**Supporting Information for ‘Ultra-short-chain PFAS in the sources of German drinking water: prevalent, overlooked, difficult to remove, and unregulated’**

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Supporting Information contains:

* Two files: Supporting Information part 1 (this Word file) and part 2 (separate Excel file)
* 12 tables, Table S2-S5 in Supporting Information part 1, Table S1, S6-S12 in Supporting Information part 2
* One figure in Supporting Information part 1
* Eight text chapters

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Table S2: List of all analyzed samples in anonymized form.

|  |  |  |
| --- | --- | --- |
| **Sample Name** | **Sample type** | **Connected with / influenced by** |
| SW 1 | Surface water | SW 2, 3 |
| SW 2 | Surface water | SW 1 |
| SW 3 | Surface water | SW 1 |
| SW 4 | Surface water | No connection |
| SW 5 | Surface water | BF 2, 3, 4 |
| SW 6 | Surface water | RW 2, 3 |
| SW 7 | Surface water | RW 4, 5 |
| SW 8 | Surface water | BF 6, 7 |
| SW 9 | Surface water | No connection |
| SW 10 | Surface water | RW 6, 7 |
| SW 11 | Surface water | BF 13 |
| SW 12 | Surface water | BF 14 |
| SW 13 | Surface water | GW 2, 3, 4 |
| SW 14 | Surface water | BF 15, 16 |
| SW 15 | Surface water | No connection |
| SW 16 | Surface water | No connection |
| BF 1 | Bank filtrate | SW 1, 2 |
| BF 2 | Bank filtrate | SW 5 |
| BF 3 | Bank filtrate | SW 5 |
| BF 4 | Bank filtrate | SW 5 |
| BF 5 | Bank filtrate | No connection |
| BF 6 | Bank filtrate | SW 8 |
| BF 7 | Bank filtrate | SW 8 |
| BF 8 | Bank filtrate | No connection |
| BF 9 | Bank filtrate | No connection |
| BF 10 | Bank filtrate | No connection |
| BF 11 | Bank filtrate | No connection |
| BF 12 | Bank filtrate | No connection |
| BF 13 | Bank filtrate | SW 11, nearby groundwater |
| BF 14 | Bank filtrate | SW 12, nearby groundwater |
| BF 15 | Bank filtrate | SW 14, nearby groundwater |
| BF 16 | Bank filtrate | SW 14, nearby groundwater |
| RW 1 | Raw water | No connection |
| RW 2 | Raw water | SW 6 |
| RW 3 | Raw water | SW 6 |
| RW 4 | Raw water | SW 7 |
| RW 5 | Raw water | SW 7 |
| RW 6 | Raw water | SW 10 |
| RW 7 | Raw water | SW 10 |
| GW 1 | Groundwater | Nearby surface water |
| GW 2 | Groundwater | SW 13 |
| GW 3 | Groundwater | SW 13 |
| GW 4 | Groundwater | SW 13 |
| GW 5 | Groundwater | No connection |
| GW 6 | Groundwater | Nearby surface water |
| GW 7 | Groundwater | No connection |

# Text S1: Liquid chromatography sample preparation

*Multi-layer solid phase extraction:* The multi-layer solid-phase extraction (mlSPE) cartridges contained 60 mg of CHROMABOND sorbens HR-XAW, CHROMABOND sorbens HR-XCW (both 45 µm) and Carbograph graphitized carbon black and were provided by Macherey Nagel (Düren, Germany). The protocol was as follows: 200 g of each water sample was adjusted to pH 5.5 ± 0.1 with formic acid or ammonia solution. Conditioning of the cartridges was performed using 1 mL methanolic ammonia solution (5%), 1 mL methanolic formic acid solution (2%), 1 mL methanol and 3 mL water. The samples were passed through the cartridge at a flow rate of approximately 5 mL/min and the cartridge was dried under a gentle stream of nitrogen for about 15 minutes. Elution was performed sequentially with 3 mL methanolic ammonia solution (5%), followed by evaporation of the extract (50°C; under a gentle stream of nitrogen), addition of 3 mL methanolic formic acid solution (2%) and 1.5 mL methanol, again followed by evaporation of the extract (50°C; under a gentle stream of nitrogen), and reconstitution in 1 mL acetonitrile:water 95:5 (v:v). The eluate was then mixed for 15 s and filtered through a syringe filter (regenerated cellulose, 0.20 µm, GE Healthcare, Little Chalfont, UK) into a 1 mL polypropylene (PP) vial (Klaus Ziemer, Langerwehe, Germany).

*Weak anion-exchange SPE:* 200 g of each water sample was weighed and enriched with Oasis WAX cartridges (Waters, Milford, MA, USA). The SPE protocol was as follows: Conditioning of the cartridges was performed with 2 mL methanolic ammonia solution (1%, v:v), 2 x 2 mL methanol and 3 x 2 mL water. After the samples were passed through the cartridges, they were rinsed with 3 mL water:methanol 4:1 (v:v) and dried under a gentle stream of nitrogen for 10 minutes. Elution was performed using 2 x 1 mL methanolic ammonia solution (1%, v:v). The eluate was then evaporated to dryness at 50 °C under a gentle stream of nitrogen, reconstituted in 0.5 mL methanol, and filtered through a syringe filter into a 0.5 mL PP vial.

# Text S2: Gas chromatography sample preparation

Sample preparation of trifluoroacetate (TFA) was performed by mixing 19 mL of the water sample with 500 µL ammonium carbonate solution (1 M) and 50 µL internal standard (IS) solution (chlorodifluoroacetic acid) in a 20 mL headspace vial. The mixture was evaporated to dryness at 90 °C overnight (8 – 14 h) in a compartment dryer. After cooling, 4 mL of the derivatization solution (75% H2SO4 (9 M) + 25% methanol) was added and the vial was immediately closed gas tight.

1,1,2,2,3,3,4,4,4-Nonafluoro-N-(2-hydroxyethyl)-N-methyl-1-butanesulfonamide (CAS 34454-97-2) and Trichloro-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (CAS 78560-45-9) were analyzed with gas chromatography mass spectrometry (GC-MS) after liquid-liquid extraction. To do this, a 1 L water sample was extracted with 20 mL hexane and the extract was evaporated in a test tube while flushing with a gentle nitrogen stream until it was reduced to 200 µL.

# Text S3: Hydrophilic interaction chromatography measurements

The column used for hydrophilic interaction chromatography (HILIC) was an Acquity ultra-high performance liquid chromatography (UHPLC) BEH Amide 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 injection volume was 5 μL, the total run time was 10 minutes and the flow rate was 500 μL/min. The employed gradient started at 100 % eluent B for 0-1 min, reduced 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.

# Text S4: Reversed-phase liquid chromatography measurements

The columns used were an Acquity UHPLC HSS T3 1.8 μm, 2.1 x 50 mm for the chromatographic run and a Luna C18(2), 5 µm 30 x 2 mm column (Phenomenex, Torrance, California, United States), which was installed after the mixing chamber of the eluents and before the injector to retain solvent blank signals for reversed-phase liquid chromatography (RPLC) measurements. The RPLC eluents consisted of 95% water and 5% methanol (v:v, eluent A) and 10% water and 90% methanol (v:v, eluent B) with 5 mM ammonium formate. The injection volume was 7.5 μL, the total run time was 8 minutes and the flow rate was 500 μL/min. The employed gradient started at 0% eluent B from 0-0.5 min, increased to 30% from 0.5-1 min, increased to 100% from 1-3.5 min and held it until 5.1 min, re-equilibrated to 0% from 5.1-5.5 min and held it until 8 min.

Table S3: Analytical information on liquid chromatography (LC) electrospray ionization (ESI) negative analytes, including used internal standard (IS) and sMRM parameters. IS: internal standard, DP: Declustering potential, EP: Entrance potential, CE: Collision energy, CXP: Collision cell exit potential.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **CAS-No.** | **Analyte** | **IS used** | **Chromatography** | **Time in min** | **Q1 mass** | **Q3 mass** | **DP in V** | **EP in V** | **CE in eV** | **CXP in V** |
| 1493-13-6 | TFMS | None | HILIC | 0.48 | 148.869 | 80 | -80 | -10 | -30 | -9 |
| 0.48 | 148.869 | 98.9 | -80 | -10 | -34 | -11 |
| 377739-43-0 | FAP | None | HILIC | 0.43 | 444.9 | 118.9 | -85 | -10 | -42 | -13 |
| 0.43 | 444.9 | 344.8 | -85 | -10 | -42 | -31 |
| 161401-25-8 | NTf2 | None | HILIC | 0.44 | 279.9 | 63.9 | -70 | -10 | -110 | -10 |
| 0.44 | 279.9 | 77.9 | -70 | -10 | -65 | -8 |
| 354-88-1 | PFEtS | None | HILIC | 0.46 | 199 | 80 | -20 | -10 | -43 | -10 |
| 0.46 | 199 | 99 | -20 | -10 | -34 | -10 |
| 422-64-0 | PFPrA | None | HILIC | 0.56 | 163 | 119 | -20 | -10 | -13 | -10 |
| 0.56 | 163 | 69 | -20 | -10 | -50 | -10 |
| 375-22-4 | PFBA | 13C4 MPFBA | RPLC | 2.48 | 213 | 169 | -52 | -10 | -20 | -10 |
| 2706-90-3 | PFPeA | 13C3 MPFPeA | RPLC | 3.19 | 263 | 219 | -40 | -10 | -13 | -10 |
| 307-24-4 | PFHxA | 13C2 MPFHxA | RPLC | 3.51 | 313 | 269 | -60 | -10 | -13 | -10 |
| 3.51 | 313 | 119 | -60 | -10 | -32 | -10 |
| 375-85-9 | PFHpA | 13C4 MPFHpA | RPLC | 3.75 | 363 | 319 | -60 | -10 | -15 | -10 |
| 3.75 | 363 | 169 | -60 | -10 | -25 | -10 |
| 335-67-1 | PFOA | 13C4 MPFOA | RPLC | 3.94 | 413 | 369 | -60 | -10 | -15 | -10 |
| 3.94 | 413 | 169 | -60 | -10 | -27 | -10 |
| 375-95-1 | PFNA | 13C5 MPFNA | RPLC | 4.11 | 463 | 419 | -60 | -10 | -18 | -10 |
| 4.11 | 463 | 169 | -60 | -10 | -29 | -10 |
| 335-76-2 | PFDA | 13C2 MPFDA | RPLC | 4.25 | 513 | 469 | -40 | -10 | -18 | -10 |
| 4.25 | 513 | 269 | -40 | -10 | -27 | -10 |
| 2058-94-8 | PFUnA | 13C2 MPFUnA | RPLC | 4.39 | 563 | 519 | -60 | -10 | -20 | -10 |
| 4.39 | 563 | 319 | -60 | -10 | -27 | -10 |
| 307-55-1 | PFDoA | 13C2 MPFDoA | RPLC | 4.53 | 613 | 569 | -60 | -10 | -23 | -10 |
| 4.53 | 613 | 219 | -60 | -10 | -29 | -10 |
| 72629-94-8 | PFTrA | 13C2 MPFDoA | RPLC | 4.67 | 663 | 619 | -80 | -10 | -23 | -10 |
| 4.67 | 663 | 169 | -80 | -10 | -41 | -10 |
| 376-06-7 | PFTeA | 13C2 MPFDoA | RPLC | 4.82 | 713 | 669 | -60 | -10 | -23 | -10 |
| 4.82 | 713 | 169 | -60 | -10 | -41 | -10 |
| 375-73-5 | PFBS | 13C2 MPFHxA | RPLC | 3.26 | 299 | 80 | -39 | -10 | -100 | -10 |
| 3.26 | 299 | 99 | -39 | -10 | -66 | -10 |
| 355-46-4 | PFHxS | 13C3 MPFHxS | RPLC | 3.74 | 399 | 80 | -32 | -10 | -100 | -10 |
| 3.74 | 399 | 99 | -32 | -10 | -88 | -10 |
| 375-92-8 | PFHpS | 13C4 MPFOA | RPLC | 3.93 | 449 | 80 | -42 | -10 | -100 | -10 |
| 3.93 | 449 | 99 | -42 | -10 | -100 | -10 |
| 1763-23-1 | PFOS | 13C4 MPFOS | RPLC | 4.09 | 499 | 80 | -35 | -10 | -100 | -10 |
| 4.09 | 499 | 99 | -35 | -10 | -100 | -10 |
| 335-77-3 | PFDS | 13C2 MPFUnA | RPLC | 4.37 | 599 | 80 | -52 | -10 | -130 | -10 |
| 4.37 | 599 | 99 | -52 | -10 | -120 | -10 |
|  | 13C4 MPFBA |  | RPLC | 2.48 | 217 | 172 | -52 | -10 | -13 | -10 |
|  | 13C2 MPFHxA |  | RPLC | 3.51 | 315 | 270 | -50 | -10 | -13 | -10 |
|  | 3.51 | 315 | 119 | -50 | -10 | -34 | -10 |
|  | 13C4 MPFOA |  | RPLC | 3.94 | 417 | 372 | -60 | -10 | -16 | -10 |
|  | 3.94 | 417 | 169 | -60 | -10 | -34 | -10 |
|  | 13C5 MPFNA |  | RPLC | 4.11 | 468 | 423 | -55 | -10 | -16 | -10 |
|  | 4.11 | 468 | 219 | -55 | -10 | -34 | -10 |
|  | 13C2 MPFDA |  | RPLC | 4.25 | 515 | 470 | -35 | -10 | -16 | -10 |
|  | 4.25 | 515 | 270 | -35 | -10 | -29 | -10 |
|  | 13C2 MPFUnA |  | RPLC | 4.39 | 565 | 520 | -60 | -10 | -21 | -10 |
|  | 4.39 | 565 | 219 | -60 | -10 | -31 | -10 |
|  | 13C2 MPFDoA |  | RPLC | 4.53 | 615 | 570 | -60 | -10 | -18 | -10 |
|  | 4.53 | 615 | 169 | -60 | -10 | -46 | -10 |
|  | 13C3 MPFHxS |  | RPLC | 3.74 | 403 | 84 | -40 | -10 | -80 | -10 |
|  | 3.74 | 403 | 103 | -40 | -10 | -64 | -10 |
|  | 13C4 MPFOS |  | RPLC | 4.09 | 503 | 80 | -40 | -10 | -88 | -10 |
|  | 4.09 | 503 | 99 | -40 | -10 | -91 | -10 |
| 27619-97-2 | 6:2 FTS | 13C2 M-6:2-FTS | RPLC | 3.92 | 427 | 81 | -100 | -10 | -75 | -10 |
|  | 13C2 M-6:2-FTS |  | RPLC | 3.92 | 429 | 81 | -92 | -10 | -78 | -10 |
| 13252-13-6 | HFPO-DA | 13C2 MPFHxA | RPLC | 3.59 | 329 | 169 | -30 | -10 | -20 | -10 |
| 3.59 | 329 | 285 | -30 | -10 | -10 | -10 |
| 423-41-6 | PFPrS | None | RPLC | 2.83 | 249 | 80 | -40 | -10 | -55 | -10 |
| 2.83 | 249 | 99 | -40 | -10 | -30 | -10 |
| 2706-91-4 | PFPeS | None | RPLC | 3.49 | 348.9 | 80 | -40 | -10 | -80 | -10 |
| 3.49 | 348.9 | 99 | -40 | -10 | -40 | -10 |
| 68259-12-1 | PFNS | None | RPLC | 4.19 | 548.8 | 80 | -80 | -10 | -120 | -10 |
| 4.19 | 548.8 | 99 | -80 | -10 | -105 | -10 |
| 79780-39-5 | PFDoS | None | RPLC | 4.65 | 698.7 | 80 | -130 | -10 | -130 | -10 |
| 4.65 | 698.7 | 99 | -130 | -10 | -120 | -10 |
| 2926-29-6 | Triflinate | None | RPLC | 0.42 | 132.9 | 69 | -60 | -10 | -20 | -10 |
| 0.42 | 132.9 | 83 | -60 | -10 | -15 | -10 |
| 80475-32-7 | DPOSA | None | RPLC | 4.05 | 526.8 | 64 | -170 | -10 | -105 | -10 |
| 4.05 | 526.8 | 120 | -170 | -10 | -40 | -10 |

# Text S5: GC method 1 – derivatization of TFA

For the measurement of TFA, the employed GC-MS system was a Hewlett Packard 6890 gas chromatograph with 5973 MSD (Hewlett Packard). An MPS 2 autosampler equipped with a temperature-controlled injection system (Gerstel, Mülheim a.d. Ruhr, Germany) was used. The used column was a Phenomenex ZB 624. Helium (5.0) was chosen as carrier gas with a flow of 1.0 – 1.3 L/min. A gaseous aliquot of 1000 µL was extracted with a heatable, gas tight plunger syringe and injected with a split ratio of 1:7. The temperature controlled injection system was programmed as follows: start temperature 75 °C, heating rate 2 °C/s, end temperature 80 °C, and final hold time 4 min. The oven temperature gradient was as follows: start temperature 35 °C, hold time 5 min, heating rate 20 °C/min, and end temperature 250 °C. As MS settings electron impact (EI) (70 eV) and single-ion monitoring (SIM) mode were chosen.

# Text S6: GC method 2 – liquid-liquid extraction

For the measurement of the liquid-liquid extracts of 1,1,2,2,3,3,4,4,4-Nonafluoro-N-(2-hydroxyethyl)-N-methyl-1-butanesulfonamide (CAS 34454-97-2) and Trichloro-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (CAS 78560-45-9) the employed GC-MS system was a GC-2010-Plus (Shimadzu, Duisburg, Germany) with GC-MS-TQ8030 (Shimadzu, Duisburg, Germany). An MPS2 autosampler and Multimode GC Inlet Optic 4 (Gerstel, Mülheim a.d. Ruhr, Germany) was used. The employed column was a Phenomenex Z5. Helium (5.0) was chosen as carrier gas with a flow of 1.0 L/min. An aliquot of 1 µL of the extract was injected in splitless mode. The temperature program of the injector started at 60 °C, followed by a heating phase of 10 °C/s until an end temperature of 280 °C, which was held for 4 min. The oven was programmed with a start temperature of 65 °C, a heating rate of 10 °C/min until the end temperature of 300 °C was reached. The end temperature was kept constant for 5 min. Measurements were performed in SIM mode (70 eV).

# Text S7: GC method 3 – headspace GC-MS

For the remaining headspace analyses, the employed GC-MS system was an Agilent 889 GC with 5977B MSD (Agilent, Waldbronn, Germany). As autosampler a Gerstel Robotic (Gerstel, Mülheim a.d. Ruhr, Germany) equipped with a temperature-controlled injection system GERSTEL KAS was used. The used column was a Phenomenex ZB624. Helium (5.0) was chosen as carrier gas with a flow of about 1.0 L/min.A gaseous aliquot of 1000 µL was taken from the sample’s headspace and injected with a split ratio of 10:1. The temperature program of the injector started at 80 °C, followed by a heating phase of 2 °C/s, until the end temperature of 85 °C was reached, which was held for 10 min. In order to ensure sufficient sample focusing at the column head, the GC-oven was programmed with a low start temperature of 35 °C, which was held for 5 min, followed by a heating phase of 10 °C/min until the final temperature of 220 °C was reached and held for 1 min. The following MS settings EI (70 eV) were chosen: a dwell time of 0.02 s and SIM mode.

Table S4: Analytical information on gas chromatography (GC) electron impact (EI) negative analytes, including manufacturer, mass spectrometry (MS) parameters, enrichment and recovery. IS: internal standard.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **CAS-No.** | **Analyte** | **Manufacturer** | **IS used** | **Time in min** | **Quantifier mass** | **1st Qualifier mass** | **2nd Qualifier mass** |
| 76-05-1 | TFA | Dr. Ehrenstorfer | Chlorodifluoro-acetic acid | 1.77 | 69 | 50 | 59 |
| 382-28-5 | 2,2,3,3,5,5,6,6-Octafluoro-4-(trifluoromethyl)-morpholine | Synquest Laboratories | Toluol D8 | 1.614 | 114 | 280 |  |
| 75-71-8 | Dichlorodifluoromethane | Dr. Ehrenstorfer | Toluol D8 | 1.659 | 85 | 87 |  |
| 40573-09-9 | 1,1,2,2,3,3-Hexafluoro-1-tri-fluoromethoxy-3-trifluorovinyloxy-propane | Unknown | Toluol D8 | 1.718 | 332 | 119 |  |
| 15290-77-4 | 1,1,2,2,3,3,4-Heptafluoro-cycloentane | Tokyo Chemical Industry Co. | Toluol D8 | 6.361 | 95 | 64 |  |
| 422-05-9 | 2,2,3,3,3-Pentafluoropropanol | Sigma Aldrich | Toluol D8 | 7.822 | 69 | 100 |  |
| 920-66-1 | HFIP | Sigma Aldrich | Toluol D8 | 10.609 | 99 | 149 |  |
| 355-93-1 | 2,2,3,3,4,4,5,5-Octafluoropentyl methacrylate | Tokyo Chemical Industry Co. | Toluol D8 | 15.741 | 69 | 95 |  |
| 17527-29-6 | 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl acrylate | Unknown | Toluol D8 | 16.122 | 99 | 418 |  |
| 85857-16-5 | Trimethoxy(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-silane | Tokyo Chemical Industry Co. | Toluol D8 | 17.035 | 91 | 121 |  |
| 2144-53-8 | 3,3,4,4,5,5,,6,6,7,7,8,8,8-Tridecafluorooctyl methacrylate | Unknown | Toluol D8 | 17.404 | 69 | 432 |  |
| 51851-37-7 | Triethoxy(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-silane | Tokyo Chemical Industry Co. | Toluol D8 | 18.845 | 163 | 119 |  |
| 34454-97-2 | 1,1,2,2,3,3,4,4,4-Nonafluoro-N-(2-hydroxyethyl)-N-methyl-1-butane-sulfonamide | Unknown | None | 7.340 | 326 | 69 | 219 |
| 78560-45-9 | Trichloro(3,3,4,4,5,5,6,6,7,7,8,8,8-trideca-fluorooctyl)silane | Tokyo Chemical Industry Co. | None | 10.980 | 215 | 185 | 173 |

Table S5: Tandem mass spectrometry (MS/MS)-parameters (Sciex 6500+) for the determination of PFAS after the TOP-assay. IS: Internal standard. DP: Declustering potential, EP: Entrance potential, CE: Collision energy, CXP: Collision cell exit potential.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| CAS-No. | Analyte | IS used | IS manufacturer | Q1 mass | Q3 mass | DP in V | EP in V | CE in eV | CXP in V |
| 375-22-4 | PFBA | 13C4 MPFBA | Wellington Laboratories | 212.9 | 168.9 | −14 | −11 | −15 | −10 |
| 2706-90-3 | PFPeA | 13C5 MPFPeA | Wellington Laboratories | 262.8 | 219 | −12 | −19 | −20 | −10 |
| 262.8 | 69 | −58 | −9 | −20 | −10 |
| 307-24-4 | PFHxA | 13C2 MPFHxA | Wellington Laboratories | 312.8 | 269 | −12 | −17 | −20 | −10 |
| 312.8 | 119 | −26 | −13 | −20 | −10 |
| 375-85-9 | PFHpA | 13C4 MPFHpA | Wellington Laboratories | 362.8 | 319 | −14 | −21 | −35 | −10 |
| 362.8 | 169 | −24 | −11 | −35 | −10 |
| 335-67-1 | PFOA | 13C4 MPFOA | Wellington Laboratories | 412.9 | 368.9 | −14 | −25 | −30 | −10 |
| 412.9 | 169 | −24 | −15 | −30 | −10 |
| 375-95-1 | PFNA | 13C5 MPFNA | Wellington Laboratories | 462.8 | 419 | −16 | −27 | −40 | −10 |
| 462.8 | 219 | −24 | −13 | −40 | −10 |
| 335-76-2 | PFDA | 13C2 MPFDA | Wellington Laboratories | 512.8 | 469 | −16 | −31 | −40 | −10 |
| 512.8 | 219 | −24 | −13 | −40 | −10 |
| 2058-94-8 | PFUnA | 13C2 MPFUnA | Wellington Laboratories | 562.8 | 518.9 | −16 | −37 | −55 | −10 |
| 562.8 | 269 | −26 | −23 | −55 | −10 |
| 307-55-1 | PFDoA | 13C2 MPFDoA | Wellington Laboratories | 612.8 | 568.9 | −18 | −37 | −50 | −10 |
| 612.8 | 169 | −34 | −11 | −50 | −10 |
| 72629-94-8 | PFTrA | 13C2 MPFDoA | Wellington Laboratories | 662.8 | 619 | −18 | −39 | −75 | −10 |
| 662.8 | 169 | −36 | −13 | −75 | −10 |
| 376-06-7 | PFTeA | 13C2 PFTeA | Wellington Laboratories | 712.8 | 669 | −20 | −41 | −75 | −10 |
| 712.8 | 169 | −36 | −13 | −75 | −10 |
| 423-41-6 | PFPrS | 13C3 PFBS | Wellington Laboratories | 248.9 | 80 | −75 | −10 | −52 | −9 |
| 248.9 | 98.9 | −75 | −10 | −36 | −11 |
| 375-73-5 | PFBS | 13C3 PFBS | Wellington Laboratories | 298.8 | 80 | −75 | −10 | −62 | −9 |
| 298.8 | 99 | −75 | −10 | −36 | −11 |
| 2706-91-4 | PFPeS | 18O2 PFHxS | Wellington Laboratories | 348.8 | 80 | −65 | −10 | −80 | −9 |
| 348.8 | 99 | −65 | −10 | −38 | −11 |
| 355-46-4 | PFHxS | 18O2 PFHxS | Wellington Laboratories | 398.8 | 80 | −105 | −10 | −90 | −9 |
| 398.8 | 99 | −105 | −10 | −80 | −11 |
| 375-92-8 | PFHpS | 13C4 PFOS | Wellington Laboratories | 448.8 | 80 | −125 | −10 | −104 | −9 |
| 448.8 | 99 | −125 | −10 | −88 | −11 |
| 1763-23-1 | PFOS | 13C4 PFOS | Wellington Laboratories | 498.8 | 99 | −125 | −10 | −98 | −11 |
| 498.8 | 80 | −125 | −10 | −114 | −9 |
| 68259-12-1 | PFNS | 13C2 PFDA | Wellington Laboratories | 548.8 | 80 | −115 | −10 | −122 | −9 |
| 548.8 | 99 | −115 | −10 | −106 | −11 |
| 335-77-3 | PFDS | 13C2 PFUnA | Wellington Laboratories | 598.8 | 80 | −110 | −10 | −132 | −9 |
| 598.8 | 99 | −110 | −10 | −118 | −11 |

# Text S8: Equations for calculations in validation

Equation for recovery (in %) calculation:

Equation for matrix effects (in %) calculation:

Equation for trueness (in %) calculation:

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Figure S1: Total concentrations of PFAS and their distribution in the samples (ordered by sample type; SW: surface water, BF: bank filtrate, RW: raw water, GW: groundwater). A) Bar plot of total concentration of all analyzed PFAS (blue) and concentration of TFA (green). The number above the bars depict the total amount of detected PFAS per sample. B) Stacked bar plot of relative abundance of all PFAS except for TFA. Blue and green colors represent short-chain and other non PFCA and PFSA PFAS, while yellow, orange and pink colors represent legacy long-chain PFAS. <LOQ was included as half its value for each substance.