.7) | 75.4 (8.81) | 82.7 (6.65) | 85.8 (33.5) | 107 (11.4) | 91.8 (19.1) | 69.6 (6.82) | 59.5 (5.40) | 37.1 (54.9) | 56.5 (19.6) | 39.3 (52.0) |
| *PFOS* | 32.0 (62.9) | 63.2 (15.6) | 72.6 (9.41) | 77.9 (7.51) | 90.6 (34.6) | 106 (13.6) | 101 (1.07) | 63.1 (8.67) | 68.7 (4.91) | 35.8 (59.6) | 53.6 (16.6) | 35.8 (50.8) |
| *PFNS* | NA | 61.7 (17.1) | 67.6 (10.3) | 63.9 (5.40) | 87.9 (32.5) | 102 (13.6) | NA | 76.4 (7.72) | 63.2 (6.81) | 36.5 (71.7) | 61.0 (19.3) | 43.1 (56.0) |
| *PFDS* | NA | 59.7 (16.6) | 63.7 (11.1) | 41.6 (12.6) | 84.9 (29.3) | 98.9 (12.3) | NA | 65.4 (2.92) | 63.7 (5.84) | 32.2 (88.6) | 53.6 (20.2) | 37.8 (50.1) |
| *PFDoDS* | NA | 55.6 (17.4) | 41.9 (18.3) | 34.9 (21.7) | 80.1 (31.1) | 81.2 (16.3) | NA | 80.2 (6.20) | 60.6 (5.12) | 21.1 (134) | 45.1 (19.6) | 31.7 (39.4) |
| *4:2 FTS* | 86.8 (35.3) | 73.6 (7.83) | 63.7 (18.5) | 93.3 (7.30) | 83.4 (11.8) | 132 (3.70) | 182 (6.00) | 106 (0.96) | 115 (4.2) | 59.2 (45.8) | 193 (3.62) | 87.0 (86.2) |
| *6:2 FTS* | 65.0 (36.3) | 75.3 (5.4) | 70.2 (17.3) | 90.2 (5.65) | 80.8 (9.05) | 101 (2.93) | 145 (0.01) | 97.5 (0.41) | 110 (5.72) | 53.6 (55.3) | 151 (2.29) | 90.8 (73.9) |
| *8:2 FTS* | 28.5 (61.1) | 75.7 (2.50) | 67.7 (14.6) | 74.8 (8.46) | 87.8 (10.8) | 91.0 (6.81) | 136.4 (2.81) | 154 (3.67) | 151 (8.6) | 74.8 (70.6) | 176 (6.01) | 91.1 (83.6) |
| *10:2 FTS* | 20.7 (58.8) | 64.4 (6.99) | 52.8 (12.3) | 40.6 (19.4) | 76.6 (5.15) | 97.4 (5.8) | 79.3 (11.7) | 44.8 (12.8) | 77.6 (18.4) | 22.0 (104) | 56.8 (15.7) | 32.4 (74.5) |
| *PFOSA* | 20.2 (43.9) | 63.1 (13.2) | 34.6 (10.5) | 12.0 (6.99) | 91.2 (0.28) | 95.6 (15.3) | 48.6 (11.1) | 32.1 (8.27) | 34.5 (28.8) | 11.6 (87.9) | 90.2 (33.8) | 55.9 (79.1) |
| *MeFOSA* | 12.1 (72.1) | 50.5 (11.5) | 20.3 (14.1) | 4.84 (23.0) | 73.1 (7.30) | 75.5 (5.46) | 43.2 (9.61) | 68.7 (21.2) | 130 (15.3) | 43.4 (85.9) | 46.4 (25.1) | 35.4 (67.5) |
| *EtFOSA* | 10.7 (60.8) | 48.9 (17.8) | 20.0 (20.2) | 5.41 (27.3) | 75.3 (8.20) | 74.7 (4.58) | 59.2 (7.09) | 115 (12.1) | 192 (13.8) | 70.0 (89.6) | 283 (24.3) | 197 (71.7) |
| *FOSAA* | 18.8 (56.4) | 48.3 (6.78) | 25.6 (18.0) | 37.3 (13.7) | 64.8 (7.21) | 68.8 (7.19) | 61.9 (8.29) | 79.3 (6.56) | 84.8 (16.8) | 38.4 (86.9) | 68.9 (10.5) | 48.5 (62.7) |
| *MeFOSAA* | 18.9 (51.1) | 62.6 (6.78) | 23.5 (10.6) | 47.1 (12.6) | 89.9 (4.16) | 86.9 (9.92) | 57.1 (8.00) | 37.4 (1.56) | 42.1 (27.8) | 15.7 (91.1) | 38.8 (26.9) | 25.7 (67.1) |
| *EtFOSAA* | 10.2 (53.7) | 51.0 (17.3) | 19.1 (18.2) | 5.32 (29.1) | 69.6 (8.19) | 72.8 (1.04) | 61.2 (4.92) | 124 (10.8) | 210 (12.8) | 79.4 (91.1) | 308 (16.3) | 236 (65.0) |
| *MeFOSE* | 3.48 (97.2) | 51.6 (34.5) | 38.9 (22.5) | 10.1 (17.0) | 88.8 (6.66) | 100.6 (6.27) | 6.50 (21.6) | 8.91 (83.5) | 33.1 (31.9) | 13.1 (90.0) | 23.0 (49.3) | 19.7 (81.2) |
| *EtFOSE* | 2.86 (159) | 39.3 (14.3) | 34.9 (14.9) | 11.1 (18.0) | 100 (29.1) | 110 (11.5) | 14.2 (23.4) | 24.8 (58.4) | 42.5 (38.0) | 15.3 (99.2) | 17.3 (48.4) | 14.3 (75.8) |
| *DecaS* | 63.6 (47.9) | 64.0 (6.63) | 38.9 (17.7) | 86.6 (6.40) | 56.1 (13.2) | 83.6 (3.47) | 120 (2.76) | 68.6 (8.58) | 68.8 (2.50) | 36.5 (45.5) | 294 (8.42) | 155 (69.7) |
| *7H-PFHpA* | 71.3 (20.2) | 82.9 (10.3) | 61.4 (8.00) | 79.9 (14.7) | 123 (16.5) | 134 (15.4) | 45.9 (6.39) | 20.7 (15.1) | 41.7 (22.4) | 17.2 (53.0) | 27.3 (24.1) | 15.2 (93.7) |
| *P37DMOA* | 22.1 (43.1) | 77.7 (7.41) | 68.8 (6.54) | 79.6 (8.20) | 86.4 (16.4) | 122 (4.85) | 76.5 (1.49) | 39.3 (1.93) | 49.9 (16.4) | 21.6 (70.2) | 47.6 (1.89) | 30.4 (80.9) |
| *PFECHS* | NA | 80.9 (11.4) | 73.8 (12.5) | 88.2 (7.90) | 88.4 (13.4) | 105 (4.93) | NA | 48.1 (0.46) | 54.9 (13.4) | 28.2 (59.1) | 61.7 (0.17) | 40.6 (76.1) |
| *9Cl-PF3ONS* | 23.4 (63.6) | 82.4 (7.82) | 72.8 (9.50) | 71.7 (5.56) | 82.7 (11.3) | 120 (2.36) | 79.1 (1.92) | 72.3 (0.95) | 60.4 (10.3) | 37.0 (70.6) | 99.1 (1.98) | 65.8 (77.2) |
| *GenX* | 80.0 (26.2) | 117 (8.27) | 87.3 (12.1) | 106 (6.86) | 74.4 (11.3) | 36.4 (7.66) | 74.3 (27.3) | 49.4 (5.69) | 65.7 (9.01) | 39.2 (23.8) | 75.6 (9.00) | 52.8 (48.0) |
| *NaDONA* | 43.1 (25.5) | 73.1 (14.1) | 68.7 (4.01) | 86.5 (8.48) | 98.3 (10.9) | 100 (15.9) | 67.4 (3.37) | 32.7 (2.7) | 40.2 (22.4) | 21.0 (59.0) | 47.7 (22.5) | 30.2 (79.5) |
| *diSAMPAP* | 9.78 (82.4) | 73.7 (25.8) | 7.18 (44.5) | 30.9 (21.2) | 90.8 (65.38) | 66.5 (29.6) | 313 (5.55) | 143 (42.7) | 109 (44.0) | 57.1 (139) | 80.4 (45.6) | 41.2 (39.8) |

Table S4. Method validation of the proposed methodology for the analysis of the 41 generic PFAS – Method AA, in addition to method validation for the established methods BB and BC. Mean Absolute recoveries (Abs%), Relative recoveries (Rel%) and Matrix effects (ME%) for sludge and biochar fortified at 3 different concentrations (2.5, 10 and 20 ng g-1), n=3 replicates.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | **Sludge** | | | **Biochar** | | |
|  | **Compound** | **Abs % (RSD)** | **Rel % (RSD)** | **ME % (RSD)** | **Abs % (RSD)** | **Rel % (RSD)** | **ME % (RSD)** |
| Method AA | *PFBA* | 121 (22.3) | 159 (30.6) | 117 (4.57) | 25.4 (13.9) | 74.8 (11.8) | 113 (25.0) |
| *PFPeA* | 115 (15.1) | 141 (33.7) | 32.2 (9.71) | 19.6 (30.0) | 40.1 (26.1) | 107 (9.41) |
| *PFHxA* | 75.1 (7.89) | 85.0 (19.4) | 42.2 (0.58) | 32.9 (16.9) | 67.7 (11.2) | 90.7 (7.36) |
| *PFHpA* | 46.4 (18.0) | 103 (33.6) | 18.2 (20.2) | 51.2 (20.7) | 157 (17.0) | 74.2 (4.08) |
| *PFOA* | 72.2 (3.55) | 103 (8.08) | 18.2 (19.4) | 67.5 (7.36) | 83.4 (6.08) | 74.7 (0.80) |
| *PFNA* | 58.9 (15.0) | 96.0 (13.3) | 17.2 (16.4) | 79.7 (10.2) | 167 (11.9) | 68.1 (11.8) |
| *PFDA* | 59.1 (22.9) | 99.3 (26.2) | 11.2 (16.2) | 72.5 (13.1) | 151 (13.4) | 109 (3.13) |
| *PFUnA* | 54.9 (17.2) | 86.7 (5.03) | 20.2 (4.36) | 72.1 (10.7) | 151 (14.6) | 70.1 (0.61) |
| *PFDoDA* | 50.2 (12.5) | 77.3 (7.27) | 19.2 (0.63) | 58.6 (4.56) | 122 (4.62) | 88.2 (6.37) |
| *PFTriDA* | 38.1 (7.21) | 53.8 (1.75) | 22.2 (7.77) | 51.7 (3.32) | 108 (6.62) | 75.9 (8.08) |
| *PFTDA* | 33.5 (13.5) | 41.3 (29.3) | 19.2 (4.37) | 37.4 (2.98) | 78.3 (10.6) | 68.4 (0.40) |
| *PFHxDA* | 32.7 (13.2) | 33.7 (9.67) | 29.2 (29.3) | 13.0 (25.7) | 27.4 (24.7) | 45.9 (37.4) |
| *PFOcDA* | 36.3 (3.03) | 35.4 (2.16) | 23.2 (55.6) | 9.91 (8.30) | 20.9 (6.49) | 23.9 (94.5) |
| *PFBS* | 39.6 (3.06) | 79.0 (8.26) | 57.2 (8.75) | 34.0 (26.6) | 102 (6.91) | 85.0 (6.30) |
| *PFPeS* | 59.9 (13.1) | 125 (18.8) | 58.2 (9.82) | 47.5 (14.2) | 147 (14.3) | 87.9 (13.5) |
| *PFHxS* | 72.6 (20.0) | 154 (22.6) | 50.2 (12.4) | 51.8 (4.56) | 163 (25.4) | 85.0 (6.56) |
| *PFHpS* | 75.6 (18.5) | 136 (13.5) | 51.2 (11.6) | 54.1 (5.24) | 67.3 (12.9) | 75.8 (1.87) |
| *PFOS* | 78.6 (17.8) | 112 (2.57) | 52.2 (8.62) | 55.0 (8.69) | 115 (1.42) | 76.6 (6.21) |
| *PFNS* | 64.4 (11.8) | 97.5 (8.92) | 51.2 (6.08) | 53.5 (6.35) | 112 (1.23) | 75.3 (2.97) |
| *PFDS* | 66.3 (20.1) | 97.9 (2.70) | 52.2 (6.27) | 53.5 (5.39) | 112 (3.78) | 74.8 (4.86) |
| *PFDoDS* | 47.1 (6.96) | 61.7 (23.5) | 51.2 (3.82) | 37.9 (7.98) | 79.0 (4.50) | 72.0 (10.0) |
| *4:2 FTS* | 21.6 (20.1) | 32.8 (8.90) | 152 (8.98) | 16.0 (19.4) | 47.1 (24.2) | 144 (17.4) |
| *6:2 FTS* | 54.9 (5.98) | 111 (13.2) | 113 (9.91) | 31.2 (21.6) | 95.6 (5.5) | 158 (19.5) |
| *8:2 FTS* | 68.3 (16.8) | 101 (5.73) | 137 (5.01) | 56.6 (19.6) | 118 (16.7) | 120 (22.5) |
| *10:2 FTS* | 60.1 (19.7) | 88.8 (4.40) | 87.2 (12.2) | 46.6 (7.07) | 97.7 (8.39) | 120 (18.7) |
| *PFOSA* | 35.7 (11.7) | 46.8 (19.8) | 45.2 (7.87) | 30.1 (13.2) | 63.0 (21.3) | 89.8 (15.2) |
| *MeFOSA* | 21.6 (30.1) | 24.5 (17.2) | 46.2 (0.48) | 10.8 (7.44) | 22.3 (8.79) | 85.7 (19.6) |
| *EtFOSA* | 21.0 (23.5) | 22.8 (14.1) | 47.2 (5.17) | 11.2 (11.7) | 23.0 (13.9) | 86.1 (16.0) |
| *FOSAA* | 37.0 (7.78) | 53.32 (1.67) | 69.2 (13.2) | 9.25 (20.5) | 19.42 (28.5) | 127 (16.1) |
| *MeFOSAA* | 42.1 (7.65) | 55.9 (22.8) | 63.2 (14.6) | 54.5 (9.41) | 114.2 (9.5) | 103 (16.3) |
| *EtFOSAA* | 21.8 (23.8) | 23.9 (13.3) | 54.2 (3.94) | 11.6 (12.1) | 23.9 (14.3) | 86.7 (15.6) |
| *MeFOSE* | 25.3 (8.94) | 34.5 (18.1) | 20.2 (24.6) | 23.4 (17.7) | 48.9 (24.8) | 99.5 (8.00) |
| *EtFOSE* | 23.9 (28.8) | 29.2 (15.8) | 32.2 (25.9) | 25.7 (21.5) | 53.9 (29.0) | 86.7 (14.1) |
| *DecaS* | 11.2 (10.2) | 20.6 (0.83) | 82.2 (9.06) | 7.12 (14.2) | 11.7 (31.2) | 108 (17.5) |
| *7H-PFHpA* | 55.6 (9.61) | 73.4 (4.72) | 31.2 (16.5) | 44.1 (16.3) | 91.4 (22.2) | 112 (17.6) |
| *P37DMOA* | 66.6 (17.4) | 99.7 (4.28) | 58.2 (9.90) | 70.0 (6.44) | 147 (7.39) | 98.5 (13.4) |
| *PFECHS* | 84.1 (18.9) | 179 (22.6) | 68.2 (13.1) | 47.5 (2.88) | 152 (30.6) | 94.6 (15.1) |
| *9Cl-PF3ONS* | 80.1 (17.4) | 118 (8.04) | 81.2 (4.38) | 49.1 (1.39) | 103 (9.05) | 104 (13.9) |
| *GenX* | 140 (27.1) | 181 (31.1) | 45.1 (2.39) | 27.9 (5.19) | 57.7 (20.0) | 68.0 (0.51) |
| *NaDONA* | 51.6 (11.8) | 80.8 (8.04) | 34.2 (14.8) | 60.6 (19.4) | 126 (13.5) | 92.0 (12.9) |
| *diSAMPAP* | 42.4 (2.08) | 42.2 (0.91) | 81.2 (30.5) | 15.0 (7.68) | 31.7 (11.7) | 39.2 (8.39) |
| *Range* | *11.2 - 140 %* | *20.6 - 181 %* | *11.2 - 137 %* | *7.12 - 79.7 %* | *11.7 - 163 %* | *23.9 - 158%* |
| *RSD (%)* | *3.03 - 30.1 %* | *0.83 - 36.6 %* | *<30.5* | *1.39 - 30.0 %* | *1.23 - 31.2 %* | *0.40 - 25 %* |
| Method BB | *4:3 acid* | 11.1 (4.5) | - | -16.7 (0.6) | 6.1 (3.1) | - | -6.2 (8.2) |
| *5:3 acid* | 12.6 (4.1) | - | -41.2 (3.7) | 8.9 (4.2) | - | -12.1 (4.1) |
| *6:3 acid* | 12.2 (3.7) | - | -46.7 (4.6) | 13.2 (5.4) | - | -4.7 (3.1) |
| *7:3 acid* | 13.9 (2.4) | - | -55.1(1.2) | 15.8 (5.6) | - | -4.1 (4.8 |
| *6:2 FTUCA* | 27.3 (5.0) | - | -30.5 (0.5) | 27.2 (5.9) | - | -11.4 (4.4) |
| *8:2 FTUCA* | 21.5 (1.2) | - | -57.6 (2.5) | 37.0 (5.7) | - | -9.5 (7.0) |
| *10:2 FTUCA* | 16.5 (3.0) | - | -74.1 (4.6) | 43.0 (4.9) | - | -15.6 (5.2) |
| *6:2 diPAP* | 28.3 (3.3) | - | -61.3 (2.1) | 56.0 (7.9) | - | -9.7 (3.0) |
| *8:2 diPAP* | 116 (1.0) | - | -62.8 (17.3) | 68.8 (4.5) | - | 31.9 (7.7) |
| *6:2 FTEO1C* | 52.9 (6.7) | - | -28.3 (3.7) | 53.7 (11.2) | - | -3.2 (12.5) |
| *8:2 FTEO1C* | 36.0 (2.3) | - | -50.4 (1.1) | 52.0 (7.3) | - | -13.0 (3.4) |
| *Range* | 11.1-116 % | - | -74.1 - 62.8 % | 6.1 - 68.8 % | - | -15.6 - 31.9 % |
| *RSD range* | 1.0-6.7 % | - | 0.5 - 17.3 % | 3.1 - 11.2 % | - | 3.0 - 12.5 % |
| Method BC | *TFMSA* | 25.9 (2.0) | - | -67.2 (2.9) | 61.1 (1.1) | - | -17.7 (1.7) |
| *PFEtS* | 35.5 (2.0) | - | -54.6 (5.8) | 67.5 (3.3) | - | -12.1 (4.1) |
| *PFPrS* | 44.9 (1.5) |  | -43.8 (7.0) | 75.5 (2.5) |  | -4.6 (3.7) |
| *PFPrA* | 2.1 (0.2) | - | -96.8 (1.3) | 42.0 (2.4) | - | -53.1 (1.7) |
| *Range* | 2.1 - 44.9 % | - | -96.8 - -43.8 % | 42 - 75.5 % | - | -53.1 - -4.6 % |
| *RSD range* | 0.2 - 2.0 % | - | 1.3 - 7.0 % | 1.1 - 3.3 % | - | 1.7 - 4.1 % |

Table S5. Mean concentrations (±standard deviation) of PFAS-congeners (ng g-1) detected in feedstock samples (F), and biochars produced at various temperatures (500-800 ºC), from food waste reject (FWR), waste timber (WT), garden waste (GW) and clean wood chips (CWC). Also showing fractions (%) of short and long chains of the detected concentrations.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **PFAS type** | **PFAS comp.** | **DSS-1** | | | | | **DSS-2** | | | | | **LSS** | | | **DWSS** | | | |
| **F** | **500** | **600** | **700** | **750** | **F** | **500** | **600** | **700** | **800** | **F** | **600** | **750** | **F** | **600** | **700** | **800** |
| PFCA | PFBA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 84±81 | n.d. | n.d. | n.d. |
| PFPeA | n.d. | n.d. | n.d. | n.d. | n.d. | 336±32 | n.d. | n.d. | n.d. | n.d. | 217±44 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| PFHxA | n.d. | n.d. | n.d. | n.d. | n.d. | 23±3 | n.d. | n.d. | n.d. | n.d. | 27±7 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| PFOA | n.d. | 0.3±0.5 | 1±1 | 0.6±0.5 | 0.2±0.4 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| PFSA | PFHpS | 4±2 | n.d. | n.d. | n.d. | n.d. | 1.4±0.6 | 1±2 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1.8±0.9 | n.d. | n.d. | n.d. |
| PFOS | 14±4 | 0.6±0.5 | 0.7±0.2 | n.d. | n.d. | 38±8 | 1.6±0.9 | n.d. | n.d. | n.d. | 13±5 | 0.3±0.5 | 0.6±0.4 | 35±10 | n.d. | n.d. | n.d. |
| PFDS | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 6±1 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| FTS | 4:2 FTS | 24±10 | n.d. | n.d. | n.d. | n.d. | 27±3 | n.d. | n.d. | n.d. | n.d. | 64±7 | n.d. | n.d. | 80±11 | n.d. | n.d. | n.d. |
| 6:2 FTS | 1±1 | n.d. | n.d. | n.d. | n.d. | 1.1±0.9 | 0.4±0.3 | n.d. | n.d. | n.d. | 1±1 | n.d. | n.d. | 5±3 | n.d. | n.d. | n.d. |
| 8:2 FTS | 1.8±0.8 | n.d. | n.d. | n.d. | n.d. | 2±1 | n.d. | n.d. | n.d. | n.d. | 1.5±0.3 | n.d. | n.d. | 6±1 | n.d. | n.d. | n.d. |
| 10:2 FTS | 1.9±0.8 | n.d. | n.d. | n.d. | n.d. | 0.4±0.7 | n.d. | n.d. | n.d. | n.d. | 2±2 | n.d. | n.d. | 1.5±0.3 | n.d. | n.d. | n.d. |
| FSA | PFOSA | n.d. | n.d. | n.d. | n.d. | n.d. | 0.3±0.5 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| EtFOSA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 7±1 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| FOSAA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1±1 | n.d. | n.d. | n.d. |
| MeFOSAA | 0.2±0.4 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1.6±0.6 | n.d. | n.d. | 0.5±0.5 | n.d. | n.d. | n.d. |
| Mics. | P37DMOA | n.d. | 0.8±0.2 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| NaDONA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Precursor compounds | 6.2 diPAP | 5.4±0.2 | n.d. | n.d. | n.d. | n.d. | 6.9±0.1 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 8.2 diPAP | 2.8±0.4 | n.d. | n.d. | n.d. | n.d. | 1.49±0.02 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 6:2 FTUCA | n.d. | n.d. | n.d. | n.d. | n.d. | 3.3±0.9 | 0.4±0.2 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
|  | **PFAStot** | **56±11** | **1.7±0.7** | **2±1** | **0.6±0.5** | **0.2±0.4** | **429±41** | **3±2** | **n.d.** | **n.d.** | **n.d.** | **340±43** | **0.3±0.5** | **0.6±0.4** | **214±88** | **n.d.** | **n.d.** | **n.d.** |
|  | **Short chain (%)** | **55** | **0** | **0** | **0.0** | **0.0** | **93** | **24** | **0** | **0** | **0** | **91** | **0.0** | **0.0** | **79** | **0** | **0** | **0** |
|  | **Long**  **Chain (%)** | **45** | **100** | **100** | **100.0** | **100.0** | **10** | **76** | **0** | **0** | **0** | **9** | **100.0** | **100.0** | **21** | **0** | **0** | **0** |
| **PFAS type** | **PFAS compound** | **WT** | | | | | **CWC** | | | | | **FWR** | | | **GW** | | | |
| **F** | **500** | **600** | **700** | **800** | **F** | **500** | **600** | **700** | **750** | **F** | **600** | **800** | **F** | **500** | **600** | **800** |
| PFCA | PFBA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 219±27 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| PFPA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 2±4 | n.d. | n.d. | n.d. | 215±16 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| PFHxA | 487±83 | n.d. | <LOQ | n.d. | n.d. | 3577±1801 | n.d. | 1±1 | 1±2 | 2±1 | n.d. | n.d. | n.d. | 113±69 | 0.4±0.6 | n.d. | n.d. |
| PFOA | n.d. | n.d. | 0.1±0.2 | <LOQ | n.d. | n.d. | n.d. | n.d. | <LOQ | <LOQ | n.d. | n.d. | n.d. | n.d. | <LOQ | n.d. | 0.6±0.1 |
| PFNA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1±1 | n.d. | n.d. |
| PFDA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | <LOQ | 0.3±0.5 |
| PFSA | PFBS | 0.2±0.4 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| PFPeS | 13±1 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| PFHpS | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 8±2 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| PFOS | 1±1 | <LOQ | n.d. | n.d. | 0.1±0.1 | 45±33 | n.d. | n.d. | <LOQ | n.d. | 9±8 | 0.59±0.07 | 0.3±0.3 | n.d. | 0.1±0.2 | n.d. | n.d. |
| PFDS | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 2±3 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| FTS | 4:2 FTS | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 223±23 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 6:2 FTS | n.d. | n.d. | 0.14±0.03 | n.d. | n.d. | 0.04±0.07 | 0.1±0.1 | 0.1±0.1 | 0.1±0.1 | n.d. | 0.3±0.4 | n.d. | n.d. | n.d. | 0.04±0.08 | 0.04±0.06 | <LOQ |
| 10:2 FTS | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1±1 | n.d. | n.d. | n.d. |
| FSA | EtFOSA | n.d. | n.d. | n.d. | n.d. | n.d. | 26±21 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| EtFOSE | 10±18 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Micselaneous | P37DMOA | n.d. | n.d. | n.d. | n.d. | n.d. | 2±3 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| NaDONA | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.5±0.4 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
|  | **PFAStot** | **511±79** | **<LOQ** | **0.3±0.2** | **<LOQ** | **0.1±0.1** | **3651±1846** | **2±4** | **1±1** | **1±2** | **2±1** | **676±62** | **0.59±0.07** | **0.3±0.3** | **114±70** | **1±1** | **0.04±0.06** | **1±1** |
|  | Short chain (%) | 98 | 0 | 52 | 0.0 | 0.0 | 98 | 100 | 100 | 100 | 100 | 97 | 0.0 | 0.0 | 99 | 44 | 100 | 0 |
|  | Long chain (%) | 2 | 0 | 48 | 0.0 | 100.0 | 2 | 0 | 0 | 0 | 0 | 3 | 100.0 | 100.0 | 1 | 79 | 0 | 100 |

Table S6. Pyrolysis treatment details, mass yield (%) and carbon yield (%) for digested sewage sludge (DSS-1 and DSS-2), limed sewage sludge (LSS), de-watered sewage sludge (DWSS), food waste reject (FWR), waste timber (WT), garden waste (GW) and clean wood chips (CWC).

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Feedstock** | **Pyrolysis temp. (°C)** | **Residence time (min)** | **Mass yield (%)** | | | **Total C (%)** | | | |
| **Biochar** | **Condensate** | **Gas** | **Feedstock** | **Biochar** | **Condensate** | **Gas** |
| DSS-1 | 500 | 20 | 54.1 | 30.6 | 15.3 | 20.5 | 13.2 | 33.6 | 1.5 |
| 600 | 20 | 50.6 | 30.4 | 19.1 | 20.5 | 13.1 | 8.0 | 1.4 |
| 700 | 20 | 53.7 | 32.8 | 13.4 | 20.5 | 13.5 | 7.7 | 1.6 |
| 800 | 20 | 53.7 | 32.8 | 13.4 | 20.5 | 13.1 | - | 1.7 |
| DSS-2 | 500 | 20 | 40.3 | 36.9 | 22.8 | 31.6 | 30.3 | 15.5 | 1.4 |
| 600 | 20 | 37.3 | 36.9 | 25.8 | 31.6 | 28.0 | 12.2 | 1.3 |
| 700 | 20 | 38.5 | 50.3 | 11.2 | 31.6 | 28.1 | 9.1 | 1.0 |
| 800 | 20 | 34.8 | 44.1 | 21.1 | 31.6 | 27.7 | 10.3 | 1.4 |
| LSS | 600 | 20 | 56.7 | 23.9 | 19.4 | 22.6 | 15.7 | 54.3 | 1.1 |
| 760 | 20 | 46.2 | 24.6 | 29.3 | 22.6 | 10.5 | 19.5 | 0.4 |
| DWSS | 600 | 40 | 40.0 | - | - | 33.7 | 31.7 | - | - |
| 700 | 40 | 38.7 | - | - | 33.7 | 29.6 | - | - |
| 800 | 40 | 33.0 | - | - | 33.7 | 31.0 | - | - |
| FWR | 600 | 20 | 39.7 | 28.3 | 32.0 | 45.9 | 30.9 | - | 1.8 |
| 800 | 20 | 38.0 | 27.5 | 34.5 | 45.9 | 32.3 | 22.4 | 1.7 |
| WT | 500 | 20 | 25.8 | 57.1 | 17.1 | 48.1 | 85.0 | 28.2 | 1.9 |
| 600 | 20 | 23.3 | 45.5 | 31.2 | 48.1 | 79.6 | 19.4 | 1.9 |
| 700 | 20 | 20.9 | 40.8 | 38.3 | 48.1 | 85.4 | 12.4 | 1.8 |
| 800 | 20 | 18.8 | 39.1 | 42.1 | 48.1 | 85.1 | 0.5 | 2.0 |
| GW | 500 | 20 | 30.1 | 41.3 | 28.6 | 46.0 | 55.4 | 30.0 | 1.8 |
| 600 | 20 | 28.7 | 29.8 | 41.5 | 46.0 | 60.2 | 14.7 | 1.7 |
| 800 | 20 | 20.8 | 31.3 | 47.9 | 46.0 | 67.3 | 5.4 | 1.9 |
| CWC | 500 | 20 | 20.0 | 36.7 | 43.3 | 50.3 | 91.4 | 28.2 | 1.3 |
| 600 | 20 | 21.5 | 35.3 | 43.2 | 50.3 | 92.5 | 24.2 | 1.3 |
| 700 | 20 | 21.0 | 29.4 | 49.6 | 50.3 | 91.4 | 12.4 | 1.4 |
| 750 | 20 | 18.5 | 15.5 | 66.0 | 50.3 | 89.9 | 8.5 | 1.9 |

Table S7. Removal efficiency (RE, %) of total PFAS in the transformation of waste feedstocks to biochars at various pyrolysis temperatures (500-800 °C).

|  |  |  |
| --- | --- | --- |
| **Feedstock** | **Pyr. Temp (°C)** | **RE (%)** |
| DSS-1 | 500 | 98.36 |
| 600 | 98.27 |
| 700 | 99.45 |
| 750 | 99.76 |
| DSS-2 | 500 | 99.69 |
| 600 | 100.00 |
| 700 | 100.00 |
| 800 | 100.00 |
| LSS | 600 | 99.95 |
| 750 | 99.91 |
| DWSS | 600 | 100.00 |
| 700 | 100.00 |
| 800 | 100.00 |
| FWR | 600 | 99.97 |
| 800 | 99.98 |
| WT | 500 | 100.00 |
| 600 | 99.99 |
| 700 | 100.00 |
| 800 | 100.00 |
| GW | 500 | 99.75 |
| 600 | 99.99 |
| 800 | 99.85 |
| CWC | 500 | 99.99 |
| 600 | 100.00 |
| 700 | 99.99 |
| 750 | 99.99 |

Table S8. Emission concentrations (ng m-3) for all PFAS detected on emitted particles and in the gaseous phase in the pyrolysis of sewage sludge feedstocks. Detectable concentrations shown as mean ± standard deviation. Also showing the fractions of gaseous and particle-based compounds (%), and the fractions of long and short chain PFAS (%).

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **PFAS type** | **PFAS compound** | **Fraction** | **DSS-1** | | | **DSS-2** | | | | | **LSS** | |
| **500** | **600** | **700** | **500** | **600** | **700** |  | **800** | **600** | **750** |
| PFCA | PFBA | Gaseous | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| Particles | n.d. | 10.76 ± 0.02 | 11.5 ± 0.4 | n.d. | 3.6 ± 0.2 | 7.4 ± 0.5 | 0.5 | 9 ± 1 | 9.4 ± 0.5 | 12 ± 2 |
| PFPeA | Gaseous | n.d. | n.d. | n.d. | n.d. | 9 ± 15 | n.d. | - | n.d. | n.d. | n.d. |
| Particles | 2.0 ± 0.4 | 26 ± 36 | n.d. | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| PFHpA | Gaseous | n.d. | 100 ± 99 | 35 ± 61 | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| 7H-PFHpA | Gaseous | n.d. | 22 ± 27 | n.d. | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| PFSA | PFBS | Gaseous | 42 ± 10 | 58 ± 16 | 46 ± 6 | n.d. | n.d. | n.d. | - | 10.9 ± 0.8 | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | - | n.d. | 0.19 ± 0.03 | n.d. |
| PFOS | Gaseous | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | 0.6 ± 0.8 | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| FTS | 6:2 FTS | Gaseous | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | 0.03 ± 0.05 | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| 8:2 FTS | Gaseous | n.d. | n.d. | n.d. | n.d. | 8 ± 14 | n.d. | - | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| FSA | PFOSA | Gaseous | n.d. | n.d. | n.d. | n.d. | 6 ± 11 | n.d. | - | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| MeFOSAA | Gaseous | 11 ± 19 | n.d. | n.d. | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| Misc. | NaDONA | Gaseous | 5 ± 9 | n.d. | 3 ± 6 | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | - | n.d. | n.d. | n.d. |
| Sum | PFAStot | Gaseous | 57 ± 23 | 181 ± 104 | 84 ± 62 | n.d. | 23 ± 23 | n.d. | - | 10.9 ± 0.8 | n.d. | 0.00 |
| Particles | 2.0 ± 0.4 | 36 ± 36 | 11.6 ±0.4 | 0.6 ± 0.8 | 3.6 ± 0.2 | 7.4 ± 0.5 | 0.5 | 9 ± 1 | 9.6 ± 0.5 | 12 ± 2 |
| Total | 59 ± 23 | 217 ± 110 | 96 ± 62 | 0.6 ± 0.8 | 27 ± 23 | 7.4 ± 0.5 | 0.5 | 20 ± 1 | 9.6 ± 0.5 | 12 ± 2 |
| Fractions of total | PFAStot | Gaseous | 97 | 83 | 88 | 0 | 87 | 0 |  | 55 | 0 | 0 |
| Particles | 3 | 17 | 12 | 100 | 13 | 100 |  | 45 | 100 | 100 |
| PFAStot | Short chain | 82 | 44 | 63 | 0 | 46 | 100 |  | 100 | 100 | 100 |
| Long chain | 18 | 56 | 37 | 100 | 54 | 0 |  | 0 | 0 | 0 |

Table S9. Emission factors (EF, mg tonne-1) for all PFAS detected on emitted particles or in the gaseous phase in the pyrolysis of sewage sludge feedstocks.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Emission factor (mg tonne-1)** | | | **DSS-1** | | | **DSS-2** | | | | **LSS** | |
| **PFAS type** | **PFAS compound** | **Fraction** | **500** | **600** | **700** | **500** | **600** | **700** | **800** | **600** | **750** |
| PFCA | PFBA | Gaseous | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Particles | n.d. | 0.172±0.001 | 0.15±0.01 | n.d. | 0.12±0.01 | 0.32±0.02 | 0.32±0.04 | 0.009±0.001 | 0.9±0.2 |
| PFPeA | Gaseous | n.d. | n.d. | n.d. | n.d. | 0.3±0.5 | n.d. | n.d. | n.d. | n.d. |
| Particles | 0.008±0.002 | 0.03±0.04 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| PFHpA | Gaseous | n.d. | 1.6±1.6 | 0.5±0.8 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 7H-PFHpA | Gaseous | n.d. | 0.4±0.4 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| PFSA | PFBS | Gaseous | 0.17±0.04 | 0.9±0.3 | 0.59±0.7 | n.d. | n.d. | n.d. | 0.39±0.03 | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.0002±0.0001 | n.d. |
| PFOS | Gaseous | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | 0.01±0.02 | n.d. | n.d. | n.d. | n.d. | n.d. |
| FTS | 6:2 FTS | Gaseous | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | 0.0004±0.0006 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 8:2 FTS | Gaseous | n.d. | n.d. | n.d. | n.d. | 0.3±0.5 | n.d. | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| FSA | PFOSA | Gaseous | n.d. | n.d. | n.d. | n.d. | 0.2±0.4 | n.d. | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| MeFOSAA | Gaseous | 0.04±0.07 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Misc. | NaDONA | Gaseous | 0.02±0.03 | n.d. | 0.04±0.07 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Particles | n.d. | n.d. | n.d. | 0.4±0.5 | n.d. | n.d. | n.d. | n.d. | n.d. |
|  | PFAStot | Gaseous | 0.23±0.09 | 2.9±1.7 | 1.1±0.8 | n.d. | 0.8±0.8 | n.d. | 0.39±0.03 | n.d. | n.d. |
| Sum | Particles | 0.008±0.002 | 0.20±0.04 | 0.15±0.01 | 0.01±0.02 | 0.12±0.01 | 0.32±0.02 | 0.32±0.04 | 0.0096±0.0005 | 0.9±0.2 |
|  | Total | 0.24±0.09 | 3.1±1.6 | 1.2±0.8 | 0.01±0.02 | 0.9±0.8 | 0.32±0.02 | 0.7±0.1 | 0.0096±0.0005 | 0.9±0.2 |
|  | PFAStot (%) | Gaseous | 97 | 94 | 88 | 0 | 87 | 0 | 55 | 0 | 0 |
|  | Particles | 3 | 6 | 12 | 100 | 13 | 100 | 45 | 100 | 100 |

Table S10. Volumes of flue gas produced per kg of biochar produced (m3 kg-1) from sewage sludge feedstocks included in the emission measurements. Vflue gas is used in Eq. 7 to derive EFPFAS.

|  |  |  |
| --- | --- | --- |
| **Feedstock** | **Pyrolysis temp. (°C)** | **Vflue gas (m3 kg-1)** |
| DSS-1 | 500 | 4 |
| 600 | 16 |
| 700 | 13 |
| DSS-2 | 500 | 25 |
| 600 | 33 |
| 700 | 43 |
| 800 | 36 |
| LSS | 600 | 1 |
| 750 | 72 |

Table S11. Mass balance for PFAS in the pyrolysis of 1 tonne of sewage sludge at temperatures between 500 and 800 °C.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **In feedstock (1 tonne)** | | **In biochar** | | | **Emitted** | | **Decomposed or trapped in pyrolysis oil** | |
| **Sample** | **PFAStot (µg)** | **Pyr temp (ºC)** | **PFAStot (mg)** | **Fbiochar (%)** | **PFAStot (mg)** | **Femitted (%)** | **PFAStot (mg)** | **Fdecomposed (%)** |
| DSS-1 | 55.6 | 500 | 0.91 | 1.64 | 0.13 | 0.231 | 54.6 | 98.13 |
| 600 | 0.96 | 1.73 | 1.56 | 2.808 | 53.1 | 95.47 |
| 700 | 0.30 | 0.55 | 0.67 | 1.203 | 54.6 | 98.25 |
| DSS-2 | 429.4 | 500 | 1.36 | 0.32 | 0.01 | 0.001 | 428 | 99.68 |
| 600 | 0.00 | 0.00 | 0.33 | 0.077 | 429.1 | 99.92 |
| 700 | 0.00 | 0.00 | 0.12 | 0.029 | 429.3 | 99.97 |
| 800 | 0.00 | 0.00 | 0.25 | 0.058 | 429.2 | 99.94 |
| LSS | 339.6 | 600 | 0.17 | 0.05 | 0.01 | 0.002 | 339.4 | 99.95 |
| 750 | 0.29 | 0.09 | 0.41 | 0.12 | 338.9 | 99.79 |

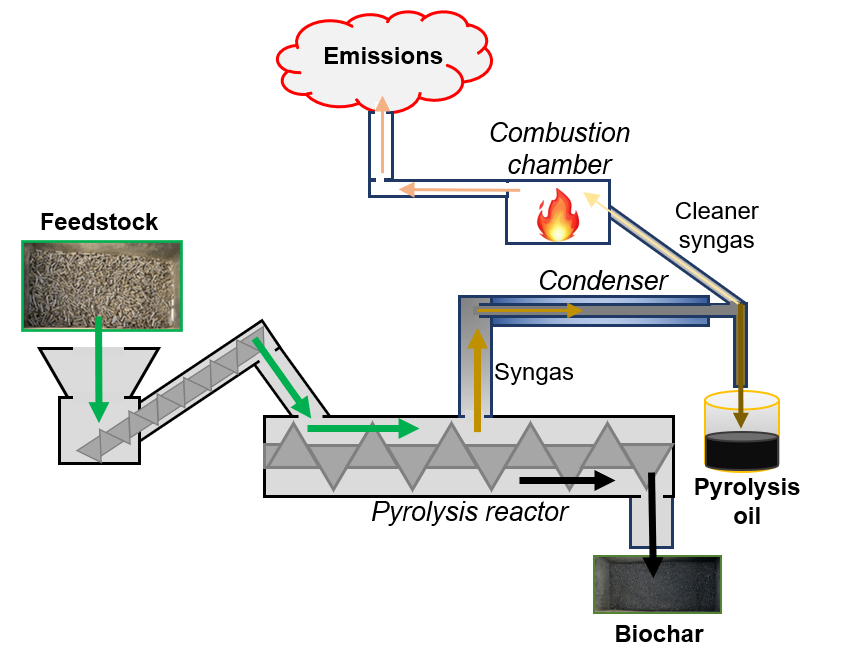


Figure S.1: Schematic overview of the pyrolysis system used.

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