Supporting Information

High Concentrations of Unidentified Extractable Organofluorine observed in Blubber from a Greenland Killer Whale (*Orcinus orca*)

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Sample information

The killer whale (*Orcinus orca*) was a 409 cm long female, young adult. The individual, which was not pregnant and had seal remains in the stomach, was harvested near Tasiilaq, East Greenland, in September 2017. Export and import permits were obtained from the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES; permit no: 17GL1167088).

Table S1. Sample amounts in grams wet weight (replication) used for different experiments and analysis. S/R = spike /recovery.

| Tissue   | PFAS S/R | Target PFAS analysis | EOF S/R | EOF analysis | TF analysis |
|----------|----------|----------------------|---------|--------------|-------------|
| Liver    | 0.5 g (3) 0.5 g (3) | 0.5 g (3) | 0.5 g (3) | 0.1 g (2) |
| Blood    | 0.5 g (3) 0.5 g (3) | 0.5 g (3) | 0.5 g (3) | 0.1 g (2) |
| Lung     | 0.5 g (3) 0.5 g (3) | 0.5 g (3) | 0.5 g (3) | 0.1 g (2) |
| Kidney   | 0.5 g (3) 0.5 g (3) | 0.5 g (2) | 0.5 g (2) | 0.1 g (2) |
| Ovary    | 0.5 g (3) 0.5 g (3) | 0.5 g (3) | 0.5 g (3) | 0.2 g (2) |
| Muscle   | 0.5 g (3) 0.5 g (3) | 0.5 g (3) | 0.5 g (3) | 0.1 g (2) |
| Skin     | 0.5 g (3) 0.5 g (3) | 0.5 g (3) | 0.5 g (3) | 0.1 g (2) |
| Blubber  | 0.5 g (6) 0.5 g (2) | 0.5 g (2) | 0.5 g (3) | 0.1 g (2) |
| Seal liver | 0.5 g (3) | 0.5 g (3) |         |             |

Sample extraction

Sample extraction for targeted analysis and suspect screening (0.5 g, n=3 replicates per tissue) was carried out using acetonitrile together with bead blending. Tissues were allowed to thaw at room temperature prior to extraction. After addition of an internal standard mix (1 ng, n=13) and 4 ml acetonitrile, samples were homogenized for 5 min at 1500 rpm using a bead blender (4.8 mm stainless steel beads, Next Advance; Bead blender 1600 miniG, SPEX Sample Prep). Extracts were centrifuged (5 min, 2000 rpm) and the supernatant transferred to a new 13 ml PP-tube. The extraction was repeated with 4 ml acetonitrile, and the combined supernatants concentrated to 1 ml under a stream of nitrogen. The extracts were purified using 25 mg ENVICarb and 50 µl glacial acetic acid and thereafter centrifuged for 10 min at 10000 rpm. 500 µl of the extracts were mixed with 500 µl of 4 mM aqueous NH₄OAc and two recovery standards (1 ng each), and thereafter subjected to instrumental analysis.
**UHPLC-MS/MS parameters**

The Xevo TQ-S triple quadrupole (Waters) was equipped with an electrospray ionization source operated in negative mode. The capillary voltage was set at 1.0 kV, and the desolvation and source temperature were set at 350°C and 150°C, respectively. The desolvation and cone gas flows were set at 150 L/h and 650 L/h, respectively.

**Table S2.** Mobile phase gradient and composition for target and non-target analysis. The LC column was maintained at 50°C throughout the run.

| Time (minutes) | Mobile phase A (%) | Mobile phase B (%) | Flow (mL/min) |
|----------------|--------------------|--------------------|---------------|
| 0              | 90                 | 10                 | 0.4           |
| 0.5            | 90                 | 10                 | 0.4           |
| 5.0            | 20                 | 80                 | 0.4           |
| 5.1            | 0                  | 100                | 0.4           |
| 8.0            | 0                  | 100                | 0.4           |
| 10.0           | 90                 | 10                 | 0.4           |

**Combustion ion chromatography – method details**

TF and EOF measurements were carried out using a Thermo-Mitsubishi combustion ion chromatograph (CIC). Sample extracts (100 µl) were placed in a ceramic sample boat containing glass wool for better dispersion of the fluids while neat material (100 mg) was weighed directly into the sample boat. All boats were baked out prior to sample combustion to minimize background contamination. The samples were combusted slowly in a combustion furnace (HF-210, Mitsubishi) at 1100 °C under a flow of oxygen (400 ml/min) and argon mixed with water vapor (200 ml/min) for approximately 5 minutes. Combustion gases were absorbed in MilliQ water during the entire length of the combustion process using a gas absorber unit (GA-210, Mitsubishi). An aliquot of the absorption solution (200 µl) was injected onto an ion chromatograph (Dionex Integriion HPIC, Thermo Fisher Scientific) equipped with an anion exchange column (Dionex IonPac AS19 2 × 50 mm guard column and 2 × 250 mm analytical column, 7.5 µm particle size) operated at 30°C. Chromatographic separation was achieved by running a gradient of aqueous hydroxide mobile phase ramping from 8 mM to 60 mM at a flow rate of 0.25 ml/min. Fluoride was detected using a conductivity detector.

**Orbitrap parameters**

The parameters of the heated electrospray ionization were as follows: Sheath gas = 45 arbitrary units (au), Aux gas = 5 au, spray voltage = 3.7 kV, capillary temperature = 350 °C, Aux gas heater = 350 °C.
Data quality for individual PFASs

Two levels of data quality were defined for target PFASs based on the availability of mass-labeled and native standards. This is described in detail in the supporting information. Level 1 (“quantitative”) was assigned to the following PFASs for which both native and exactly-matched ISs were available: perfluorobutanoate (PFBA), perfluoro-pentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluoroocotanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDa), perfluoroundecanoate (PFUnDA), perfluorododecanoate (PFDoDA), perfluorohexane sulfonate (PFHxS), perfluoroocane sulfonate (PFOS), perfluorooctane sulfonamide (FOSA), and N-ethyl perfluoroctane sulfonamidoacetic acid (EtFOSAA). Level 2 (“semi-quantitative”) was assigned to the following substances which lacked exactly-matched ISs: perfluorotridecanoate (PFTrDA), perfluorotetradecanoate (PFTeDA), perfluoropentadecanoate (PFPeDA), perfluorobutane sulfonate (PFBS), perfluorododecanoate (PFDS), 3-perfluoropropyl propanoic acid (3:3 FTCA), 3-perfluoropentyl propanoic acid (5:3 FTCA), 3-perfluoroheptyl propanoic acid (7:3 FTCA), 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (9Cl-PF3ONS), 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (11Cl-PF3OUdS) and dodecafluoro-3H-4,8-dioxa-nonanoate (ADONA).
Table S3. PFAS (native, internal standards and recovery standards) included in this study, MS quantification parameters and method quantification limits.

| Compound Abbreviation<sup>a</sup> | Precursor Ion | Quantitative Product ion | Qualitative Product ion | Internal standard | IS transition | Native used for quantification | Data quality<sup>b</sup> | MDL (ng/g) |
|----------------------------------|--------------|--------------------------|-------------------------|------------------|--------------|-------------------------------|---------------------------|------------|
| PFBA                            | 213          | 169                      | 149                     | <sup>13</sup>C₃-PFBA | 217>172      | PFBA                          | 1            | 0.204     |
| PFPeA                           | 263          | 219                      | 169                     | <sup>13</sup>C₅-PFPeA | 266>223      | PFPeA                         | 1            | 0.073     |
| PFHxA                           | 313          | 269                      | 119                     | <sup>13</sup>C₂-PFHxA | 315>270      | PFHxA                         | 1            | 0.073     |
| PFHpA                           | 363          | 319                      | 169                     | <sup>13</sup>C₃-PFHxA | 367>322      | PFHpA                         | 1            | 0.073     |
| PFOA                            | 413          | 169                      | 369                     | <sup>13</sup>C₄-PFOA | 417>372      | PFOA                          | 1            | 0.073     |
| PFNA                            | 463          | 419                      | 219                     | <sup>13</sup>C₅-PFNA | 468>423      | PFNA                          | 1            | 0.073     |
| PFDA                            | 513          | 469                      | 269                     | <sup>13</sup>C₂-PFDA | 515>470      | PFDA                          | 1            | 0.073     |
| PFUnDA                          | 563          | 519                      | 269                     | <sup>13</sup>C₂-PFUnDA | 565>520      | PFUnDA                        | 1            | 0.073     |
| PFDoDA                          | 613          | 569                      | 169                     | <sup>13</sup>C₂-PFDoDA | 615>570      | PFDoDA                        | 1            | 0.204     |
| PFTrDA                          | 663          | 619                      | 169                     | <sup>13</sup>C₂-PFTrDA | 615>570      | PFTrDA                        | 2            | 1.38      |
| PFTeDA                          | 713          | 669                      | 169                     | <sup>13</sup>C₂-PFTeDA | 615>570      | PFTeDA                        | 2            | 1.38      |
| PFPeDA                          | 763          | 719                      | 169                     | <sup>13</sup>C₂-PFPeDA | 615>570      | PFHxDA                        | 2            | 1.38      |
| PFBS                            | 299          | 80                       | 99                      | <sup>18</sup>O₂-PFBS | 403>84       | PFBS                          | 2            | 0.065     |
| PFHxS                           | 399          | 80                       | 99                      | <sup>18</sup>O₂-PFHxS | 403>84       | PFHxS                         | 1            | 0.065     |
| PFOS                             | 499          | 80                       | 99                      | <sup>13</sup>C₄-PFOS | 503>80       | PFOS                          | 1            | 0.070     |
| PFDS                             | 599          | 80                       | 99                      | <sup>13</sup>C₄-PFDS | 503>80       | PFDS                          | 2            | 0.070     |
| FOSA                             | 498          | 78                       | 478                     | <sup>13</sup>C₄-FOSA | 506>78       | FOSA                          | 1            | 0.080     |
| Et-FOSAA                         | 584          | 419                      | 526                     | D₅-EtFOSAA       | 589>419      | EtFOSAA                       | 1            | 1.41      |
| 9Cl-PF3ONS                        | 531          | 351                      | 83                      | <sup>13</sup>C₃-PF3ONS | 503>80       | 9Cl-PF3ONS                    | 2            | 1.43      |
| 11Cl-PF3OUdS                     | 631          | 451                      | 83                      | <sup>13</sup>C₃-PF3OUdS | 503>80       | 11Cl-PF3OUdS                  | 2            | 0.204     |
| ADONA                            | 377          | 251                      | 85                      | <sup>13</sup>C₄-PFOS | 503>80       | ADONA                         | 2            | 0.204     |
| 3:3 FTCA                         | 241          | 117                      | 177                     | <sup>13</sup>C₄-PFOA | 417>372      | 3:3 FTCA                      | 2            | 10.07     |
| 5:3 FTCA                         | 341          | 237                      | 217                     | <sup>13</sup>C₃-PFOA | 417>372      | 5:3 FTCA                      | 2            | 1.40      |
| 7:3 FTCA                         | 441          | 337                      | 148                     | <sup>13</sup>C₃-PFOA | 417>372      | 7:3 FTCA                      | 2            | 1.40      |
| <sup>13</sup>C₃PFOA             | 421          | 376                      | -                       | -                | -             | -                             | -            | -         |
| <sup>13</sup>C₄PFOS             | 507          | 80                       | -                       | -                | -             | -                             | -            | -         |

<sup>a</sup> All native and internal standards were obtained from Wellington Laboratories (Guelph, ON, Canada)

<sup>b</sup> 1 = Quantitative (native standard and exact matched mass labelled standard), 2 = Semi-quantitative (native standard but no exact matched mass labelled standard).
**Fluorine mass balance calculations**

Fluorine mass balance calculations were done by converting the concentration for the measured PFAS concentration \(C_{PFAS}; \text{ng PFAS/g}\), into corresponding fluoride concentration \(C_{F\_PFAS}; \text{ng F/g}\) using the following equation:

\[
\text{Eq 1. } C_{F\_PFAS} = n_F \times \frac{MW_F}{MW_{PFAS}} \times C_{PFAS}
\]

- \(C_{F\_PFAS}\) = The corresponding fluoride concentration
- \(n_F\) = The number of fluorine atoms in PFAS
- \(MW_F\) = The molecular weight of fluorine
- \(MW_{PFAS}\) = The molecular weight of the PFAS.
- \(C_{PFAS}\) = The measured PFAS concentration using LC-MS/MS

The total known extractable fluorine concentration \((\Sigma C_{F\_PFAS}; \text{ng F/g})\) is obtained by summing the fluorine concentrations from all individual PFASs. Then the total concentration of unidentified, extractable organic fluorine \((C_{F\_extr.unknown}; \text{ng F/g})\) can be determined by subtracting \(\Sigma C_{F\_PFAS}\) from the total extractable organic fluorine concentration \((C_{F\_EOF}; \text{ng F/g})\) as measured directly by CIC, according to equation 2.

\[
\text{Eq 2. } C_{F\_EOF} = \Sigma C_{F\_PFAS} + C_{F\_extr.unknown}
\]

The total fluorine concentration \((C_{F\_TF}; \text{ng F/g})\) was measured with direct CIC measurements. The TF concentration is the sum of \(C_{F\_EOF}\) and the total non-extractable fluorine concentration \((C_{F\_non\ extr.}; \text{ng F/g})\), as shown in equation 3.

\[
\text{Eq 3. } C_{F\_TF} = C_{F\_EOF} + C_{F\_non\ extr.}
\]
Table S4. Native PFAS recoveries per tissue, overall average recovery (%), and relative standard deviation (RSD) assessed by spike-recovery experiments (n=3, spike amount = 5 ng)

| Compound | blood | lung | blubber | muscle | skin | kidney | liver | ovary | Average recovery (%) | RSD (%) |
|----------|-------|------|---------|--------|------|--------|-------|-------|----------------------|---------|
| PFBA     | 125   | 81   | 116     | 124    | 111  | 116    | 110   | 56    | 98.4                 | 3.3     |
| PFPeA    | 107   | 113  | 108     | 96     | 94   | 92     | 79    | 86    | 95.2                 | 7.9     |
| PFHxA    | 103   | 115  | 104     | 107    | 117  | 108    | 115   | 105   | 108.5                | 19.4    |
| PFHpA    | 129   | 109  | 94      | 115    | 111  | 245    | 153   | 141   | 135.4                | 3.0     |
| PFOA     | 101   | 90   | 94      | 103    | 108  | 117    | 89    | 107   | 102.8                | 10.1    |
| PFNA     | 108   | 103  | 97      | 115    | 111  | 104    | 95    | 96    | 106.6                | 9.0     |
| PFDA     | 93    | 120  | 100     | 106    | 105  | 113    | 89    | 82    | 104.0                | 7.1     |
| PFUnDA   | 91    | 89   | 109     | 114    | 130  | 117    | 101   | 79    | 107.5                | 5.5     |
| PFDoDA   | 99    | 113  | 91      | 108    | 107  | 105    | 105   | 91    | 103.5                | 12.3    |
| PFTrDA   | 110   | 110  | 102     | 131    | 164  | 122    | 118   | 56    | 117.4                | 3.9     |
| PFTeDA   | 203   | 201  | 183     | 185    | 239  | 183    | 186   | 157   | 194.7                | 8.2     |
| PFBS     | 62    | 68   | 80      | 80     | 81   | 76     | 63    | 77    | 79.1                 | 4.2     |
| PFHxS    | 81    | 100  | 109     | 108    | 106  | 113    | 78    | 99    | 109.9                | 3.2     |
| PFDS     | 111   | 88   | 127     | 115    | 146  | 118    | 96    | 103   | 109.1                | 5.3     |
| FOSA     | 128   | 116  | 130     | 124    | 138  | 126    | 99    | 127   | 121.7                | 10.2    |
| Et-FOSAA | 0     | 0    | 0       | 129    | 142  | 112    | 125   | 116   | 82.7                 | 1.3     |
| 9Cl-PF3ONS| 157  | 158  | 156     | 166    | 190  | 166    | 135   | 163   | 161.3                | 11.4    |
| 11Cl-PF3OuDS| 245 | 227  | 205     | 212    | 266  | 217    | 215   | 287   | 234.6                | 8.6     |
| NaDONA   | 86    | 77   | 85      | 88     | 89   | 95     | 79    | 102   | 87.6                 | 11.3    |
| 3:3 FTCA | 39    | 18   | 24      | 33     | 38   | 54     | 41    | 39    | 35.3                 | 3.4     |
| 5:3 FTCA | 57    | 55   | 52      | 64     | 79   | 77     | 71    | 74    | 64.6                 | 6.0     |
| 7:3 FTCA | 95    | 45   | 75      | 90     | 96   | 105    | 90    | 88    | 86.6                 | 4.9     |

Table S5. Reference, literature and obtained PFAS concentrations (in ng/g ± standard deviation) in SRM 1957 (Organic Contaminants in Non-Fortified Human Serum (Freeze-Dried)).

|         | PFHpA | PFOA | PFNA | PFDA | PFUnDA | PFHxS | PFOS |
|---------|-------|------|------|------|--------|-------|------|
| NIST    | 0.305 | 5.0  | 0.878| 0.39 | 0.172  | 4.0   | 21.1 |
|         | ± 0.036| ± 0.4| ± 0.068| ± 0.1| ± 0.031| ± 0.75| ± 1.2|
| Gebbink (2015) | 0.20 | 3.86 | 0.72 | 0.24 | 0.11 | 3.25 | 18.5 |
|         | ± 0.02| ± 0.13| ± 0.04| ± 0.01| ± 0.01| ± 0.06| ± 0.07|
| Yeung (2013) | 0.20 | 4.10 | 0.76 | 0.29 | 0.12 | 4.14 | 19.3 |
|         | ± 0.06| ± 0.35| ± 0.08| ± 0.03| ± 0.12| ± 0.458| ± 1.18|
| This study | 0.19 | 4.00 | 0.61 | 0.13 | 0.02 | 3.91 | 19.2 |
|         | ± 0.02| ± 0.23| ± 0.06| ± 0.02| ± 0.03| ± 1.90| ± 8.89|
Table S6. Results of EOF PFOS and NaF spike-recovery experiments.

| Tissue     | PFOS spike (ng) | NaF spike (ng F) | Expected recovery<sup>a</sup> (ng F) | Theoretical recovery (%) | Recovery<sup>b</sup> (%) | Average recovery (%), RSD (%) |
|------------|-----------------|------------------|-------------------------------------|--------------------------|---------------------------|-------------------------------|
| Seal liver |                 |                  |                                     |                          |                           |                               |
|            | 80              | -                | 52                                  | 100                      | 71                        |                               |
|            | 130             | -                | 84                                  | 100                      | 69                        |                               |
|            | 250             | -                | 162                                 | 100                      | 70                        |                               |
|            | 500             | -                | 324                                 | 100                      | 66                        |                               |
|            | 1000            | -                | 647                                 | 100                      | 72                        |                               |
|            | 1000            | -                | 647                                 | 100                      | 68                        |                               |
|            | 1000            | -                | 647                                 | 100                      | 64                        | 68.5, 2.5                    |
|            | -               | 250              | 0                                   | 0                        | 0                         | 0, -                         |
|            | -               | 500              | 0                                   | 0                        | 0                         |                               |
|            | -               | 750              | 0                                   | 0                        | 0                         |                               |
|            | -               | 750              | 0                                   | 0                        | 0                         |                               |
|            | -               | 1000             | 0                                   | 0                        | 0                         |                               |
|            | -               | 2000             | 0                                   | 0                        | 0                         |                               |

<sup>a</sup> PFOS concentration converted to fluorine equivalents according to Eq. 1
<sup>b</sup> Recovery calculated as \([\text{measured concentration}/(\text{background concentration} + \text{spike})*100]\)

Table S7. Results of tissue specific EOF spike-recovery experiments.

| Tissue     | n   | PFOS spike (ng) | NaF spike (ng F) | Expected recovery<sup>a</sup> (ng F) | Theoretical recovery (%) | Average recovery<sup>b</sup> (%) | RSD (%) |
|------------|-----|-----------------|------------------|-------------------------------------|--------------------------|-------------------------------|--------|
| Seal Liver | 3   |                 |                  |                                     |                          | 65                            | 5      |
| KW Blood   | 3   |                 |                  |                                     |                          | 71                            | 14     |
| KW Lung    | 3   |                 |                  |                                     |                          | 65                            | 5      |
| KW Kidney  | 2   | 250             | 250              | 161                                 | 100                      | 70                            | 21     |
| KW Ovary   | 3   |                 |                  |                                     |                          | 50                            | 14     |
| KW Muscle  | 3   |                 |                  |                                     |                          | 60                            | 3      |
| KW Skin    | 3   |                 |                  |                                     |                          | 49                            | 6      |
| KW Blubber | 2   |                 |                  |                                     |                          | 100                           | 15     |

<sup>a</sup> PFOS concentration converted to fluorine equivalents according to Eq. 1
<sup>b</sup> Recovery calculated as \([\text{measured concentration}/(\text{background concentration} + \text{spike})*100]\)
Table S8. Average target PFAS ± standard deviation (from replicate extractions), EOF (corrected for average PFOS recovery) and TF concentrations (ng/g). Concentrations below LOD are marked in italics.

|       | Liver   | Blood   | Lung    | Kidney  | Ovary   | Skin    | Muscle  | Blubber |
|-------|---------|---------|---------|---------|---------|---------|---------|---------|
| PFPeA | <0.073  | <0.073  | <0.073  | <0.073  | 2.69±4.66 | <0.073  | <0.073  | <0.073  |
| PFHxA | <0.073  | <0.073  | <0.073  | <0.073  | 0.07±0.11 | <0.073  | <0.073  | 0.10±0.12 |
| PFHxS | 0.13±0.12 | 0.20±0.01 | <0.073  | <0.073  | 0.07±0.11 | <0.073  | <0.073  | <0.073  |
| PFOA  | 0.20±0.02 | 0.20±0.01 | 0.59±0.26 | 0.07±0.11 | <0.073  | <0.073  | <0.073  | <0.073  |
| PFNA  | 9.05±1.32 | 7.04±0.66 | 2.74±0.74 | 3.71±0.40 | 2.99±0.03 | 0.17±0.30 | 0.67±0.23 | <0.073  |
| PFDA  | 21.01±3.67 | 8.60±1.31 | 2.45±0.33 | 3.71±0.09 | 3.12±0.68 | 0.51±0.02 | 0.20±0.20 | 0.40±0.23 |
| PFUnDA| 96.35±22.56 | 29.37±6.02 | 12.91±1.44 | 13.78±0.99 | 12.44±0.31 | 3.03±0.09 | 2.07±0.58 | 1.30±0.76 |
| PFDaDA| 11.58±1.36 | 2.87±0.21 | 2.56±0.09 | 2.19±0.19 | 2.26±0.48 | 0.84±0.27 | 0.47±0.11 | 0.20±0.23 |
| PFTrDA| 30.61±16.13 | 10.30±0.50 | 16.56±1.98 | 12.58±2.35 | 15.62±2.66 | 4.89±0.33 | 2.86±0.61 | 1.90±1.10 |
| PFTeDA| 6.52±1.06 | 2.02±0.29 | 3.94±0.42 | 2.65±0.59 | 3.59±1.81 | 0.51±0.87 | <1.38   | <1.38   |
| PFPeDA| 12.91±1.32 | 1.96±0.35 | 6.78±0.45 | 5.23±1.11 | 6.18±1.36 | 3.55±0.98 | <1.38   | <1.38   |
| PFBS  | <0.26   | <0.26   | <0.26   | <0.26   | <0.26   | <0.26   | <0.26   | <0.26   |
| PFHxS | 0.93±0.24 | 2.09±0.22 | 0.70±0.44 | 0.66±0.12 | 0.93±0.24 | <0.065  | <0.065  | <0.065  |
| PFOS  | 109.89±41.23 | 34.76±7.79 | 34.01±1.84 | 33.17±3.95 | 26.42±4.48 | 4.87±0.09 | 6.01±1.32 | 2.80±1.6 |
| Br-PFOS| 8.73±3.83 | 4.83±1.77 | 3.15±0.17 | 2.65±0.32 | 1.67±0.62 | <0.070  | 0.40±0.20 | <0.070  |
| L-PFDS| 1.07±0.32 | 0.20±0.01 | 0.49±0.16 | 0.33±0.23 | 0.33±0.11 | 0.17±0.29 | <0.070  | <0.070  |
| Br-PFDS| 0.27±0.19 | <0.070   | <0.070   | <0.070   | <0.070   | <0.070   | <0.070   | <0.070   |
| L-FOSA| 25.15±4.73 | 5.86±0.47 | 6.91±1.08 | 11.32±2.30 | 2.87±1.20 | 0.67±0.27 | 3.06±0.80 | 1.90±1.14 |
| Br-FOSA| 4.06±1.19 | 0.98±0.20 | 0.98±0.04 | 1.52±0.31 | 0.40±0.20 | <0.076  | 0.13±0.12 | 0.30±0.20 |
| 7:3 FTCA| 13.65±1.79 | 4.63±0.68 | <1.402    | <1.402    | <1.402    | <1.402    | <1.402    | <1.402    |
| ΣPFOS | 118.62±45.1 | 39.59±9.60 | 37.15±2.0 | 35.83±4.3 | 28.09±5.1 | 4.87±0.90 | 6.41±1.5  | 2.80±1.6  |
| ΣFOSA | 29.20±5.90 | 6.84±0.70 | 7.89±1.1  | 12.84±2.7 | 3.27±1.4 | 0.67±0.30 | 3.19±0.9  | 2.20±1.3  |
| ΣC_{PFAS} | 352.1±100.6 | 115.9±20.5 | 94.8±9.4  | 93.6±13.0 | 81.6±18.9 | 19.4±4.3  | 16.5±4.4  | 9.5±5.7   |
| ΣC_{F,PFAS} | 239.8±43.7 | 78.8±9.1  | 64.6±1.3  | 63.5±7.4  | 55.9±3.0 | 13.5±0.3  | 11.1±1.8  | 6.28±0.90 |
| C_{F,EOF} | 195.7±15.3 | 54.9±8.4  | 33.1±0.9  | 58.7±6.3  | <41.8    | <41.8     | 27.1±15.1 | 229.0±132.4 |
| C_{F,TF}  | 404.21±97.8 | 284.70±49.3 | 1004.84±123.3 | 612.30±117.9 | 185.90±6.9 | 192.25±20.3 | 217.62±11.1 | 1315.47±5.8 |

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**Figure S1.** MS/MS spectra of selected compounds detected using target/suspect screening.