Supporting Information

# Non-Targeted Analysis of Surface and Groundwaters Impacted by Historic PFAS Waste Sites

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## 1. Instrumental Methods, Sample Collection and Preparation, and Data Processing Parameters

### *1.1 Preparation of surface-active foam fractionation (SAFF) sample*

The SAFF concentrate was collected from a SAFF unit undergoing pilot testing for surface and groundwater PFAS remediation and its concentrate was examined here to measure the specific PFAS collected and concentrated within the watershed.[1] The SAFF concentrate was collected in May 2023 when the SAFF unit was installed at Tablyn Park in Lake Elmo, MN. After collection the SAFF concentrate was transferred to the Minnesota Department of Health. As the concentrate was expected to contain elevated concentrations of PFAS due to the concentration processes employed in the technology, the concentrate was first analyzed for relative concentrations of target PFAS to inform appropriate dilution factors prior to sample preparation. From these relative estimates it was determined that 820×dilution factor would be used by diluting 500 µL of SAFF sample into 410 mL of laboratory-grade water. The SAFF concentrate was then prepared and analyzed alongside other study samples as described in the main text.

**Figure S1**. Summary of the data processing workflow steps adapted from Whitehead *et al.* (2025). For each step the number of samples, features, occurrences, and/or annotations are given.

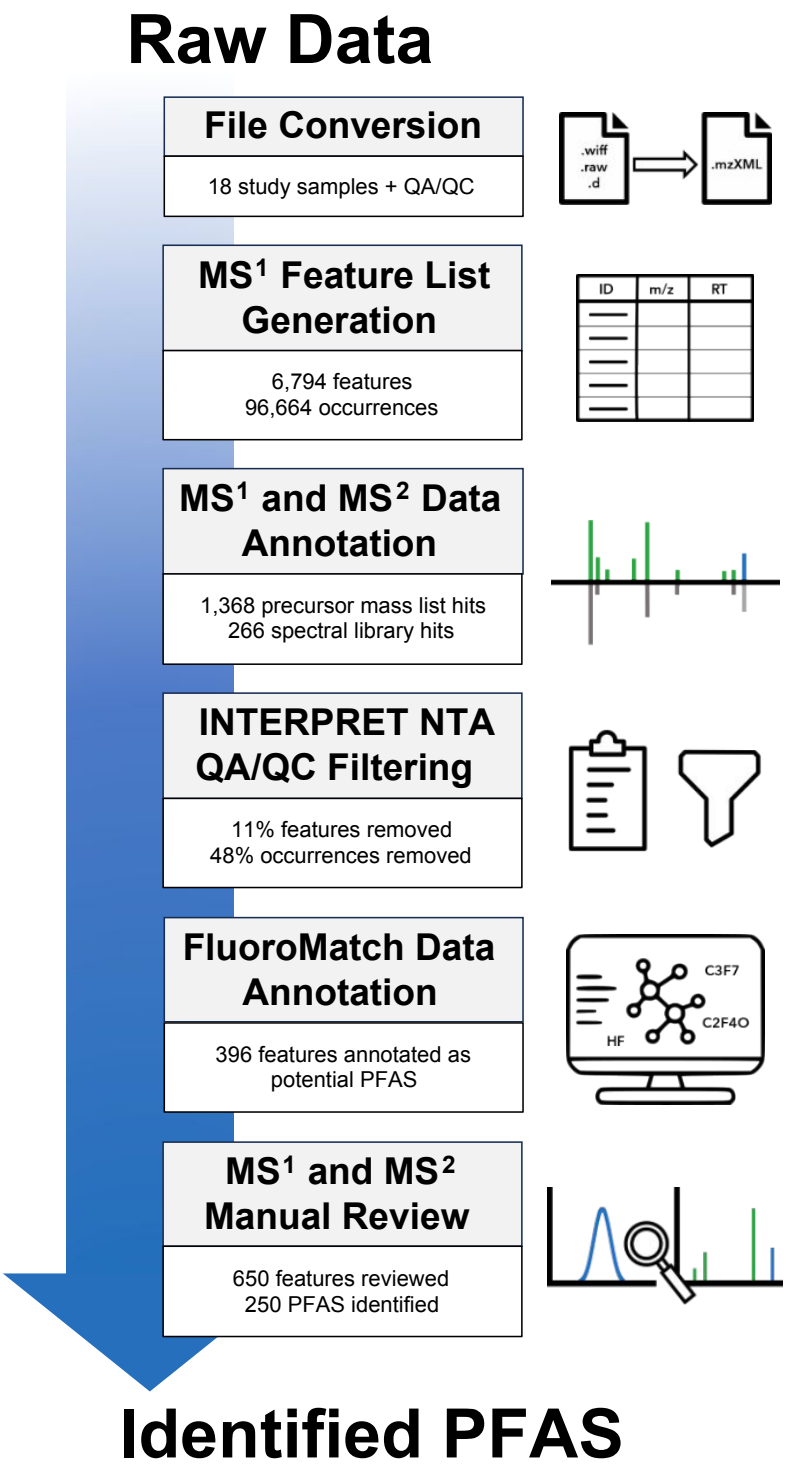

**Table S1.** Native and isotopically-labeled compounds included in the MN study and their concentrations across different samples.

| Type | Name | Acryonym | Formula | DTXSID | Final, in-vial concentration in study samples and pooled matrix control (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #1 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #2 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #3 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #4 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #5 (ng/mL) |
|---|---|---|---|---|---|---|---|---|---|---|
| Native standard | Perfluorobutanoic acid | PFBA | C4HF7O2 | DTXSID4059916 | | 10.24 | 25.60 | 64.00 | 160.00 | 400.00 |
| Native standard | Perfluoropentanoic acid | PFPeA | C5HF9O2 | DTXSID6062599 | | 5.12 | 12.80 | 32.00 | 80.00 | 200.00 |
| Native standard | Perfluorohexanoic acid | PFHxA | C6HF11O2 | DTXSID3031862 | | 2.56 | 6.40 | 16.00 | 40.00 | 100.00 |
| Native standard | Perfluoroheptanoic acid | PFHpA | C7HF13O2 | DTXSID1037303 | | 2.56 | 6.40 | 16.00 | 40.00 | 100.00 |
| Native standard | Perfluorooctanoic acid | PFOA | C8HF15O2 | DTXSID8031865 | | 2.56 | 6.40 | 16.00 | 40.00 | 100.00 |
| Native standard | Perfluorononanoic acid | PFNA | C9HF17O2 | DTXSID8031863 | | 2.56 | 6.40 | 16.00 | 40.00 | 100.00 |
| Native standard | Perfluorodecanoic acid | PFDA | C10HF19O2 | DTXSID3031860 | | 2.56 | 6.40 | 16.00 | 40.00 | 100.00 |
| Native standard | Perfluoroundecanoic acid | PFUnA | C11HF21O2 | DTXSID8047553 | | 2.56 | 6.40 | 16.00 | 40.00 | 100.00 |
| Native standard | Perfluorododecanoic acid | PFDoA | C12HF23O2 | DTXSID8031861 | | 2.56 | 6.40 | 16.00 | 40.00 | 100.00 |
| Native standard | Perfluorotridecanoic acid | PFTrDA | C13HF25O2 | DTXSID90868151 | | 2.56 | 6.40 | 16.00 | 40.00 | 100.00 |
| Native standard | Perfluorotetradecanoic acid | PFTeDA | C14HF27O2 | DTXSID3059921 | | 2.56 | 6.40 | 16.00 | 40.00 | 100.00 |
| Native standard | Perfluorobutanesulfonic acid | PFBS | C4HF9O3S | DTXSID5030030 | | 2.27 | 5.68 | 14.19 | 35.48 | 88.70 |
| Native standard | Perfluoropentanesulfonic acid | PFPeS | C5HF11O3S | DTXSID8062600 | | 2.41 | 6.02 | 15.06 | 37.64 | 94.10 |
| Native standard | Perfluorohexanesulfonic acid | PFHxS | C6HF13O3S | DTXSID7040150 | | 2.34 | 5.85 | 14.62 | 36.56 | 91.40 |
| Native standard | Perfluoroheptanesulfonic acid | PFHpS | C7HF15O3S | DTXSID8059920 | | 2.44 | 6.10 | 15.25 | 38.12 | 95.30 |
| Native standard | Perfluorooctanesulfonic acid | PFOS | C8HF17O3S | DTXSID3031864 | | 2.38 | 5.94 | 14.85 | 37.12 | 92.80 |
| Native standard | Perfluorononanesulfonic acid | PFNS | C9HF19O3S | DTXSID8071356 | | 2.46 | 6.16 | 15.39 | 38.48 | 96.20 |
| Native standard | Perfluorodecanesulfonic acid | PFDS | C10HF21O3S | DTXSID3040148 | | 2.47 | 6.18 | 15.44 | 38.60 | 96.50 |
| Native standard | Perfluorododecanesulfonic acid | PFDoS | C12HF25O3S | DTXSID20873011 | | 2.48 | 6.21 | 15.52 | 38.80 | 97.00 |
| Native standard | 4:2 Fluorotelomer sulfonic acid | 4:2 FTS | C6H5F9O3S | DTXSID30891564 | | 9.60 | 24.00 | 60.00 | 150.00 | 375.00 |
| Native standard | 6:2 Fluorotelomer sulfonic acid | 6:2 FTS | C8H5F13O3S | DTXSID6067331 | | 9.73 | 24.32 | 60.80 | 152.00 | 380.00 |
| Native standard | 8:2 Fluorotelomer sulfonic acid | 8:2 FTS | C10H5F17O3S | DTXSID00192353 | | 9.83 | 24.58 | 61.44 | 153.60 | 384.00 |
| Native standard | Perfluorooctanesulfonamide | PFOSA | C8H2F17NO2S | DTXSID3038939 | | 2.56 | 6.40 | 16.00 | 40.00 | 100.00 |
| Native standard | N-Methylperfluorooctanesulfonamide | NMeFOSA | C9H4F17NO2S | DTXSID1067629 | | 2.56 | 6.40 | 16.00 | 40.00 | 100.00 |
| Native standard | N-Ethylperfluorooctane sulfonamide | NEtFOSA | C10H6F17NO2S | DTXSID1032646 | | 2.56 | 6.40 | 16.00 | 40.00 | 100.00 |
| Native standard | 2-(N-Methylperfluorooctanesulfonamido)acetic acid | NMeFOSAA | C11H6F17NO4S | DTXSID10624392 | | 2.56 | 6.40 | 16.00 | 40.00 | 100.00 |

| Type | Name | Acryonym | Formula | DTXSID | Final, in-vial concentration in study samples and pooled matrix control (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #1 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #2 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #3 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #4 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #5 (ng/mL) |
|---|---|---|---|---|---|---|---|---|---|---|
| Native standard | 2-(N-Ethylperfluorooctanesulfonamido)acetic acid | NEtFOSAA | C12H8F17NO4S | DTXSID5062760 | | 2.56 | 6.40 | 16.00 | 40.00 | 100.00 |
| Native standard | N-Methyl-N-(2-hydroxyethyl)perfluorooctanesulfonamide | NMeFOSE | C11H8F17NO3S | DTXSID7027831 | | 25.60 | 64.00 | 160.00 | 400.00 | 1000.00 |
| Native standard | N-Ethyl-N-(2-hydroxyethyl)perfluorooctane sulfonamide | NEtFOSE | C12H10F17NO3S | DTXSID6027426 | | 25.60 | 64.00 | 160.00 | 400.00 | 1000.00 |
| Native standard | Perfluoro-2-methyl-3-oxahexanoic acid | HFPO-DA | C6HF11O3 | DTXSID70880215 | | 5.12 | 12.80 | 32.00 | 80.00 | 200.00 |
| Native standard | 4,8-Dioxa-3H-perfluorononanoic acid | ADONA | C7H2F12O4 | DTXSID40881350 | | 4.84 | 12.10 | 30.24 | 75.60 | 189.00 |
| Native standard | Perfluoro-3-methoxypropanoic acid | PFMPA | C4HF7O3 | DTXSID70191136 | | 5.12 | 12.80 | 32.00 | 80.00 | 200.00 |
| Native standard | Perfluoro(4-methoxybutanoic acid) | PFMBA | C5HF9O3 | DTXSID60500450 | | 5.12 | 12.80 | 32.00 | 80.00 | 200.00 |
| Native standard | Perfluoro-3,6-dioxaheptanoic acid | NFDHA | C5HF9O4 | DTXSID30382063 | | 5.12 | 12.80 | 32.00 | 80.00 | 200.00 |
| Native standard | Perfluoro(2-((6-chlorohexyl)oxy)ethanesulfonic acid) | 9Cl-PF3ONS | C8HClF16O4S | DTXSID80892506 | | 4.79 | 11.97 | 29.92 | 74.80 | 187.00 |
| Native standard | 11-Chloroperfluoro-3-oxaundecanesulfonic acid | 11Cl-PF3OUdS | C10HClF20O4S | DTXSID40892507 | | 4.84 | 12.10 | 30.24 | 75.60 | 189.00 |
| Native standard | Perfluoro-2-ethoxyethanesulfonic acid | PFEESA | C4HF9O4S | DTXSID50379814 | | 4.56 | 11.39 | 28.48 | 71.20 | 178.00 |
| Native standard | 3:3 Fluorotelomer carboxylic acid | 3:3 FTCA | C6H5F7O2 | DTXSID00379268 | | 10.24 | 25.60 | 64.00 | 160.00 | 400.00 |
| Native standard | 2H,2H,3H,3H-Perfluorooctanoic acid | 5:3 FTCA | C8H5F11O2 | DTXSID20874028 | | 51.20 | 128.00 | 320.00 | 800.00 | 2000.00 |
| Native standard | 3-(Perfluoroheptyl)propanoic acid | 7:3 FTCA | C10H5F15O2 | DTXSID90382620 | | 51.20 | 128.00 | 320.00 | 800.00 | 2000.00 |
| Extracted internal standard (EIS) | Perfluoro-n-(13C4)butanoic acid | 13C4-PFBA | [13C]4HF7O2 | DTXSID201028085 | 10.00 | 10.00 | 10.00 | 10.00 | 10.00 | 10.00 |
| Extracted internal standard (EIS) | Perfluoro-n-(13C5)pentanoic acid | 13C5-PFPeA | [13C]5HF9O2 | DTXSID401337529 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 |
| Extracted internal standard (EIS) | Perfluoro[1,2,3,4,6-13C5]hexanoic acid | 13C5-PFHxA | C[13C]5HF11O2 | DTXSID801028083 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Extracted internal standard (EIS) | Perfluoro-n-[1,2,3,4-13C4]heptanoic acid | 13C4-PFHpA | C3[13C]4HF13O2 | DTXSID801337533 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Extracted internal standard (EIS) | Perfluoro-n-[13C8]octanoic acid | 13C8-PFOA | [13C]8HF15O2 | DTXSID501337534 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Extracted internal standard (EIS) | Perfluoro-n-(13C9)nonanoic acid | 13C9-PFNA | [13C]9HF17O2 | DTXSID201337535 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 |
| Extracted internal standard (EIS) | Perfluoro-n-(1,2,3,4,5,6-13C6)decanoic acid | 13C6-PFDA | C4[13C]6HF19O2 | DTXSID50925719 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 |

| Type | Name | Acryonym | Formula | DTXSID | Final, in-vial concentration in study samples and pooled matrix control (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #1 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #2 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #3 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #4 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #5 (ng/mL) |
|---|---|---|---|---|---|---|---|---|---|---|
| Extracted internal standard (EIS) | Perfluoro-n-[1,2,3,4,5,6,7-13C7]undecanoic acid | 13C7-PFUnA | C4[13C]7HF21O2 | DTXSID101028082 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 |
| Extracted internal standard (EIS) | Perfluoro[1,2-13C2]dodecanoic acid | 13C2-PFDoA | C10[13C]2HF23O2 | DTXSID001028089 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 |
| Extracted internal standard (EIS) | Perfluoro-n-[1,2-13C2]tetradecanoic acid | 13C2-PFTeDA | C12[13C]2HF27O2 | DTXSID301028088 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 |
| Extracted internal standard (EIS) | Perfluoro-1-[1,2,3-13C3]butanesulfonic acid | 13C3-PFBS | C[13C]3HF9O3S | DTXSID201350167 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Extracted internal standard (EIS) | Perfluoro-1-[1,2,3-13C3]hexanesulfonic acid | 13C3-PFHxS | C3[13C]3HF13O3S | DTXSID901350170 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Extracted internal standard (EIS) | Perfluoro-[13C8]octanesulfonic acid | 13C8-PFOS | [13C]8HF17O3S | DTXSID601350171 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Extracted internal standard (EIS) | Perfluoro-1-[13C8]octanesulfonamide | 13C8-PFOSA | [13C]8H2F17NO2S | DTXSID001337591 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Extracted internal standard (EIS) | 2-(N-Methyl-d3-perfluorooctanesulfonamido)acetic acid | D3-NMeFOSAA | C11H3D3F17NO4S | DTXSID701337609 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 |
| Extracted internal standard (EIS) | 2-(N-Ethyl-d5-perfluorooctanesulfonamido)acetic acid | D5-NEtFOSAA | C12H3D5F17NO4S | DTXSID001337610 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 |
| Extracted internal standard (EIS) | 1H,1H,2H,2H-perfluoro-1-[1,2-13C2]-hexanesulfonic acid | 13C2-4:2FTS | C4[13C]2H5F9O3S | DTXSID101350176 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 |
| Extracted internal standard (EIS) | 1H,1H,2H,2H-perfluoro-1-[1,2-13C2]-octanesulfonic acid | 13C2-6:2FTS | C6[13C]2H5F13O3S | DTXSID801350177 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 |
| Extracted internal standard (EIS) | 1H,1H,2H,2H-Perfluoro-1-[1,2-13C2]-decanesulfonic acid | 13C2-8:2FTS | C8[13C]2H5F17O3S | DTXSID501350178 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 |
| Extracted internal standard (EIS) | 2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)(13C3)propanoic acid | 13C3-HFPO-DA | C3[13C]3HF11O3 | DTXSID50892477 | 10.00 | 10.00 | 10.00 | 10.00 | 10.00 | 10.00 |
| Extracted internal standard (EIS) | 2-(N-Methyl-d3-perfluoro-1-octanesulfonamido)ethan-d4-ol | D7-NMeFOSE | C11HD7F17NO3S | DTXSID701337611 | 25.00 | 25.00 | 25.00 | 25.00 | 25.00 | 25.00 |
| Extracted internal standard (EIS) | N-Ethyl-d5-N-(2-hydroxyethyl-d4)perfluorooctane sulfonamide | D9-NEtFOSE | C12HD9F17NO3S | DTXSID401337612 | 25.00 | 25.00 | 25.00 | 25.00 | 25.00 | 25.00 |
| Extracted internal standard (EIS) | N-Ethyl-d5-perfluorooctanesulfonamide | D5-NEtFOSA | C10HD5F17NO2S | DTXSID001337608 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |

| Type | Name | Acryonym | Formula | DTXSID | Final, in-vial concentration in study samples and pooled matrix control (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #1 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #2 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #3 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #4 (ng/mL) | Final, in-vial concentration in pooled matrix calibrant concentration #5 (ng/mL) |
|---|---|---|---|---|---|---|---|---|---|---|
| Extracted internal standard (EIS) | N-Methyl-d3-perfluorooctanesulfonamide | D3-NMeFOSA | C9HD3F17NO2S | DTXSID301337607 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Non-extracted internal standard (NIS) | Perfluoro-n-(2,3,4-13C3)butanoic acid | 13C3-PFBA | C[13C]3HF7O2 | DTXSID301337564 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 |
| Non-extracted internal standard (NIS) | Perfluoro-n-[1,2,3,4-13C4]-octanoic acid | 13C4-PFOA | C4[13C]4HF15O2 | DTXSID70892999 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Non-extracted internal standard (NIS) | Perfluoro-n-(1,2-13C2)decanoic acid | 13C2-PFDA | C8[13C]2HF19O2 | DTXSID20894100 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 |
| Non-extracted internal standard (NIS) | heptadecafluoro(1,2,3,4-13C4)octane-1-sulfonic acid | 13C4-PFOS | C4[13C]4HF17O3S | DTXSID80894101 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Non-extracted internal standard (NIS) | Perfluoro-n-(1,2,3,4,5-13C5)nonanoic acid | 13C5-PFNA | C4[13C]5HF17O2 | DTXSID70894099 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 |
| Non-extracted internal standard (NIS) | Perfluoro[1,2-13C2]hexanoic acid | 13C2-PFHxA | C4[13C]2HF11O2 | DTXSID901028086 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Non-extracted internal standard (NIS) | Perfluoro-1-hexane[18O2]sulfonic acid | 18O2-PFHxS | [18O]2C6HF13OS | | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |

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158 **Table S2.** Chromatographic parameters used in data acquisition.

| | | | |
|---|---|---|---|
| **Mobile phase A** | | 95/5 water/acetonitrile with 2 mM ammonium acetate | |
| **Mobile phase B** | | 100% acetonitrile | |
| **Column** | | Agilent Infinity Lab Poroshell 120 EC-C18 (2.1x100 mm, 2.7 µm) | |
| **Column temperature (°C)** | | 40 | |
| **Injection volume (µL)** | | 10 | |
| **Time (min)** | **% A** | **% B** | **Flow rate (mL/min)** |
| 0.0 | 98 | 2 | 0.35 |
| 0.1 | 98 | 2 | 0.35 |
| 4 | 70 | 30 | 0.4 |
| 7 | 45 | 55 | 0.4 |
| 9 | 25 | 75 | 0.4 |
| 10 | 5 | 95 | 0.4 |
| 10.4 | 98 | 2 | 0.4 |
| 11.8 | 98 | 2 | 0.4 |
| 12 | 98 | 2 | 0.35 |

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**Table S3.** MS parameters used in data acquisition.

| **Ion source parameters** | |
|---|---|
| Ion source | TurbolonSpray |
| Polarity | Negative |
| Curtain gas (psi) | 15 |
| Ion source gas 1 (psi) | 60 |
| Ion source gas 2 (psi) | 60 |
| Gas temperature (°C) | 350 |
| Voltage (V) | -4500 |
| **$MS^1$ (TOFMS) parameters** | |
| Starting mass (Da) | 100 |
| Ending mass (Da) | 1250 |
| Accumulation time (ms) | 100 |
| Declustering potential (V) | -50 |
| Declustering potential spread (V) | 0 |
| Collision energy (V) | -5 |
| Collision energy spread (V) | 0 |
| CAD gas | 7 |
| **$MS^2$ (TOFMSMS) parameters** | |
| Starting mass (Da) | 50 |
| Ending mass (Da) | 1250 |
| Accumulation time (ms) | 50 |
| Declustering potential (V) | -40 |
| Declustering potential spread (V) | 0 |
| Collision energy (V) | -30 |
| Collision energy spread (V) | 15 |
| CAD gas | 7 |
| **DDA precursor ion selection parameters** | |
| Maximum candidate ions | 15 |
| Intensity threshold exceeds (counts/s) | 100 |
| Dynamic background subtraction | Selected |
| Exclude former candidate ions | Selected *(exclude for 4 seconds after 3 occurrences)* |
| Mass tolerance (ppm) | 5 |
| Inclusion list | Selected (*includes native and isotopically-labeled compounds)* |
| Q1 resolution | Unit |

**Table S4.** Parameters used for MSConvert to generate .mzXML files and .ms2 files.

| Option/Filter | Value |
|---|---|
| **.mzXML for mzmine processing** | |
| Output format | mzXML |
| Binary encoding precision | 64-bit |
| Write index, zlib compression, TPP compatibility | Selected |
| Peak Picking MS Level | 1 - |
| MS Level Subset | 1 - |
| Number of Data Points Subset | 2 - |
| Polarity Subset | Negative |
| **.ms2 for FluoroMatch processing** | |
| Output format | ms2 |
| Binary encoding precision | 64-bit |
| Write index, zlib compression, TPP compatibility | Selected |
| Peak Picking MS Level | 2 - 2 |
| MS Level Subset | 2 - 2 |
| Number of Data Points Subset | 2 - |
| Polarity Subset | Negative |

167 **Table S5.** Modules and parameters used in mzmine.

| mzmine Module | Module Parameter | Threshold or Value Used |
|---|---|---|
| Crop Filtering | | |
| | MS Level | All |
| | RT range | 1.0 – 12 min |
| | Filter out empty scans | Selected |
| Mass Detection | | |
| | MS Level | 1 |
| | RT range | 1.0 – 12 min |
| | Mass detector | Centroid |
| | Noise threshold | 1.0E3 |
| | Detect isotope signals below noise level | Selected |
| Mass Detection | | |
| | Mass Level | 2 |
| | RT range | 1.0 – 12 min |
| | Mass detector | Centroid |
| | Noise threshold | 1.0E2 |
| ADAP Chromatogram Building | | |
| | MS Level | 1 |
| | RT range | 1.0 – 12 min |
| | Minimum consecutive scans | 1 |
| | Minimum intensity for consecutive scans | 1.0E2 |
| | Minimum absolute height | 1.0E3 |
| | m/z tolerance | 0.002 m/z or 10 ppm |
| Chromatogram Resolving | | |
| | Algorithm | Local minimum |
| | MS/MS scan pairing | Selected |
| | *MS/MS scan pairing:* MS1 to MS2 precursor tolerance | 0.02 m/z or 10 ppm |
| | *MS/MS scan pairing:* Retention time filter | Use tolerance of 0.2 min |
| | *MS/MS scan pairing:* Minimum required signals | 1 |
| | Dimension | Retention time |
| | Chromatographic threshold | 90% |
| | Minimum search range RT (absolute) | 0.05 |
| | Minimum relative height | 0% |
| | Minimum absolute height | 1.0E3 |
| | Min ratio of peak top/edge | 1.70 |
| | Peak Duration Range | 0.01-0.5 |
| | Minimum scans (data points) | 3 |
| $^{13}C$ Isotope Filter | | |
| | m/z tolerance | 0.002 m/z or 10 ppm |
| | Retention time tolerance | 0.5 min |
| | Maximum charge | 1 |
| | Require monoisotopic shape | Selected |
| | Representative isotope | Most intense |
| Isotope Pattern Finder | | |
| | Chemical elements | H, C, N, O, S |
| | m/z tolerance (feature-to-scan) | 0.0005 m/z or 10 ppm |
| | Maximum charge | 1 |
| Alignment | | |
| | m/z tolerance | 0.002 m/z or 10 ppm |

| | | |
|---|---|---|
| | Weight for m/z | 20 |
| | Retention time tolerance | 0.5 min |
| | Weight for RT | 10 |
| Gap-filling | | |
| | Intensity tolerance | 10% |
| | m/z tolerance | 0.002 m/z or 10 ppm |
| | Retention time tolerance | 0.5 min |
| | Minimum scans (data points) | 1 |
| Duplicate Peak Filter | | |
| | Filter mode | New Average |
| | m/z tolerance | 0.002 m/z or 10 ppm |
| | Retention time tolerance | 0.5 min |
| Local compound database search | | |
| | Database file | PFASStructPrecursorForMZmine |
| | Columns | Name, mz, comment |
| | m/z tolerance | 0.002 m/z or 10 ppm |
| Spectral library search | | |
| | Imported spectral libraries | AMOS ESI-<br>PFAS single spectra |
| | Scans for matching | MS2 (all scans) |
| | Precursor m/z tolerance | 0.002 m/z or 10 ppm |
| | Spectral m/z tolerance | 0.002 m/z or 10 ppm |
| | Remove precursor | Unselected |
| | Minimum matched signals | 1 |
| | Similarity | Weighted cosine similarity |
| | *Similarity: Weights* | MassBank |
| | *Similarity: Minimum cos similarity* | 0.700 |
| | *Similarity: Handle unmatched signals* | Keep all and match to zero |

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**Table S6.** Parameters used by INTERPRET NTA for QA/QC processing.

| Input Parameter | Value Used |
|---|---|
| Positive mode adducts | [M+Na]+, [M+NH4]+, [M+K]+ |
| Negative mode adducts | [M+Cl]-, [M+HCO2]-, [M+CH3CO2]-, [M+FA]- |
| Neutral losses | [M-H2O], [M-CO2] |
| Adduct / duplicate mass accuracy units | ppm |
| Adduct / duplicate mass accuracy | 10 |
| Adduct /duplicate RT accuracy (mins) | 0.05 |
| Tracer mass accuracy units | ppm |
| Tracer mass accuracy | 5 |
| Tracer RT accuracy (mins) | 0.1 |
| Tracer plot y-axis scaling | log |
| Tracer plot trendlines shown | yes |
| Min. replicate hits (%) | 66 |
| Min. replicate hits in blanks (%) | 66 |
| Max. replicate CV | 0.8 |
| MRL standard deviation multiplier: | 3 |
| Parent ion mass accuracy (ppm) | 5 |
| Discard features below this RT (mins) | 0.0 |
| Search DSSTox for possible structures | Yes |
| Search Cheminformatics Hazard Module | No |
| Search DSSTox by | Mass |
| Save top result only? | No |

**Table S7.** Input parameters used for FluoroMatch Modular.

| **Input Parameter** | **Value used** | **Default value** |
|---|---|---|
| Retention time window (min) | Default | 0.1 |
| Mass accuracy window for experimental and *in-silico* fragments (ppm) | Default | 10 |
| Mass accuracy window for matching experimental and *in-silico* precursors (Da) | Default | 0.01 |
| MS/MS isolation window (Da) | Default | 0.4 |
| Threshold for determining minimum signal intensity for MS/MS ions | 10 | 1000 |
| Comment column | 1 | NA |
| m/z column | 2 | NA |
| RT column | 3 | NA |
| First numeric row | 2 | NA |
| Upper limit for mass defect filter | Default | 0.12 |
| Lower limit for mass defect filter | Default | -0.11 |
| Minimum number of MS/MS scans | Default | 1 |

177 **Table S8.** Input parameters used in SIRIUS processing.

| Option/Filter | Value |
|---|---|
| **SIRIUS – Molecular formula identification** | |
| Instrument | Q-TOF |
| Filter by isotope pattern | Unselected |
| MS2 mass accuracy (ppm) | 10 |
| MS/MS isotope scorer | Ignore |
| Candidates stored | 10 |
| Min candidates per ion stored | 1 |
| Use heuristic above m/z | 300 |
| Use heuristic only above m/z | 650 |
| Possible ionization | [M-H]- |
| *Elements allowed:* | |
| H | 0 - inf |
| C | 0 - inf |
| N | 0 - 5 |
| O | 0 - inf |
| P | 0 - 1 |
| S | 0 - 3 |
| Cl | 0 - 5 |
| Br | 0 - 1 |
| I | 0 - 1 |
| F | 0 - inf |
| *Formula prediction excluded for high MW compounds* | |
| **ZODIAC – Network-based improvement of molecular formula ranking** | |
| Considered candidates 300 m/z | 10 |
| Considered candidates 800 m/z | 50 |
| Use 2-step approach | Selected |
| *Edge Filters:* Edge threshold | 0.95 |
| *Edge Filters:* Min local connections | 10 |
| *Gibbs Sampling:* Iterations | 20,000 |
| *Gibbs Sampling:* Burn-in | 2,000 |
| *Gibbs Sampling:* Separate runs | 10 |
| **CSI:FingerID – Fingerprint Prediction & Structure Database Search** | |
| Fallback adducts | [M-H]- |
| Search databases | PubChem |
| **CANOPUS – Compound Class Prediction** | |
| *No parameters to set* | |

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**Table S9.** Parameters used to perform ion identity and spectral similarity networking in mzmine.

| | | |
|---|---|---|
| **Correlation grouping** | | |
| | RT tolerance (absolute) | 0.1 min |
| | Minimum feature height | 0.0 |
| | Intensity threshold for correlation | 0.0 |
| | Minimum samples filter: min samples in all | Max of 1 sample or 10% |
| | Minimum samples filter: min samples in group | Max of 0 samples or 0% |
| | Minimum samples filter: min %-intensity overlap | 60% |
| | Feature shape correlation | Unselected |
| | Feature height correlation: minimum samples | 2 |
| | Feature height correlation: measure | Pearson |
| | Feature height correlation: min correlation | 70% |
| **Ion identity networking** | | |
| | m/z tolerance (intra-sample) | 0.002 m/z or 10 ppm |
| | Check | Average |
| | Min height | 0.0 |
| | Ion identity library: MS mode | Negative |
| | Ion identity library: maximum charge | 2 |
| | Ion identity library: maximum molecules/cluster | 3 |
| | Ion identity library: adducts | [M]-, [M-H]-, [M+Na]-, [M+Cl]-, [M+FA]- |
| | Ion identity library: modifications | [M-H2O], [M-NH3], [M-CO], [M-CO2] |
| | Annotation refinement: minimum size | 2 |
| | Annotation refinement: delete small networks without major ion | Selected |
| | Annotation refinement: delete networks without monomer | Selected |
| **MS/MS spectral networking** | | |
| | m/z tolerance (MS2) | 0.002 m/z or 10 ppm |
| | Only best MS2 scan | Selected |
| | Minimum matched signals | 3 |
| | Min cosine similarity | 0.8 |
| | Check MS2 neutral loss similarity: maximum DP for differences matching | 25 |
| | Signal filters: remove residual precursor m/z | 10 |
| | Signal filters: Crop to top N signals | 250 |
| | Signal filters: signal threshold | 50 |
| | Signal filters: intensity filter at >N signals | 98 |

**Table S10.** Parameters used to perform homologous series identification using enviHomolog.

| Input Parameter | Value Used |
|---|---|
| m/z tolerance | 3 ppm |
| Max m/z difference between homologs | 200 Da |
| Min m/z difference between homologs | 5 Da |
| Max retention time difference between homologs | 120 seconds |
| Min retention time difference between homologs | 10 seconds |

## 2. Detection Frequency and Recovery of Native and Isotopically-labeled Compounds

### *2.1 Isotopically-labeled Compounds*

The detection frequencies and maximal CV observed for all isotopically-labeled compounds across all study samples are listed in **Table S11**. Feature detection frequencies ranged from 86-100% with an average max CV of 0.68 with a CV range of 0.39-1.22. **Table S11** breaks down detection frequencies and CVs based on the sample type. Detection frequencies were 100% in blanks and ranged from 86-100% in samples. Max CVs were always lower in blanks than study samples, which had average max CVs of 0.44 and 0.68, respectively. One isotopically-labeled compound, 13C4-PFBA, was not detected in any sample. Manual review of the feature list confirmed that no feature was present, and review of extracted ion chromatograms of this feature showed no peak for the expected m/z at the expected retention time. It is possible that this compound had poor sensitivity or other factors that limited its measurement. No trends with respect to PFAS chain length or functional group were obvious within the detection frequency or max CV data.

The recovery of isotopically-labeled compounds can be used to assess losses or gains due to the sample preparation method and/or the sample matrix. The average recovery of each isotopically-labeled compound is shown in **Figure S2** and is broken down based on the sample condition. These conditions are defined based on whether the compound was subjected to sample preparation and the presence of sample matrix. Sample preparation is anticipated to cause lower response due to sample recovery, while matrix is anticipated to yield lower response due to ion suppression. As expected, **Figure S2** does show relatively higher abundance of all isotopically-labeled compounds in samples that did not undergo sample preparation relative to those that did. Comparing matrix influence, as shown in **Figure S2**, the abundance of isotopically-labeled compounds is comparable for prepared samples with and without matrix, highlighting that sample preparation was the primary source of PFAS losses rather than ion suppression, except for in Point1-GW where suppression was large due to saturation of analyte signal, exceeding the instrumental dynamic range, in the sample itself.

The percent recovery of isotopically-labeled compounds was determined by dividing the individual response of an isotopically-labeled compound in each study sample by the average isotopically-labeled compound response for control and blank samples, which underwent sample preparation but did not have sample matrix (Eq 1).

$$Percent\ Recovery = \frac{Individual\ compound\ response\ in\ study\ sample}{Average\ compound\ response\ in\ \text{"No matrix"}\ samples} \times 100$$

A boxplot displaying the recovery of all isotopically-labeled compounds for each study sample is shown in **Figure S3.** For PFAS targeted analyses, isotopically-labeled compound recovery in samples is typically expected within ~30% of the expected value. Here, a ± 30% threshold is shown as gray horizontal bars in **Figure S3.** Three samples, Point1-GW, Point2-SW, and Mixed-GW1 had median isotopically-labeled compound recoveries outside the 70-130% range. During sample preparation each of these samples were noted to be difficult or slow to extract using the SPE cartridge, potentially contributing to loss. Qualitative and quantitative results presented here for Point2-SW and Mixed-GW1 are likely to be underreported or underestimated as a consequence of poor recovery. Manual review of extracted ion chromatograms for Point1-GW demonstrated signal saturation of several native compounds that impacted the performance of co-eluting compounds, including isotopically-labeled compounds. To account for this saturation,

the sample extract for Point1-GW was diluted 25× and 200× (using the method blank as a diluent) and reanalyzed to appropriately measure signal abundance for analytes. The boxplot also shows nearly all samples have high-recovery outlier points. As shown in **Table S12,** high-recovery outlier points were primarily due to two compounds, D3-NMeFOSA and D5-NEtFOSA, which had average percent recovery of 144% and 160%, respectively. The cause of these compounds to be over-recovered in samples is not known.

**Table S11.** Observed detection frequencies and max CVs for isotopically-labeled compounds.

| Chemical Name | Mass | Observed Mass | Mass Error (PPM) | Retention Time (min) | Observed Retention Time (min) | Retention Time Difference (min) | Detection Frequency in Blanks | Detection Frequency in Samples | Max CV in Blanks | Max CV in Samples |
|---|---|---|---|---|---|---|---|---|---|---|
| 13C2-4:2FTS | 329.9883 | 329.9877 | -1.8 | 5.42 | 4.95 | -0.47 | 100 | 100 | 0.35 | 1.21 |
| 13C2-6:2FTS | 429.9819 | 429.9810 | -2.1 | 6.23 | 6.21 | -0.02 | 100 | 100 | 0.37 | 1.22 |
| 13C2-8:2FTS | 529.9755 | 529.9742 | -2.5 | 7.25 | 7.24 | -0.01 | 100 | 100 | 0.55 | 0.80 |
| 13C2-PFDA | 515.9740 | 515.9738 | -0.4 | 7.48 | 7.47 | -0.01 | 100 | 100 | 0.49 | 0.67 |
| 13C2-PFDoA | 615.9676 | 615.9672 | -0.7 | 8.46 | 8.42 | -0.04 | 100 | 93 | 0.38 | 0.47 |
| 13C2-PFHxA | 315.9868 | 315.9864 | -1.3 | 5.10 | 5.20 | 0.10 | 100 | 100 | 0.42 | 0.61 |
| 13C2-PFTeDA | 715.9612 | 715.9605 | -1.0 | 9.28 | 9.26 | -0.02 | 100 | 86 | 0.66 | 0.68 |
| 13C3-HFPO-DA | 287.9917 | 287.9917 | -0.1 | 5.45 | 5.45 | 0.00 | 100 | 100 | 0.39 | 0.51 |
| 13C3-PFBS | 302.9603 | 302.9602 | -0.4 | 5.28 | 5.27 | -0.01 | 100 | 100 | 0.48 | 0.80 |
| 13C3-PFHxS | 402.9539 | 402.9530 | -2.3 | 6.68 | 6.65 | -0.03 | 100 | 100 | 0.41 | 0.60 |
| 13C4-PFHpA | 367.9903 | 367.9902 | -0.3 | 5.89 | 5.87 | -0.02 | 100 | 100 | 0.40 | 0.41 |
| 13C4-PFOA | 417.9871 | 417.9869 | -0.5 | 6.47 | 6.44 | -0.03 | 100 | 100 | 0.36 | 1.00 |
| 13C4-PFOS | 503.9509 | 503.9501 | -1.6 | 7.75 | 7.71 | -0.04 | 100 | 100 | 0.43 | 0.63 |
| 13C5-PFHxA | 318.9969 | 318.9968 | -0.2 | 5.21 | 5.20 | -0.01 | 100 | 100 | 0.44 | 0.50 |
| 13C5-PFNA | 468.9873 | 468.9871 | -0.4 | 7.00 | 6.98 | -0.02 | 100 | 100 | 0.55 | 0.58 |
| 13C5-PFPeA | 269.0001 | 269.0000 | -0.2 | 4.34 | 4.33 | -0.01 | 100 | 100 | 0.38 | 0.53 |
| 13C6-PFDA | 519.9874 | 519.9868 | -1.2 | 7.79 | 7.48 | -0.31 | 100 | 100 | 0.50 | 0.71 |
| 13C7-PFUnA | 570.9876 | 570.9871 | -0.9 | 7.96 | 7.97 | 0.01 | 100 | 97 | 0.55 | 0.83 |
| 13C8-PFOA | 422.0005 | 422.0004 | -0.3 | 6.47 | 6.44 | -0.03 | 100 | 100 | 0.34 | 0.67 |
| 13C8-PFOS | 507.9643 | 507.9631 | -2.4 | 7.15 | 7.64 | 0.49 | 100 | 100 | 0.42 | 0.96 |
| 13C8-PFOSA | 506.9803 | 506.9799 | -0.8 | 8.93 | 8.94 | 0.01 | 100 | 97 | 0.42 | 0.43 |
| 13C9-PFNA | 473.0007 | 473.0004 | -0.6 | 7.01 | 6.97 | -0.04 | 100 | 100 | 0.51 | 0.80 |
| 18O2-PFHxS | 403.9497 | 403.9523 | 6.4 | 6.68 | 6.65 | -0.03 | 100 | 100 | 0.41 | 0.62 |
| D3-NMeFOSA | 515.9880 | 515.9872 | -1.5 | 10.10 | 10.20 | 0.10 | 100 | 93 | 0.40 | 0.53 |
| D3-NMeFOSAA | 573.9934 | 573.9932 | -0.4 | 7.51 | 7.50 | -0.01 | 100 | 100 | 0.52 | 0.83 |
| D5-NEtFOSA | 532.0162 | 532.0155 | -1.2 | 10.40 | 10.45 | 0.05 | 100 | 93 | 0.33 | 0.45 |
| D5-NEtFOSAA | 590.0216 | 590.0212 | -0.7 | 7.73 | 7.71 | -0.02 | 100 | 97 | 0.47 | 0.85 |
| D7-NMeFOSE | 624.0605 | 624.0595 | -1.6 | 10.00 | 10.09 | 0.09 | 100 | 97 | 0.35 | 0.39 |
| D9-NEtFOSE | 640.0887 | 640.0877 | -1.5 | 10.30 | 10.36 | 0.06 | 100 | 97 | 0.39 | 0.55 |

**Figure S2.** Average abundance of each isotopically-labeled compound broken down by the sample condition or composition. Error bars represent the standard deviation of the measured abundance for each isotopically-labeled tracer across the sample condition. Sample conditions include those with sample matrix (i.e., ground or surface water) that went through sample preparation (green bars), those that do not have a sample matrix (i.e., method/trip/field/equipment blanks and controls) that went through sample preparation (blue bars) and those that do not have sample matrix and did not go through sample preparation (laboratory blanks and controls).

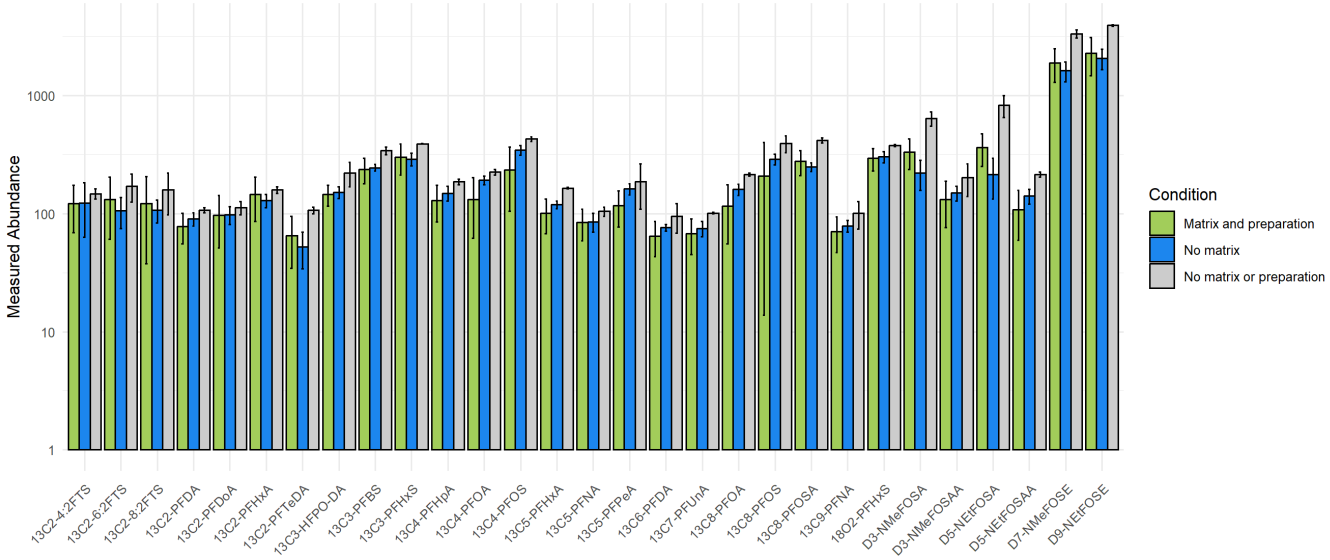

**Figure S3.** Boxplot displaying the percent recovery of isotopically-labeled compounds for all 18 study samples. Outliers are shown as open red circles. Gray horizontal bars indicate the typical acceptable range of percent recoveries for targeted analyses of PFAS (70-130%).

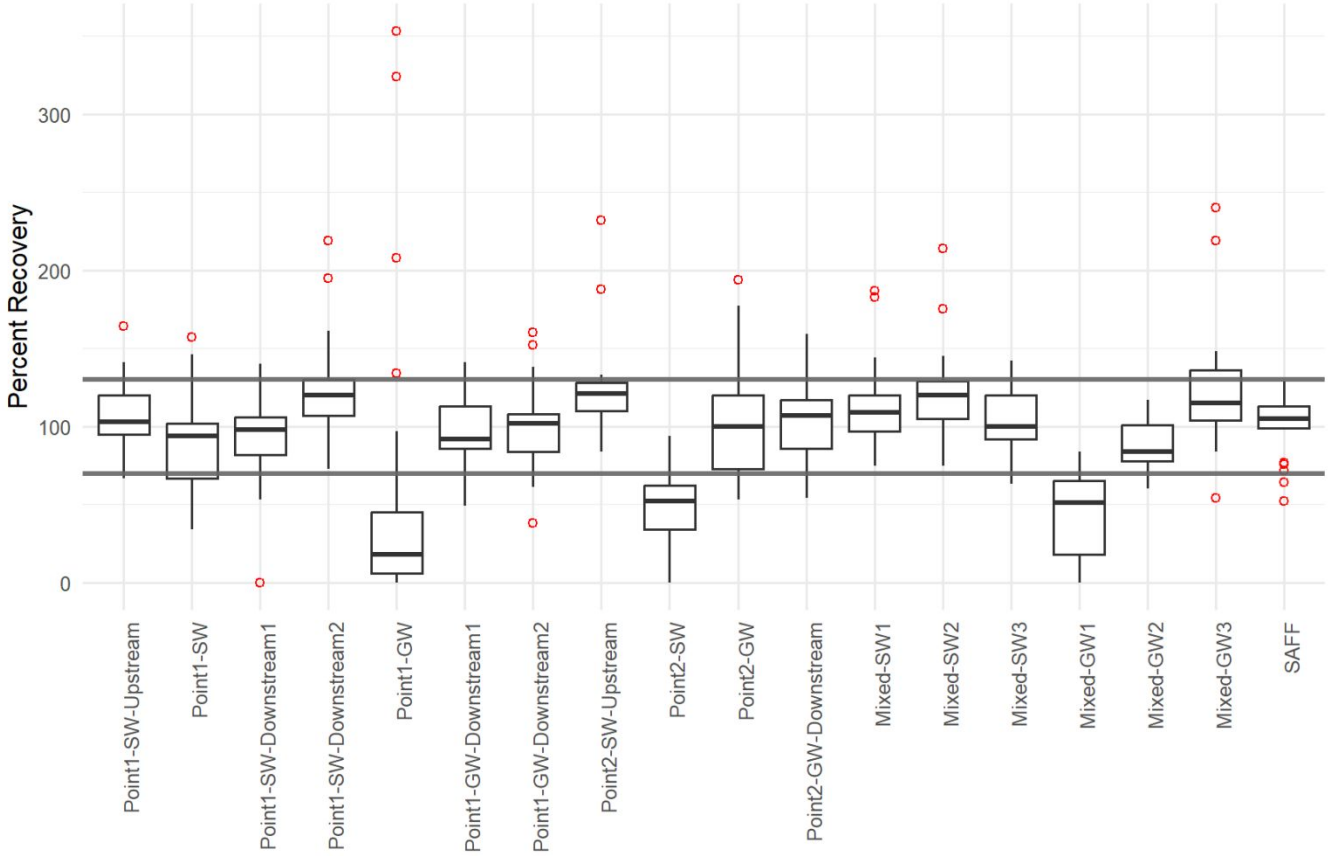

**Table S12.** Average, minimum, and maximum observed percent recovery of each isotopically-labeled compound across all 18 study samples. Occurrences of 0% recovery (isotopically-labeled compound not detected) were excluded in the table below.

| Compound | Minimum Percent Recovery | Average Percent Recovery | Maximum Percent Recovery |
|---|---|---|---|
| 13C5-PFPeA | 11 | 77 | 108 |
| 13C2-PFDoA | 6 | 78 | 132 |
| 13C4-PFOS | 18 | 83 | 129 |
| 13C4-PFOA | 18 | 85 | 121 |
| D5-NEtFOSAA | 18 | 86 | 134 |
| 13C7-PFUnA | 21 | 88 | 132 |
| 13C8-PFOA | 13 | 89 | 138 |
| 13C2-PFDA | 27 | 90 | 124 |
| 13C8-PFOS | 25 | 91 | 353 |
| 13C2-8:2FTS | 42 | 91 | 145 |
| 13C6-PFDA | 26 | 91 | 132 |
| 13C5-PFHxA | 55 | 93 | 131 |
| 13C3-HFPO-DA | 40 | 93 | 116 |
| 13C9-PFNA | 20 | 93 | 124 |
| 13C3-PFBS | 18 | 95 | 130 |
| 13C2-4:2FTS | 45 | 97 | 149 |
| 13C2-PFTeDA | 50 | 98 | 144 |
| D3-NMeFOSAA | 12 | 99 | 139 |
| 13C4-PFHpA | 58 | 99 | 134 |
| 18O2-PFHxS | 44 | 102 | 128 |
| 13C3-PFHxS | 46 | 102 | 208 |
| 13C2-6:2FTS | 55 | 105 | 145 |
| D9-NEtFOSE | 1 | 106 | 161 |
| 13C5-PFNA | 16 | 107 | 137 |
| D7-NMeFOSE | 11 | 109 | 156 |
| 13C8-PFOSA | 21 | 110 | 145 |
| 13C2-PFHxA | 65 | 118 | 324 |
| D3-NMeFOSA | 24 | 144 | 219 |
| D5-NEtFOSA | 25 | 160 | 240 |

*2.2 Native Compounds*

The detection frequencies and maximal CVs observed for all native compounds across select study samples where they were spiked is listed in **Table S13.** Feature detection frequencies were 100% in samples where native compounds were spiked. Detection frequencies in blanks were generally at 0%, except for 3 compounds: PFOS (100%), N-EtFOSE (43%) and N-MeFOSE (14%). These detections of native compounds in blanks were accounted for in samples using the blank subtraction and MRL filters within INTERPRET NTA processing. For samples where native compounds were spiked the average max CV was 0.47 with a range of 0.33-1.06. This average and range are similar to the values observed for the isotopically-labeled compounds and were found to be acceptable.

273 **Table S13.** Observed detection frequencies and max CVs for native compounds.

| Chemical Name | Mass | Observed Mass | Mass Error (PPM) | Retention Time (min) | Observed Retention Time (min) | Retention Time Difference (min) | Detection Frequency in Blanks | Detection Frequency in Spikes | Max CV in Blanks | Max CV in Spikes |
|---|---|---|---|---|---|---|---|---|---|---|
| PFBA | 213.9865 | 213.9864 | -0.36 | 3.12 | 3.11 | -0.01 | 0 | 100 | 0.00 | 0.34 |
| PFMPA | 229.9814 | 229.9812 | -0.83 | 3.64 | 3.64 | 0.00 | 0 | 100 | 0.00 | 0.41 |
| 3:3 FTCA | 242.0178 | 242.0175 | -1.14 | 3.77 | 3.86 | 0.09 | 0 | 100 | 0.00 | 0.35 |
| PFPeA | 263.9833 | 263.9831 | -0.69 | 4.32 | 4.33 | 0.01 | 0 | 100 | 0.00 | 0.38 |
| PFMBA | 279.9782 | 279.9780 | -0.71 | 4.67 | 4.63 | -0.04 | 0 | 100 | 0.00 | 0.45 |
| HFPO-DA | 285.9851 | 285.9853 | 0.74 | 5.49 | 5.45 | -0.04 | 0 | 100 | 0.00 | 0.55 |
| NFDHA | 295.9731 | 295.9729 | -0.72 | 5.07 | 5.09 | 0.02 | 0 | 100 | 0.00 | 0.39 |
| PFBS | 299.9503 | 299.9500 | -0.90 | 5.26 | 5.26 | 0.00 | 0 | 100 | 0.00 | 0.33 |
| PFHxA | 313.9801 | 313.9798 | -0.92 | 5.20 | 5.19 | -0.01 | 0 | 100 | 0.00 | 0.36 |
| PFEESA | 315.9452 | 315.9450 | -0.58 | 5.59 | 5.61 | 0.02 | 0 | 100 | 0.00 | 0.52 |
| 4:2 FTS | 327.9816 | 327.9813 | -0.82 | 4.98 | 4.97 | -0.01 | 0 | 100 | 0.00 | 0.36 |
| 5:3 FTCA | 342.0114 | 342.0107 | -2.02 | 5.49 | 5.52 | 0.03 | 0 | 100 | 0.00 | 0.37 |
| PFPeS | 349.9471 | 349.9467 | -1.07 | 6.02 | 6.02 | 0.00 | 0 | 100 | 0.00 | 0.42 |
| PFHpA | 363.9769 | 363.9765 | -1.09 | 5.82 | 5.86 | 0.04 | 0 | 100 | 0.00 | 0.35 |
| ADONA | 377.9761 | 377.9765 | 0.94 | 6.01 | 6.08 | 0.07 | 0 | 100 | 0.00 | 0.52 |
| PFHxS | 399.9439 | 399.9435 | -0.95 | 6.65 | 6.65 | 0.00 | 0 | 100 | 0.00 | 0.42 |
| PFOA | 413.9737 | 413.9733 | -0.97 | 6.44 | 6.40 | -0.04 | 0 | 100 | 0.00 | 0.53 |
| 6:2 FTS | 427.9752 | 427.9757 | 1.21 | 6.29 | 6.15 | -0.14 | 0 | 100 | 0.00 | 0.52 |
| 7:3 FTCA | 442.0050 | 442.0045 | -1.14 | 6.81 | 6.80 | -0.01 | 0 | 100 | 0.00 | 0.40 |
| PFHpS | 449.9407 | 449.9404 | -0.64 | 7.14 | 7.19 | 0.05 | 0 | 100 | 0.00 | 0.37 |
| PFNA | 463.9705 | 463.9683 | -4.76 | 6.96 | 6.95 | -0.01 | 0 | 100 | 0.00 | 0.42 |
| PFOSA | 498.9535 | 498.9529 | -1.16 | 8.91 | 8.92 | 0.01 | 0 | 100 | 0.00 | 0.41 |
| PFOS | 499.9375 | 499.9370 | -0.99 | 7.71 | 7.68 | -0.03 | 100 | 100 | 0.54 | 0.53 |
| NMeFOSA | 512.9691 | 512.9686 | -1.03 | 10.21 | 10.20 | -0.01 | 0 | 100 | 0.00 | 0.39 |
| PFDA | 513.9673 | 513.9669 | -0.81 | 7.44 | 7.45 | 0.01 | 0 | 100 | 0.00 | 0.49 |
| NEtFOSA | 526.9848 | 526.9841 | -1.29 | 10.45 | 10.46 | 0.01 | 0 | 100 | 0.00 | 0.33 |
| 8:2 FTS | 527.9688 | 527.9684 | -0.75 | 7.25 | 7.24 | -0.01 | 0 | 100 | 0.00 | 0.46 |
| 9Cl-PF3ONS | 531.9029 | 531.9025 | -0.67 | 8.08 | 8.09 | 0.01 | 0 | 100 | 0.00 | 0.56 |
| PFNS | 549.9343 | 549.9339 | -0.73 | 8.13 | 8.15 | 0.02 | 0 | 100 | 0.00 | 0.37 |
| PFUnA | 563.9641 | 563.9622 | -3.41 | 7.91 | 7.95 | 0.04 | 0 | 100 | 0.00 | 1.06 |
| NMeFOSAA | 570.9746 | 570.9742 | -0.71 | 7.59 | 7.56 | -0.03 | 0 | 100 | 0.00 | 0.93 |
| NEtFOSAA | 584.9903 | 584.9896 | -1.12 | 7.61 | 7.59 | -0.02 | 0 | 100 | 0.00 | 0.76 |
| PFDS | 599.9311 | 599.9307 | -0.68 | 8.59 | 8.60 | 0.01 | 0 | 100 | 0.00 | 0.53 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| PFDoA | 613.9609 | 613.9601 | -1.35 | 8.36 | 8.39 | 0.03 | 0 | 100 | 0.00 | 0.79 |
| NMeFOSE | 617.0158 | 617.0159 | 0.20 | 10.11 | 10.11 | 0.00 | 14 | 100 | 1.20 | 0.36 |
| NEtFOSE | 631.0311 | 631.0314 | 0.41 | 10.38 | 10.38 | 0.00 | 43 | 100 | 0.09 | 0.45 |
| 11Cl-PF3OUdS | 631.8965 | 631.8958 | -1.06 | 8.98 | 8.98 | 0.00 | 0 | 100 | 0.00 | 0.37 |
| PFTrDA | 663.9577 | 663.9569 | -1.26 | 8.83 | 8.83 | 0.00 | 0 | 100 | 0.00 | 0.46 |
| PFDoS | 699.9247 | 699.9239 | -1.17 | 9.47 | 9.47 | 0.00 | 0 | 100 | 0.00 | 0.40 |
| PFTeDA | 713.9545 | 713.9539 | -0.90 | 9.27 | 9.26 | -0.01 | 0 | 100 | 0.00 | 0.44 |

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## 3. INTERPRET NTA QA/QC Processing

### *3.1 Summary of INTERPRET NTA Outputs*

INTERPRET NTA was used to perform QA/QC filtering on the $MS^1$ feature list generated by mzmine. Summary metrics for each of the outputs produced by INTERPRET NTA are given in **Table S14.** A heatmap displaying the processing outcomes for all features across all study samples is shown in **Figure S4**. This heatmap demonstrates that QA/QC samples (blanks, control, and method spike) had few features compared to pooled matrix calibrants and study samples. The decision trees displayed in **Figure S5** and **S6** display the fate of occurrences and features across each QA/QC step (e.g., replicate, CV, and MRL checks), respectively. These trees are summarized in **Table S15** and show that 11% of all features at 48% of all occurrences were filtered during INTERPRET NTA QA/QC processing.

**Table S14.** Summarized metrics from INTERPRET NTA QA/QC processing and outputs.

| **INTERPRET NTA Output** | **Summary Quality Metrics** |
|---|---|
| Isotopically-labeled Compound Summary Tables[1] | \|mass error\|=0.1-6.4 ppm<br>\|RT error\|=0.0-0.49 min<br>max CV=0.33-1.22 |
| CV Scatter Plots[2] | 1.2% of unfiltered isotopically-labeled compound occurrences above CV=0.8 threshold |
| Run Sequence Plots[3] | Minor decrease in abundance across sequence; specific sample outliers |
| Occurrence Decision Tree[4] | 48% of unfiltered occurrences removed |
| Feature Decision Tree[4] | 11% of unfiltered features removed |
| Confusion Matrices[5] | TPR=97-100%; TNR=38-100%; FNR=0-5%; FPR=0-62% |

[1]Values from Table S11
[2]Values calculated from Figure S7
[3]Qualitative interpretation from Figure S8
[4]From Table S15 and as represented in Figure S5 (occurrences) and Figure S6 (features)
[5]Values from SI Section 3.1 and 3.2

**Figure S4.** Heatmap displaying the processing outcomes all features across all study samples. Features are represented across the x-axis and samples along the y-axis. Each cell represents the potential occurrence of a feature in that sample and the cell is shaded to denote the data quality decision for that occurrence. Cells shaded gray are non-detect (either those that had no occurrence in the input detection matrix or those found to be below the calculated MRL). Cells shaded red are occurrences where the CV of the measured abundance across the sample replicates exceeded the threshold of 0.8. Cells shaded white are those where the feature was reproducibility detected above the MRL with a CV less than 0.8.

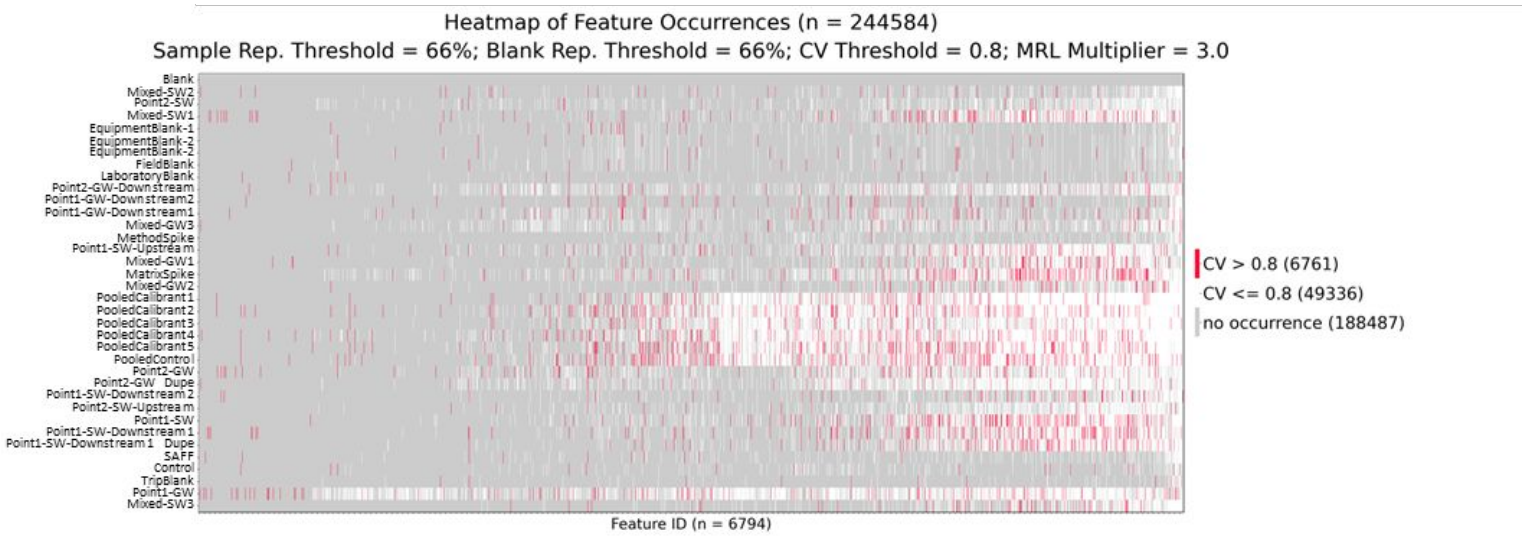


**Figure S5.** Decision tree recording the fate of occurrences for each filtering step during INTERPRET NTA processing. For each filter the threshold used is shown in the underlined text to the left and the number of occurrences either kept, removed, or flagged are shown in the boxes. Boxes colored white represent occurrences that remain in the final output, those colored gray represent occurrences that are removed from the final output, and those colored red represent occurrences that are optionally removed or flagged in the final output.

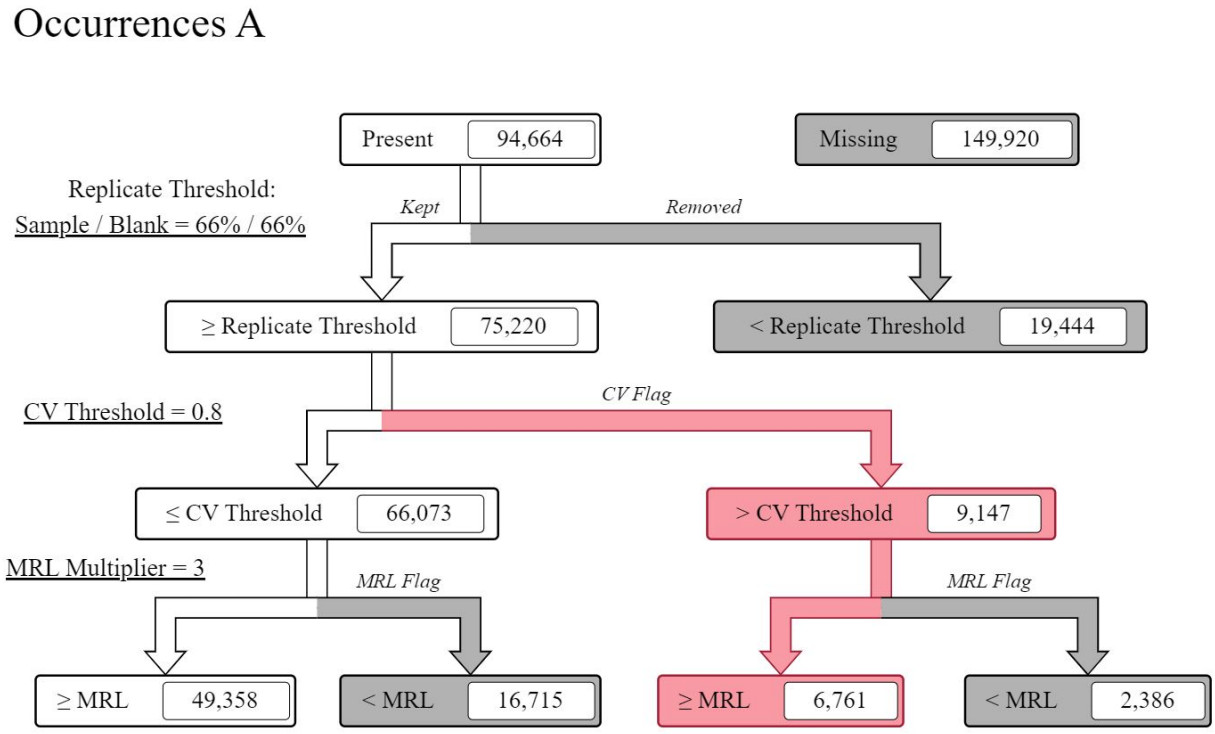


**Figure S6**. Decision tree recording the fate of features for each filtering step during INTERPRET NTA processing. For each filter the threshold used is shown in the underlined text to the left and the number of features either kept, removed, or flagged are shown in the boxes. Boxes colored white represent features that remain in the final output, those colored gray represent features that are removed from the final output, and those colored red represent features that are optionally removed or flagged in the final output.

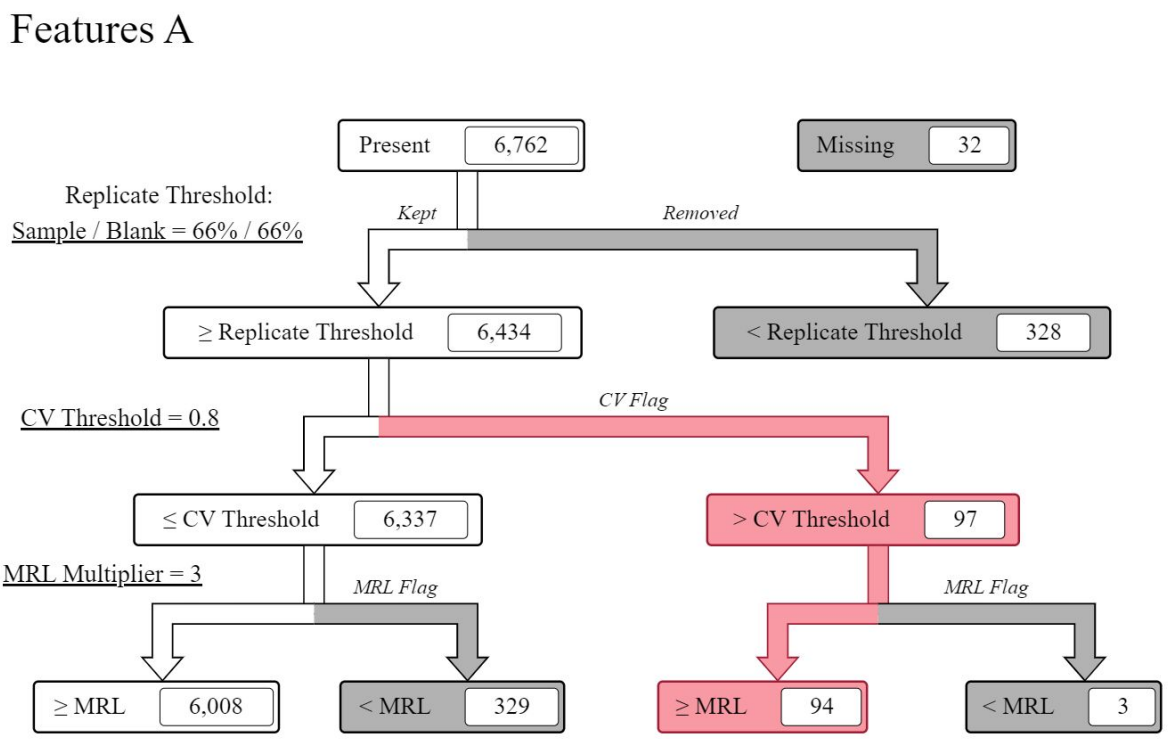


**Table S15.** Feature and occurrence decision tree counts for each filtering step for the MS1-level feature list processed with INTERPRET NTA.

| **Features** | | | |
|---|---|---|---|
| Filter | Number of features kept | Number of features removed | Percentage of features removed |
| Incoming | 6,762 | 0 | 0 |
| Replicate Threshold | 6,434 | 328 | 5 |
| CV Threshold | 6,337 | 97 | 2 |
| MRL Threshold | 6,008 | 329 | 5 |
| **Total** | 6,008 | 754 | 11 |
| **Occurrences** | | | |
| Filter | Number of occurrences kept | Number of occurrences removed | Percentage of occurrences removed |
| Incoming | 94,664 | 0 | 0 |
| Replicate Threshold | 75,220 | 19,444 | 21 |
| CV Threshold | 66,073 | 9,147 | 12 |
| MRL Threshold | 49,358 | 16,715 | 25 |
| **Total** | 49,358 | 45,306 | 48 |

*3.2 Isotopically-labeled compound performance*

A tracer file containing both the extracted and non-extracted isotopically-labeled compounds was prepared and input to track the performance of these spiked chemicals across all study samples. Performance of isotopically-labeled compounds were tracked using (1) CV scatter plots displaying mean abundance versus CV, (2) run sequence plots displaying tracer abundance across the analytical runs, and (3) confusion matrices to examine true positive, false positive, true negative, and false negative rates.

3.2.1 A scatterplot displaying the mean abundance against the measured CV of blanks and study samples is shown in **Figure S7**. Detections of isotopically-labeled compounds (tracers) are displayed as red circles and other detections are shown as open circles. The right scatterplot show that as mean abundance decreases the CV increases for tracer chemicals, which is expected. Very few tracer occurrences, 0% in blanks and 1% in samples, had CVs measured above the set CV threshold of 0.8.

3.2.2 Run sequence plots displaying tracer abundance based on sample type (blank or sample) for all isotopically-labeled compounds are shown in **Figure S8.** The run sequence order goes from the first injection in batch #1 through the final injection in batch #3. From these plots we can see each isotopically-labeled compound has a slight decrease in abundance across the run sequence in both the blanks and the study samples. This temporal effect appears systematic and may be the result of instrument sensitivity decreasing over time, but (1) as this decrease is relatively small, (2) injection replicates were randomized, and (3) the reported CVs are not artificially high, run sequence corrections were not implemented.

3.2.3 The performance of isotopically-labelled compounds was also assessed using confusion matrices, according to Sobus *et al.* (2025).[2] Confusion matrix statistics are broken down below at both the feature and occurrence level in the input detection matrices and in INTERPRET NTA-filtered final occurrence matrix.

**Input Detection Matrices**

False positive rates were 0% for both features and detections in the input detection matrices. False negative rates were low at 3.33% and 5.09% for features and detections, respectively. For features, the 3.33% false negative rate is due to the isotopically-labeled compound, 13C4-PFBA, which was not detected in any sample, as described above. For detections the false negative rate of 5.09% is due to all missing detection for 13C4-PFBA (n=125) and other missing detections (n=66).

**Unfiltered Features:**

| | | **Expected to map to isotopically-labeled compounds** | | |
|---|---|---|---|---|
| | | **Yes** | **No** | **Sum** |
| **Mapped to isotopically-labeled compounds** | **Yes** | 29 | 0 | 29 |
| | **No** | 1 | 6,765 | 6,766 |
| | **Sum** | 30 | 6,765 | 6,795 |

TPR = (29/30) × 100 = 96.67%
FNR = (1/30) × 100 = 3.33%
TNR = (6,765/6,765) × 100 = 100%
FPR = (0/6,765) × 100 = 0%

**Detections:**

| | | Expected to map to isotopically-labeled compounds | | |
|---|---|---|---|---|
| | | **Yes** | **No** | **Sum** |
| **Mapped to isotopically-labeled compounds** | **Yes** | 3,560 | 0 | 3,560 |
| | **No** | 191 | 330,769 | 330,960 |
| | **Sum** | 3,751 | 330,769 | 334,520 |

TPR = (3,560/3,751) × 100 = 94.91%
FNR = (191/3,751) × 100 = 5.09%
TNR = (330,769/330,769) × 100 = 100%
FPR = (0/330,769) × 100 = 0%

**Final Occurrence Matrix**

False negative rates for both features and occurrences in the final occurrence matrix cannot be calculated from isotopically-labeled tracers, as they are not expected in the final occurrence matrix due to the blank subtraction step performed by INTERPRET NTA. As the method blank contained concentrations of spiked isotopically-labeled compounds at equal levels as as other samples the response of these compounds in samples should be similar to what is observed in the blank, and accounted for during blank subtraction.

False positive rates were high at 62.07% for features in the final occurrence matrix. This is due to 18 isotopically-labeled compounds that were present in the final occurrence matrix that should have been removed during blank subtraction. False positive rates in the occurrences of the final occurrence matrix however were low at 1.63%. The reason for the disparity in false positive rates between features and occurrences becomes apparent when examining the final occurrence matrix. Manual review highlighted that half (n=9) of the isotopically-labeled features present in the final occurrence matrix had a measurement in just a single sample. The remaining 9 features were typically detected in few samples, between 6-34%. The 58 occurrences of isotopically-labeled compounds in the final occurrence matrix were found primarily in other study blanks (n=14) and control samples (n=40) rather than in true study samples (n=14). The presence of isotopically-labeled compounds present in these other blanks and control samples is due to their increased response in matrix-free or low matrix conditions relative to the method blank, which was used to perform blank subtraction.

**Filtered Features:**

| | Expected to map to isotopically-labeled compounds | |
|---|---|---|

| | | Yes | No | Sum |
|---|---|---|---|---|
| **Mapped to isotopically-labeled compounds** | **Yes** | NA | 18 | 18 |
| | **No** | NA | 11 | 11 |
| | **Sum** | NA | 29 | 29 |

TPR = *NA*
FNR = *NA*
TNR = (11/29) × 100 = 37.93%
FPR = (18/29) × 100 = 62.07%

**Occurrences:**

| | | Expected to map to isotopically-labeled compounds | | |
|---|---|---|---|---|
| | | **Yes** | **No** | **Sum** |
| **Mapped to isotopically-labeled compounds** | **Yes** | NA | 58 | 58 |
| | **No** | NA | 3,502 | 3,502 |
| | **Sum** | NA | 3,560 | 3,560 |

TPR = *NA*
FNR = *NA*
TNR = (3,502/3,560) × 100 = 98.37%
FPR = (58/3,560) × 100 = 1.63%

**Figure S7.** CV scatter plot generated by INTERPRET NTA. These are displayed as the mean abundance versus the measured CV in study blanks (left) and study samples (right). Detections of isotopically-labeled compounds are shown as red circles (tracers) and other detections are shown as open circles.

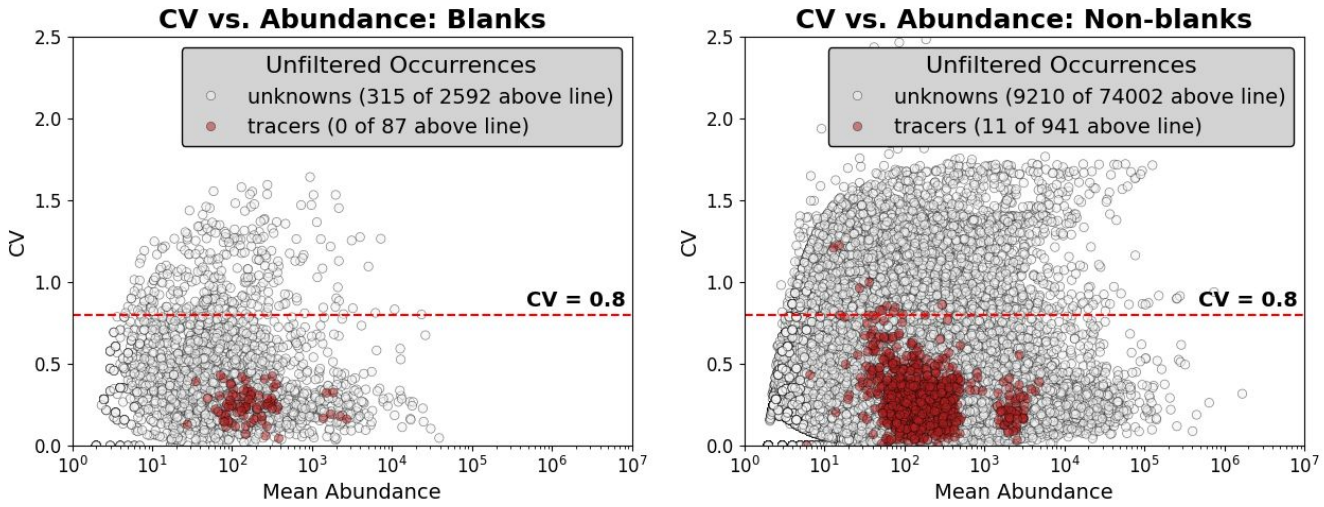
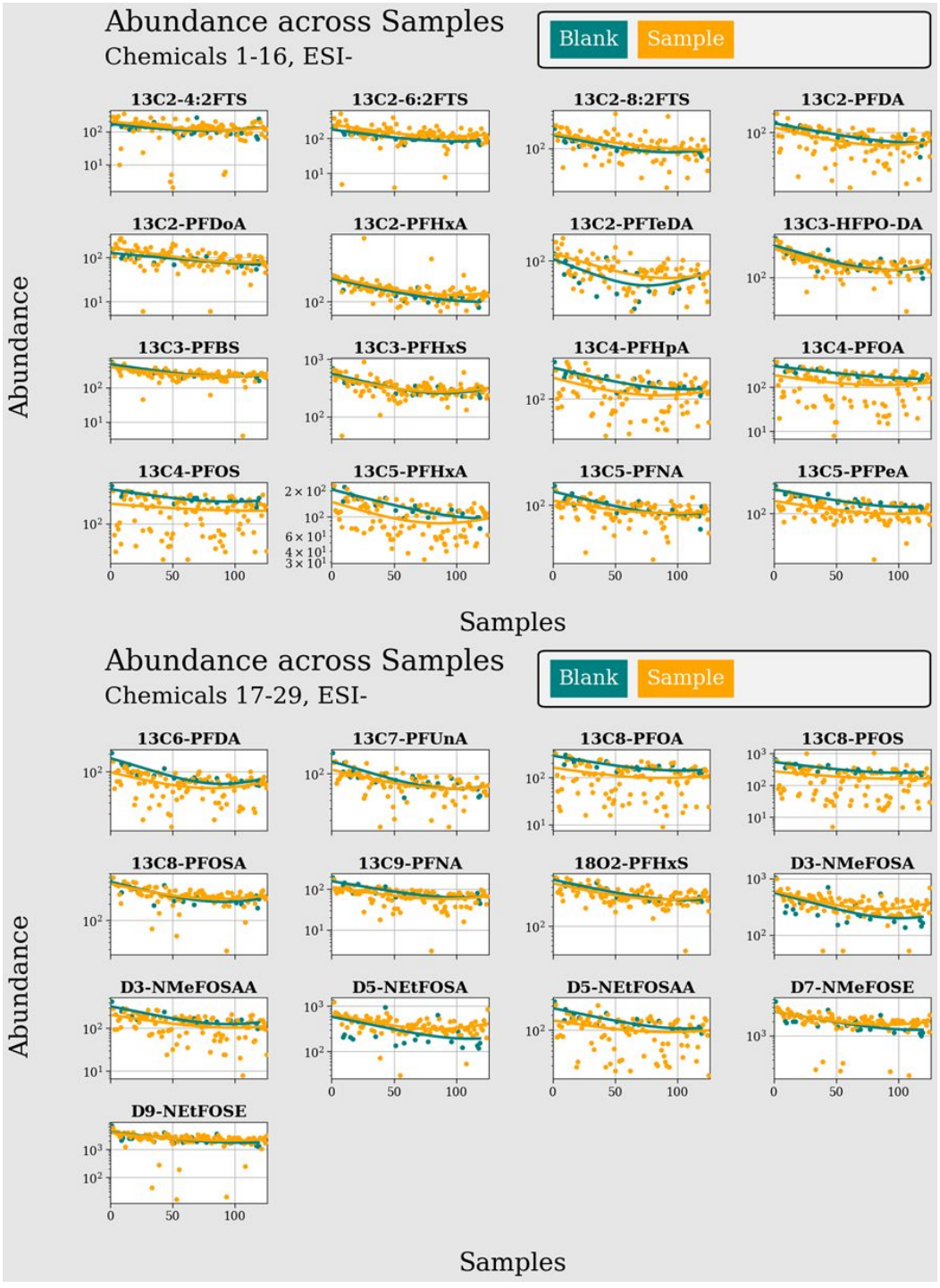


**Figure S8**. Run sequence plots of isotopically-labeled compounds generated by INTERPRET NTA. These are displayed as the run sequence position versus the measured abundance. Points on each plot and the trendlines are colored based on their grouping, either study blanks (teal) or study samples (yellow-orange).



*3.3 Native compound performance*

A tracer file containing just the native compounds was prepared and input to track the performance of spiked native compounds across select study samples. Performance of native compounds were tracked using (1) CV scatter plot displaying mean abundance versus CV and (2) confusion matrices to examine true positive, false positive, true negative, and false negative rates.

3.3.2 A scatterplot displaying the mean abundance against the measured CV of study blanks and samples is shown in **Figure S9**. Detections of native compounds (tracers) are displayed as red circles and other detections are shown as open circles. The right scatterplot displays as mean abundance decreases the CV increases for native compounds, which is expected for these data. Few native occurrences, 1.6% in samples, had CVs measured above the set CV threshold of 0.8.

3.3.3 The performance of native compounds was also assessed using the confusion matrices, according to Sobus *et al.* (2025).[2] These are broken down below at both the feature and occurrence levels based on the input detection matrices and the INTERPRET NTA filtered final occurrence matrix. The examination of false positive rates and false negative rates are examined only in samples where native compounds were spiked at sufficient levels and expected to be detectable. These samples included QA/QC controls (standard in neat solvent, method spike, and matrix spike) and three pooled matrix calibrants (for the mid-range and higher concentrations).

**Input Detection Matrices**

False negative and false positive rates were 0% for both features and detections in the input detection matrices. All native compounds were measured in the samples and injections where they were spiked at sufficient levels.

**Unfiltered Features:**

| | | **Expected to map to native compounds** | | |
|---|---|---|---|---|
| | | **Yes** | **No** | **Sum** |
| **Mapped to isotopically-labeled compounds** | **Yes** | 40 | 0 | 40 |
| | **No** | 0 | 6,754 | 6,754 |
| | **Sum** | 40 | 6,754 | 6,794 |

$$TPR = (40/40) \times 100 = 100\%$$
$$FNR = (1/30) \times 100 = 0\%$$
$$TNR = (6{,}754/6{,}754) \times 100 = 100\%$$
$$FPR = (0/6{,}754) \times 100 = 0\%$$

**Detections:**

| | **Expected to map to native compounds** | |
|---|---|---|

| | | Yes | No | Sum |
|---|---|---|---|---|
| **Mapped to isotopically-labeled compounds** | **Yes** | 1,040 | 0 | 1,040 |
| | **No** | 0 | 79,409 | 79,409 |
| | **Sum** | 1,040 | 79,409 | 80,449 |

TPR = (1,040/1,040) × 100 = 100%
FNR = (0/1,040) × 100 = 0%
TNR = (79,409/79,409) × 100 = 100%
FPR = (0/79,409) × 100 = 0%

**Final Occurrence Matrix**

False positive rates for both features and occurrences in the final occurrence matrix canot be calculated for native spiked chemicals as they are expected in the final occurrence matrix due to their intentional spiking.

False negative rates were 0% and 0.42% for features and occurrences in the final occurrence matrix, respectively. Only one occurrence of a single feature was not present in the final occurrence matrix. Review of this feature using the Decision Documentation sheet produced in the INTERPRET NTA output showed this occurrence was removed during INTERPRET NTA filtering in a pooled matrix calibrant sample due to the measured CV exceeding the set threshold of 0.8. The variability of peak areas for this occurrence were confirmed in both the input detection matrix and in the extracted ion chromatogram of the feature which showed poor reproducibility in peak shape and area in that sample.

**Filtered Features:**

| | | Expected to map to native compounds | | |
|---|---|---|---|---|
| | | **Yes** | **No** | **Sum** |
| **Mapped to isotopically-labeled compounds** | **Yes** | 40 | NA | 40 |
| | **No** | 0 | NA | 0 |
| | **Sum** | 40 | NA | 40 |

TPR = (40/40) x 100 = 100%
FNR = (0/40) x 100 =100%
TNR = NA
FPR = NA

**Occurrences:**

| | | Expected to map to native compounds | | |
|---|---|---|---|---|
| | | **Yes** | **No** | **Sum** |
| **Mapped to isotopically-labeled compounds** | **Yes** | 239 | NA | 239 |
| | **No** | 1 | NA | 1 |
| | **Sum** | 240 | NA | 240 |

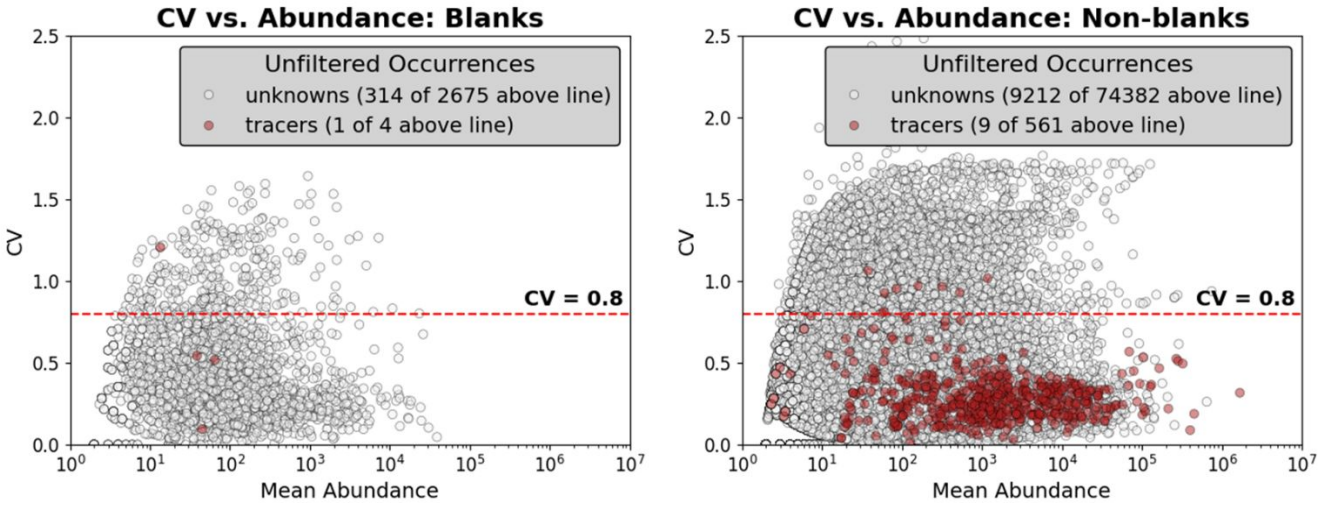
TPR = (239/240) x 100 =99.58%

FNR = (1/240) x 100 = 0.42%

TNR = NA

FPR = NA

**Figure S9.** CV scatter plot generated by INTERPRET NTA. These are displayed as the mean abundance versus the measured CV in study blanks (left) and study samples (right). Detections of native compounds are shown as red circles (tracers) and other detections are shown as open circles.



## 4. Identified PFAS and their Fate and Transport

### *4.1 Dilution Calculations*

The concentrations of chemicals measured in both groundwater at and downstream to point source #1 (n=24) determined in Pu *et al.* (2025), were used to estimate the rates of dilution from upstream to downstream.[3] First, the distribution of dilution factors from the point source (Point1-GW) to each downstream site (Point1-GW-Downstream1 and Point1-GW-Downstream2) were compared with a Mann-Whitney U test to determine if dilution factors were comparable between each downstream site. A boxplot of the dilution factors measured at each site is shown in **Figure S12**. Dilution factors were found to be comparable ($p = 0.101$). The dilution factors for each site were then combined to create one distribution of dilution factors (**Figure S13**). The median (50$^{th}$ percentile) and 2.5$^{th}$ percentiles were taken from this distribution and were found to be 639-fold and 55-fold, respectively.

### *4.2 Estimating Limits of Detection*

Limits of detection for the PFAS measured were then estimated to identify the minimum detectable concentrations that would need to be present in sample extracts. First, the concentrations measured for all PFAS as determined in Pu *et al.* (2025), across all surface and groundwater samples (excluding SAFF, n=15) were plotted as a distribution, as shown in **Figure S14**. The 5$^{th}$ percentile of this distribution was then taken to simulate an approximate limit of detection for the PFAS identified here. This gave a limit of detection (pre-enrichment) of 0.003 ng/mL, or a post-enrichment, in-vial concentration of 0.255 ng/mL.

### *4.3 Predicting Concentrations Downstream*

The estimated dilution factors and limit of detection was then applied to the concentrations measured of PFAS identified at Point1-GW that were not measured at any downstream site (n=176). When using the 50th percentile dilution factor of 639× and an estimated limit of detection of 0.003 ng/mL, approximately 95% of the concentrations measured at Point1-GW would fall below the limit of detection if transported downstream, as shown in **Figure S13.** When using the 2.5th percentile dilution factor of 55× and an estimated limit of detection of 0.003 ng/mL, approximately 56% of the concentrations measured at Point1-GW would fall below the limit of detection if transported downstream, as shown in **Figure S15.**

**Table S16.** PFAS identified at a Schymanski *et al.* (2014) scale confidence level 1 with their observed detection frequencies across all study samples (n=18).

| LEVEL 1 PFAS | DETECTION FREQUENCY IN STUDY SAMPLES |
|---|---|
| PFOS | 89 |
| PFOA | 89 |
| PFHpA | 78 |
| PFHxA | 78 |
| PFHxS | 78 |
| PFBA | 78 |
| PFPeA | 72 |
| PFBS | 67 |
| PFHpS | 61 |
| PFPeS | 61 |
| PFNA | 33 |
| PFDA | 33 |
| NEtFOSAA | 28 |
| PFOSA | 22 |
| 6:2 FTS | 17 |
| PFMBA | 11 |
| PFMPA | 11 |
| NMeFOSAA | 11 |
| PFNS | 6 |
| 5:3 FTCA | 6 |
| PFDS | 6 |
| PFUnA | 6 |
| 8:2 FTS | 6 |
| PFEESA | 6 |
| 3:3 FTCA | 6 |
| PFDOA | 6 |
| HFPO-DA | 6 |
| 4:2 FTS | 6 |
| ADONA | 6 |
| NFDHA | 6 |
| NEtFOSE | 6 |
| NMeFOSE | 6 |

548 **Table S17.** Homologous series identification across all study samples.

| Series Number | PFAS Subclass | Level of Fluorination | Number of Carbons Observed in Series | Representative Formula | Representative SMILES |
|---|---|---|---|---|---|
| 1 | Perfluorinated sulfonic acids | Perfluorinated | C1-C10 | C8HF17O3S | OS(=O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 2 | Polyfluorinated sulfonic acids | Polyfluorinated | C3-C11 | C8H2F16O3S | OS(=O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)C(F)(F)F |
| 3 | Polyfluorinated sulfonic acids | Polyfluorinated | C7-C8, C10 | C8H3F15O3S | OS(=O)(=O)CC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 4 | Polyfluorinated sulfonic acids | Polyfluorinated | C6, C8, C10 | C8H5F13O3S | OS(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 5 | Unsaturated sulfonic acid | Unsaturated | C4, C11-C12 | C12HF23O3S | OS(=O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)=C(F)C(F)(F)F |
| 6 | Polyfluorinated sulfonic acids | Unsaturated + H substituted | C4-C11 | C8H2F14O3S | OS(=O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)C(\F)=C(/F)C(F)(F)F |
| 7 | Chlorinated sulfonic acids | Perfluorinated | C6, C8 | C8HClF16O3S | OS(=O)(=O)C(F)(Cl)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 8 | Keto sulfonic acids | Perfluorinated | C4-C11 | C8HF15O4S | OS(=O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(=O)C(F)(F)F |
| 9 | Ether sulfonic acid | Perfluorinated | C3-C9 | C8HF17O4S | OS(=O)(=O)C(F)(F)C(F)(F)OC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 10 | Ether sulfonic acid | Polyfluorinated | C6-C9 | C8H7F11SO4 | FC(C(F)C(F)(F)C(F)(F)C(F)(F)F)C(F)C(F)OCS(=O)(=O)O |
| 11 | Ether sulfonic acid | Polyfluorinated | C8-C10 | C8H8F10SO4 | FC(C(F)OCS(=O)(O)=O)C(F)C(F)(F)C(F)C(F)C(F)(F)F |
| 12 | Ether sulfonic acid | Unsaturated | C6-C11 | C8HF13O4S | F/C(=C(/F)C(F)(F)C(F)(F)OC(F)(F)S(=O)(O)=O)/C(F)=C(\F)C(F)(F)F |
| 13 | Ether sulfonic acid | Unsaturated | C8-C11 | C8HF13O5S | F/C(=C(/F)C(F)(F)F)/C(F)=C(\F)C(F)(F)OC(F)(F)OC(F)(F)S(=O)(O)=O |
| 14 | Polyfluorinated hydroxy sulfonic acid | Polyfluorinated | C5-C6, C8-C9 | C8H5F13O4S | OC(CC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)S(O)(=O)=O |
| 15 | Perfluorinated sulfinic acids | Perfluorinated | C3-C5, C7-C8 | C8HF17O2S | OS(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 16 | Cyclic sulfonic acid | Unsaturated | C4-C12 | C8HF15O3S | FC1(C(F)(F)C(F)(F)F)C(F)(F)C(F)(C(F)(F)C(F)(F)C1(F)F)S(=O)(=O)O |
| 17 | Bifunctional sulfonic acid | Perfluorinated | C7-C15 | C8H2F16O6S2 | FC(F)(C(F)(F)C(F)(F)C(F)(F)S(=O)(=O)O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)S(=O)(=O)O |
| 18 | Bifunctional sulfonic acid | Polyfluorinated | C8-C15 | C8H3F15O6S2 | FC(S(O)(=O)=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)S(=O)(=O)O |
| 19 | Bifunctional sulfonic acid | Unsaturated | C9-C16, C18, C20 | C9H2F16O6S2 | O=S(O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)\C(F)=C(/F)C(F)(F)C(F)(F)S(=O)(=O)O |
| 20 | Bifunctional sulfonic and carboxylic acid | Perfluorinated | C5, C7-C12, C14-C15 | C8H2F14O5S | FC(F)(C(=O)O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)S(=O)(O)=O |
| 21 | Perfluorinated carboxylic acids | Perfluorinated | C3-C12 | C8HF15O2 | OC(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 22 | Polyfluorinated carboxylic acid | Polyfluorinated | C4-C8 | C8H2F14O2 | OC(=O)C(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 23 | Polyfluorinated carboxylic acid | Polyfluorinated | C5-C8 | C8H3F13O2 | OC(=O)CC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 24 | Polyfluorinated carboxylic acid | Polyfluorinated | C6-C8 | C8H5F11O2 | OC(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 25 | Polyfluorinated carboxylic acid | Unsaturated + H substituted | C5-C8 | C8H2F12O2 | OC(=O)\C=C(\F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 26 | Ether carboxylic acid | Unsaturated | C5-C12 | C8HF13O3 | OC(=O)C(F)(F)OC(F)(F)C(F)(F)C(F)(F)C(\F)=C(/F)C(F)(F)F |
| 27 | Ether carboxylic acid | Polyfluorinated | C5-C8 | C8H3F13O3 | OC(=O)COC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 28 | Ether carboxylic acid | Perfluorinated | C4-C5, C7-C11 | C8HF15O3 | OC(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)OC(F)(F)C(F)(F)F |
| 29 | Sulfonamides and Sulfonamidos | Perfluorinated | C5-C11 | C8H4F13NO4S | OC(=O)CNS(=O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 30 | Sulfonamides and Sulfonamidos | Perfluorinated | C4-C7 | C6H6F9NO2S | CCNS(=O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 31 | Sulfonamides and Sulfonamidos | Perfluorinated | C3-C8 | C8H2F17NO2S | NS(=O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |

| | | | | | |
|---|---|---|---|---|---|
| 32 | Sulfonamides and Sulfonamidos | Perfluorinated | C6-C12 | C12H8F17NO4S | CCN(CC(O)=O)S(=O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |
| 33 | Sulfonamides and Sulfonamidos | Perfluorinated | C8-C11 | C9H10F9NO4S | CCCN(CC(O)=O)S(=O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F |

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**Figure S10.** Venn diagram displaying the relationship of 208 PFAS that were identified in the ground and surface waters at each point source. Point source #1 is the Oakdale Disposal Site (ODS) and point source #2 is the Washington County Landfill (WCL). Groundwater is abbreviated as "GW" and surface water is abbreviated as "SW".

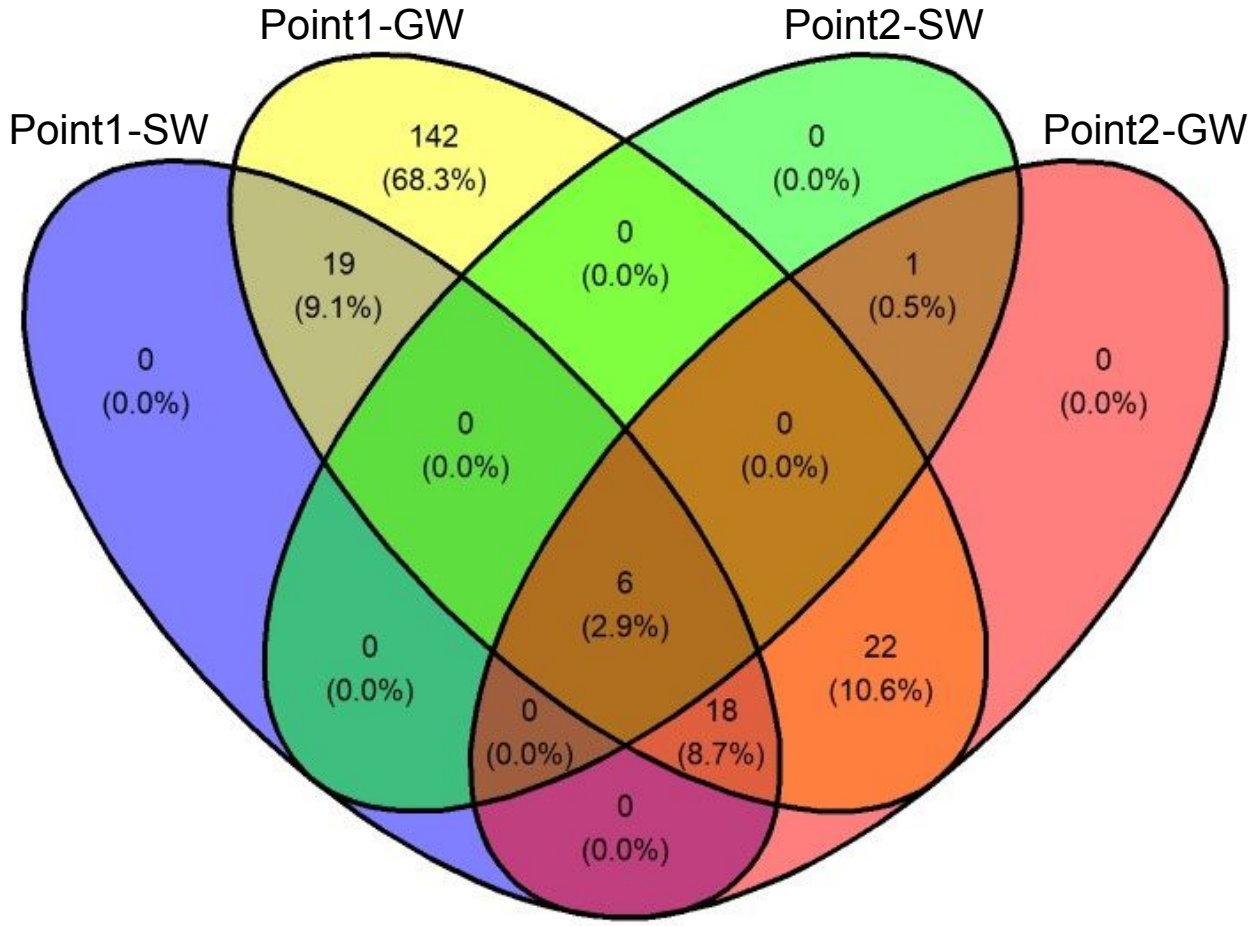
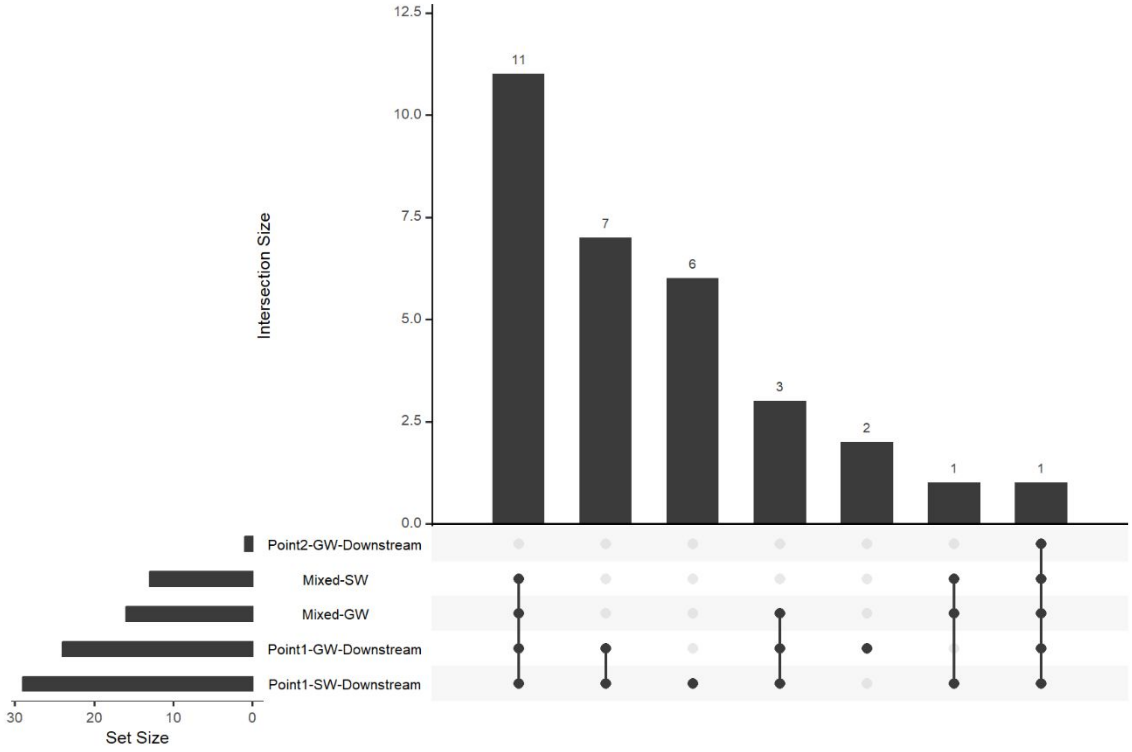


**Figure S11.** UpSet plot showing the relationship of 33 PFAS measured at one or more downstream location(s). Sites with more than one downstream location (e.g., Mixed-GW1, Mixed-GW2, and MixedGW3) were combined here.



561 **Table S18.** Homologous series and individual PFAS measured in at least one downstream
562 ground or surface water sample.

| Series Number | PFAS Subclass or Name | Level of Fluorination | Number of Carbons Observed in Series Measured Downstream | Representative Formula |
|---|---|---|---|---|
| 1 | Perfluorinated sulfonic acids | Perfluorinated | C3-8 | C8HF17O3S |
| 2 | Polyfluorinated sulfonic acids | Polyfluorinated | C8-C10 | C8H2F16O3S |
| 3 | Polyfluorinated sulfonic acids | Polyfluorinated | C8 | C8H3F15O3S |
| 8 | Keto sulfonic acids | Perfluorinated | C8, C10 | C8HF15O4S |
| 9 | Ether sulfonic acid | Perfluorinated | C8 | C8HF17O4S |
| 19 | Bifunctional sulfonic acid | Unsaturated | C12, C14, C16 | C9H2F16O6S2 |
| 21 | Perfluorinated carboxylic acids | Perfluorinated | C3-C10 | C8HF15O2 |
| 22 | Polyfluorinated carboxylic acid | Polyfluorinated | C8 | C8H2F14O2 |
| 23 | Polyfluorinated carboxylic acid | Polyfluorinated | C8 | C8H3F13O2 |
| 28 | Ether carboxylic acid | Perfluorinated | C8, C9 | C8HF15O3 |
| 31 | Sulfonamides and Sulfonamidos | Perfluorinated | C3-C4, C8 | C8H2F17NO2S |
| | N-Methyl-N-(2-hydroxyethyl)perfluorooctanesulfonamide | Perfluorinated | | C11H8F17NO3S |
| | N-Ethyl-N-(2-hydroxyethyl)perfluorooctane sulfonamide | Perfluorinated | | C12H10F17NO3S |
| | 2-(Difluoromethyl)-4-(2-methylpropyl)-5-[(methylthio)carbonyl]-6-(trifluoromethyl)-3-pyridinecarboxylic acid | Polyfluorinated | | C14H14F5NO3S |

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564 **Table S19.** Transformation pathways and products identified using the EPA Chemical Transformation Simulator (CTS) tool with the
565 PFAS environmental reaction library. Six homologous series and four individual PFAS identified were found to have at least one
566 transformation product/pathway identified below.

| Feature ID | Series Number | Final DTXSID or CAS-RN | Formula | SMILES | CTS Pathways | CTS products |
|---|---|---|---|---|---|---|
| 848 | | DTXSID30895360 | C6H3F7O2 | OC(=O)C=CC(F)(F)C(F)(F)C(F)(F)F | Reduction and/or hydroxylation with oxidation | Fluorotelomer carboxylic acids and/or perfluorinated carboxylic acids |
| 1567 | | DTXSID70880215 | C6HF11O3 | OC(=O)C(F)(OC(F)(F)C(F)(F)C(F)(F)F)C(F)(F)F | Decarboxylation | Polyfluorinated ether without headgroup |
| 1736 | | DTXSID30382063 | C5HF9O4 | OC(=O)C(F)(F)OC(F)(F)C(F)(F)OC(F)(F)F | Decarboxylation | Polyfluorinated ether without headgroup |
| 2440 | 30 | DTXSID501026626 | C6H6F9NO2S | CCNS(=O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F | Dealkylation and hydrolysis | Perfluorinated sulfonic acids |
| 2749 | 24 | DTXSID20874028 | C8H5F11O2 | OC(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F | Oxidation and hydroxylation | Perfluorinated carboxylic acids |
| 3083 | 25 | DTXSID30891463 | C8H2F12O2 | OC(=O)\C=C(\F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F | Reduction and/or hydroxylation with oxidation | Fluorotelomer carboxylic acids and/or perfluorinated carboxylic acids |
| 3348 | | DTXSID00897154 | C11H12F7NO5 | CCOC(=O)[C@@H](CCC(O)=O)NC(=O)C(F)(F)C(F)(F)C(F)(F)F | Hydrolysis | Perfluorinated carboxylic acids |
| 3809 | 26 | DTXSID001035131 | C8HF13O3 | OC(=O)C(F)(F)OC(F)(F)C(F)(F)C(F)(F)C(\F)=C(/F)C(F)(F)F | Decarboxylation | Polyfluorinated ether without headgroup |
| 4361 | 4 | DTXSID6067331 | C8H5F13O3S | OS(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F | Desulfonation and oxidation | Fluorotelomer carboxylic acids |
| 4729 | 29 | DTXSID401026647 | C8H4F13NO4S | OC(=O)CNS(=O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F | Deacetylation and hydrolysis | Perfluorinated sulfonic acids |

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**Figure S12**. Boxplot of the dilution factors for chemicals measured at each site downstream to Point1-GW. Dilution factors for each site were compared with a Mann-Whitney U test and were found to be comparable (p =0.101).

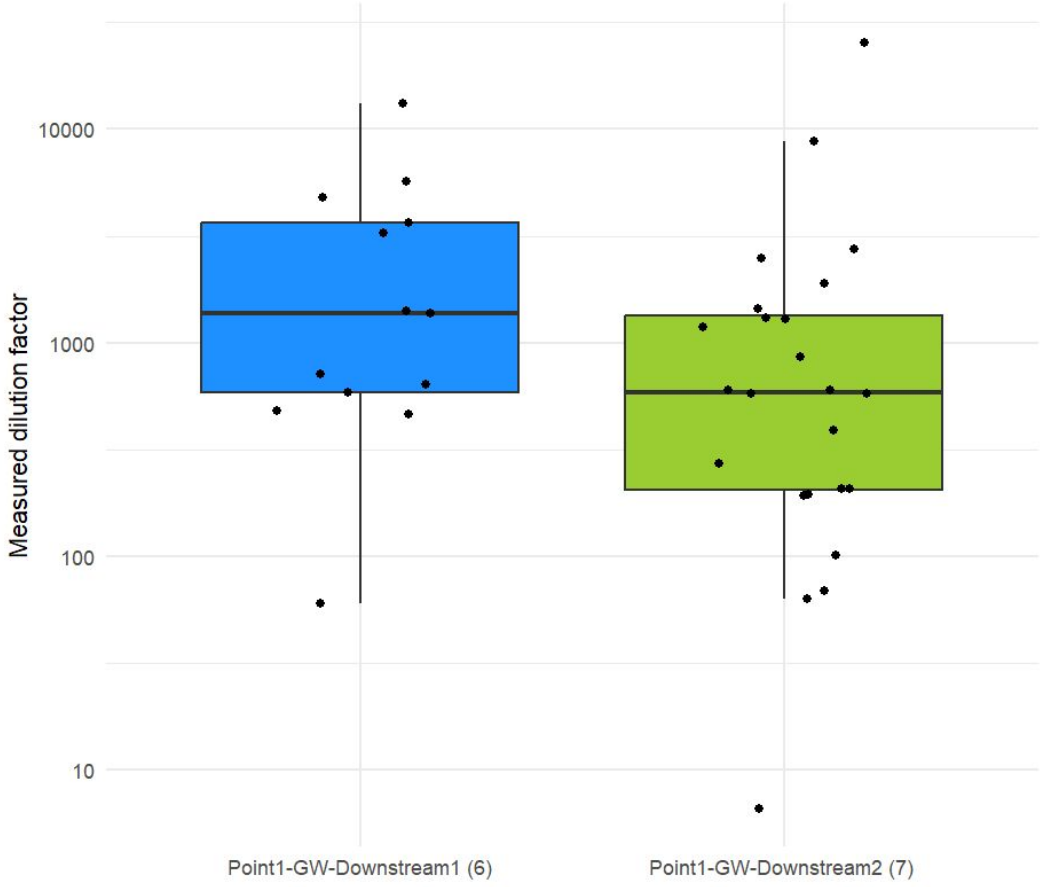


**Figure S13.** Histogram plot of the distribution of dilution factors for chemicals measured at both Point1-GW and Point1-GW-Downstream1 and Point1-GW-Downstream2. The red vertical line represents the 2.5$^{th}$ percentile of and the black line represents the 50$^{th}$ percentile (median) of the distribution.

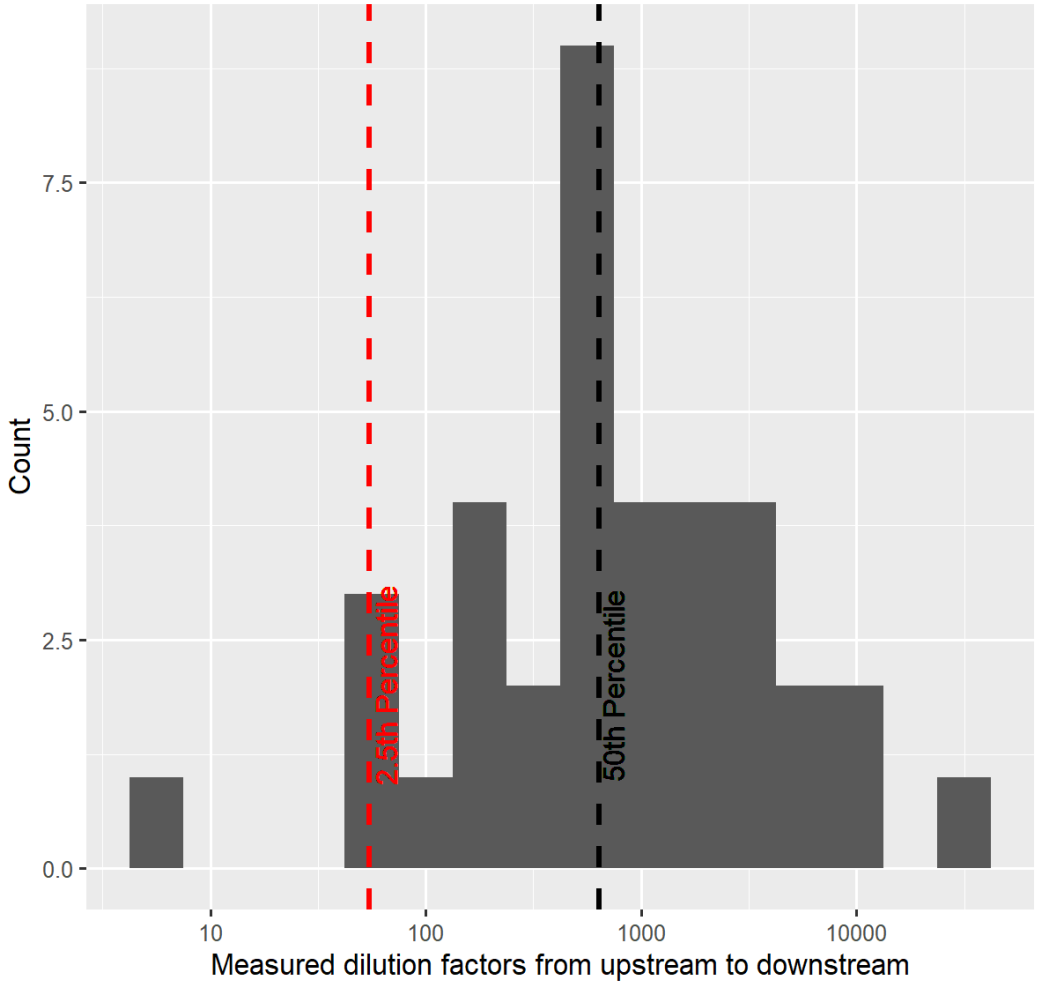


**Figure S14.** Histogram plot of the distribution of concentrations estimated in all ground and surface water samples. The black vertical line represents the 5th percentile of the distribution that was used to estimate a limit of detection of 0.003 ng/mL (pre-enrichment).

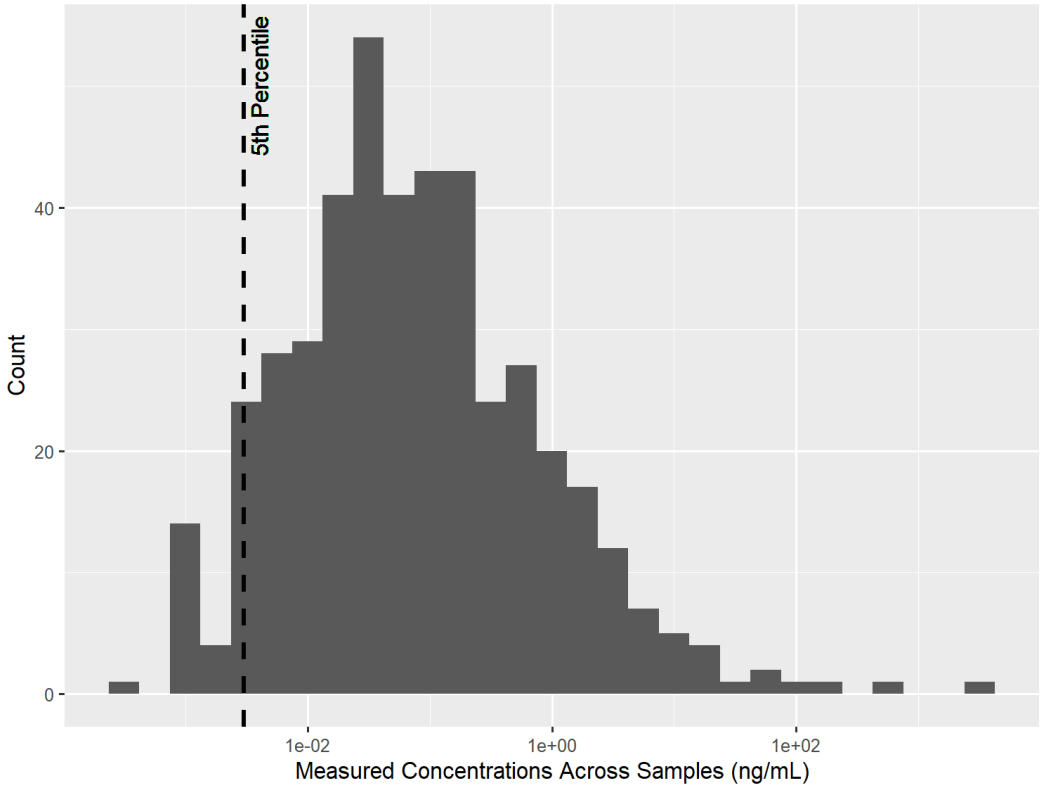
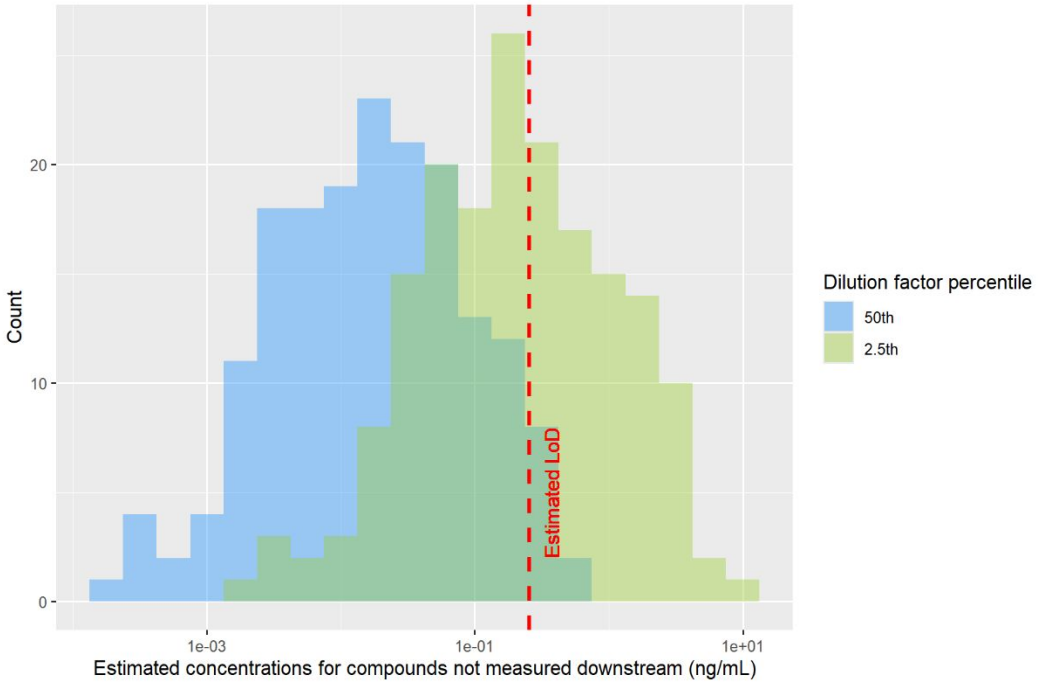


**Figure S15.** Histogram of the concentrations estimated for compounds not measured downstream from Point1-GW compared to estimated limit of detection. Two distributions are given, one for a the median (50$^{th}$ percentile) dilution factor in blue and another for the 2.5$^{th}$ dilution factor in green. The estimated limit of detection (0.255 ng/mL for post-enrichment, in-vial) is given as a red vertical line.



## 5. References

(1) *MPCA brings cutting-edge technology to Minnesota to remove PFAS from water*. Minnesota Pollution Control Agency, 2022. https://www.pca.state.mn.us/news-and-stories/mpca-brings-cutting-edge-technology-to-minnesota-to-remove-pfas-from-water (accessed 2024 November 20th).

(2) Sobus, J. R.; Sayre-Smith, N. A.; Chao, A.; Ferland, T. M.; Minucci, J. M.; Carr, E. T.; Brunelle, L. D.; Batt, A. L.; Whitehead, H. D.; Cathey, T.; Boyce, M.; Ulrich, E. M.; McCord, J. P.; Williams, A. J. Automated QA/QC reporting for non-targeted analysis: a demonstration of "INTERPRET NTA" with de facto water reuse data. *Analytical and Bioanalytical Chemistry.* **2025**.

(3) Pu, S.; Whitehead, H. D.; McCord, J. P.; Dahlmeier, A.; Saravia, S.; Rushing, R.; DeVault, M.; Sobus, J. R. Assessing Sample and Chemical Data Quality for Quantitative Non-Targeted Analysis of Environmental Study Sample. *In preparation.* **2025**.