**Trophic transfer of PFAS potentially threatens vulnerable Saunders's gull (*Larus saundersi*) via the food chain in the coastal wetlands of the Yellow Sea, China**

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**Figure S1**. Sample extraction methods

 

**Figure S2**. The contribution (%) of variables of two principal component

**Table S1**. UHPLC-ESIMS/MS conditions for target PFAS

|  |  |
| --- | --- |
| Instrument | Waters Acquity UHPLC system (Milford, MA, USA) coupled to a Xevo Triple-Quadrupole (Xevo-TQD) AB SCIEX 5500 mass spectrometer (SCIEX Corp, Framingham, MA, USA) with an electrospray ionization (ESI) source |
| Analytical column | Shimadzu Shim-pack G1ST-C18 column (2.1 × 100 mm, 2 μm) |
| Column temperature | 40℃ |
| Injection volume | 5 μL |
| Mobile phase | A: methanol; B: 5 mM ammonium acetate in ultrapure water |
| LC Gradient | Duration (min) | Flow (ml/min) | A (%) | B (%) |
| 0.8 | 0.3 | 40 | 60 |
| 2.9 | 0.3 | 90 | 10 |
| 0.9 | 0.3 | 90 | 10 |
| 1.4 | 0.3 | 40 | 60 |
| 2 | 0.3 | 40 | 60 |
| ESI detection parameters | Curtain gas at 35 psiIon spray voltage at 4500 VTemperature at 500℃Ion source gas 1: 50 psiIon source gas 2: 60 psicollision gas: "medium." |
| MS detection parameters | Entrance potential at 10 VCollision cell exit potential at 13 VDeclustering potential at 80 V |

**Table S2**. Precursors and productions at optimum collision energy (eV) values for 14 PFAS and 9 surrogate standards.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Analytes | Molecular weight | Precursorion（m/z） | Production（m/z） | Collision energy (eV) | Retention time (min) |
| PFBA | 214.04 | 212.70 | 168.70\* | 11 | 2.81 |
| PFPeA | 264.05 | 263 | 219\*/175 | 15,15 | 3.32 |
| PFHxA | 314.05 | 313 | 269\*/119 | 11,18 | 3.63 |
| PFHpA | 364.06 | 363 | 319\*/169 | 15,15 | 3.87 |
| PFOA | 414.07 | 413 | 369\*/169 | 13,21 | 4.09 |
| PFNA | 464.08 | 463 | 419\*/169 | 16,15 | 4.28 |
| PFDA | 514.08 | 513 | 469\*/269 | 14,16 | 4.50 |
| PFUnDA | 564.09 | 563 | 519\*/269 | 13,21 | 4.72 |
| PFDoDA | 614.10 | 613 | 569\*/269 | 15,25 | 4.96 |
| PFTeDA | 714.11 | 713 | 669\*/169 | 15,31 | 5.48 |
| L-PFBS | 300.19 | 299 | 80\*/99 | 33,42 | 3.34 |
| L-PFHxS | 400.20 | 399 | 80\*/99 | 40,35 | 3.86 |
| L-PFOS | 500.22 | 499 | 80/99\* | 64,34 | 4.25 |
| L-PFDS | 600.22 | 599 | 80\*/99 | 50,45 | 4.96 |
| 13C4 PFBA | 217 | 217 | 172\* | 11 |  |
| 13C2 PFHxA | 315 | 315 | 270\* | 11 |  |
| 13C4 PFOA | 417 | 417 | 372\* | 13 |  |
| 13C5 PFNA | 468 | 468 | 423\* | 16 |  |
| 13C2 PFDA | 515 | 515 | 470\* | 14 |  |
| 13C2 PFUnDA | 565 | 565 | 520\* | 13 |  |
| 13C8 PFDoDA | 615 | 615 | 570\* | 15 |  |
| 13C4 PFHxS | 403 | 403 | 103\* | 35 |  |
| 13C4 PFOS | 503 | 503 | 99\* | 34 |  |

Note: \* Quantification ion

**Table S3**. Matrix spike recoveries (RE) of target compounds for five sample matrix with the relative standard deviation (RSD) values

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Bird | Clamworm | Bivalve | Shrimp | Sediment |
|  | RE% | RSD% | RE% | RSD% | RE% | RSD% | RE% | RSD% | RE% | RSD% |
| PFBA | 104.19 | 3.06 | 106.68 | 5.55 | 102.32 | 3.84 | 104.51 | 4.21 | 106.59 | 6.10 |
| PFPeA | 82.65 | 6.64 | 106.88 | 5.74 | 96.38 | 9.83 | 109.25 | 8.43 | 108.01 | 5.05 |
| PFBS | 94.95 | 14.82 | 79.29 | 4.33 | 82.68 | 17.71 | 85.87 | 17.81 | 80.10 | 19.96 |
| PFHxA | 106.94 | 4.89 | 114.70 | 3.96 | 105.52 | 4.85 | 113.38 | 3.06 | 106.41 | 5.04 |
| PFHxS | 119.74 | 4.44 | 109.87 | 8.85 | 116.82 | 6.28 | 112.96 | 2.44 | 121.63 | 8.16 |
| PFOA | 83.62 | 6.15 | 113.83 | 7.46 | 107.43 | 4.71 | 103.66 | 4.10 | 107.97 | 13.08 |
| PFHpA | 84.07 | 9.79 | 95.29 | 12.67 | 87.62 | 18.58 | 85.07 | 15.37 | 78.46 | 10.69 |
| PFOS | 106.94 | 7.15 | 105.71 | 3.66 | 111.81 | 8.42 | 97.30 | 12.51 | 119.77 | 13.40 |
| PFNA | 116.61 | 4.24 | 115.38 | 4.82 | 121.07 | 1.61 | 112.80 | 1.44 | 112.98 | 7.23 |
| PFDA | 108.13 | 8.51 | 107.41 | 9.43 | 115.45 | 7.70 | 106.60 | 3.03 | 108.98 | 14.22 |
| PFUnDA | 111.61 | 0.79 | 107.37 | 19.04 | 113.07 | 8.10 | 102.91 | 12.74 | 112.79 | 6.72 |
| PFDS | 112.58 | 4.39 | 108.71 | 14.80 | 120.29 | 3.98 | 111.97 | 3.68 | 102.95 | 14.78 |
| PFDoDA | 111.27 | 2.86 | 116.24 | 3.03 | 113.90 | 9.50 | 109.07 | 16.55 | 115.40 | 4.50 |
| PFTeDA | 87.40 | 15.68 | 72.98 | 12.49 | 95.33 | 17.58 | 111.22 | 6.42 | 115.93 | 4.24 |

**Table S4**. The input and output parameters of in the Ecopath model.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Group name | Trophic level | Biomass in habitat area (t/km²) | Concentration of PFAS (ng/g) | Production / biomass (/year) | Consumption / biomass (/year) | Ecotrophic Efficiency | Production / consumption (/year) |
| Gull | 4.70 | 0.10 | 593.72 | 0.10 | 4.33 | 0.00 | 0.02 |
| Shrimp | 4.40 | 142.86 | 9.42 | 7.60 | 28.90 | 0.20 | 0.26 |
| Bivalve | 4.09 | 428.57 | 27.49 | 2.00 | 8.60 | 0.20 | 0.23 |
| Clamworm | 3.50 | 0.71 | 103.23 | 9.00 | 33.00 | 0.30 | 0.27 |
| Sediment | 1.00 | 18.00 | 1.67 | - | - | 0.89 | - |

**Table S5.** Diet composition matrix for Saunders's gull Ecopath model.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Prey \ predator | Gull | Shrimp | Bivalve | Clamworm |
| Gull | 0 | 0 | 0 | 0 |
| Shrimp | 0.29 | 0 | 0 | 0 |
| Bivalve | 0.23 | 0.5 | 0 | 0 |
| Clamworm | 0.38 | 0.4 | 0.8 | 0 |
| Sediment | 0.1 | 0.1 | 0.2 | 0.2 |

**Table S6**. Concentrations of 13 PFAS in chest muscle from juvenile and adult gull.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| ng/g ww | Juvenile (n=3) | Adult (n=5) | LOD | LOQ |
| Mean±SD | Median (range) | Mean±SD | Median (range) |
| PFOA | 234.19±383.86 | 13.33(11.82-677.44) | 144.11±69.77 | 170.35(21.18-189.38) | 0.02 | 0.06 |
| PFBA | 86.19±149.28 | nd(nd-258.57) | 222.71±199.20 | 130.39(15.50-517.70) | 0.01 | 0.03 |
| PFUNDA | 81.71±47.94 | 68.9(41.47-134.75) | 2.67±3.13\* | 0.64(nd-6.31) | 0.03 | 0.09 |
| PFDA | 49.12±30.10 | 41.43(23.62-82.32) | 1.81±3.51\* | 0.39(nd-8.07) | 0.01 | 0.03 |
| PFNA | 16.87±15.03 | 9.43(7.00-34.17) | 7.42±10.58 | 3.91(1.08-26.21) | 0.03 | 0.1 |
| PFDODA | 21.27±10.51 | 21.62(10.59-31.60) | 2.92±5.76\* | 0.12(nd-13.18) | 0.04 | 0.12 |
| PFHPA | 8.44±14.62 | nd(nd-25.33) | 4.63±5.75 | 1.63(nd-12.36) | 0.02 | 0.06 |
| PETeDA | 2.48±0.84 | 2.81(1.53-3.12) | 1.91±4.21 | nd(nd-9.43) | 0.04 | 0.12 |
| PFPeA | 2.7±4.68 | nd(nd-8.10) | 0.31±0.70 | nd(nd-1.56) | 0.03 | 0.1 |
| PFHxA | 1.80±3.12 | nd(nd-5.41) | nd | nd | 0.03 | 0.1 |
| ∑PFCAs | 504.77±506.98 | 273.03(155.08-1086.21) | 388.49±246.02 | 325.16(66.69-714.06) |  |  |
| PFOS | 398.03±292.53 | 274.54(187.49-732.05) | 16.13±23.52\* | 6.48(0.62-57.78) | 0.05 | 0.15 |
| PFHxS | 1.46±2.53 | nd(nd-4.38) | 2.77±2.60 | 2.85(nd-6.64) | 0.01 | 0.03 |
| PFBS | nd | nd | nd | nd | 0.01 | 0.03 |
| PFDS | nd | nd | nd | nd | 0.02 | 0.06 |
| ∑PFSAs | 399.49±290.96 | 274.54(191.87-732.05) | 18.90±25.77\* | 10.01(0.62-64.41) |  |  |
| ∑PFAS | 904.26±433.12 | 1005.08(429.62-1278.07) | 407.40±246.37\* | 389.57(67.31-722.60) |  |  |

\* represents statistically difference at p < 0.05 between juvenile and adult gull group. “nd” means not detected.

**Table S7** The explanation of Variance Explained (%) with the increase of the number of principal components

|  |  |
| --- | --- |
| No | Eigen |
| Eigenvalue | Variance Explained (%) | Cumulation of Variance Explained (%) |
| 1 | 5.06 | 36.15 | 36.15 |
| 2 | 3.77 | 26.95 | 63.11 |
| 3 | 1.40 | 9.97 | 73.08 |
| 4 | 1.05 | 7.49 | 80.57 |
| 5 | 0.96 | 6.87 | 87.44 |
| 6 | 0.82 | 5.87 | 93.31 |
| 7 | 0.54 | 3.86 | 97.17 |
| 8 | 0.24 | 1.70 | 98.87 |
| 9 | 0.09 | 0.62 | 99.48 |
| 10 | 0.04 | 0.30 | 99.79 |
| 11 | 0.02 | 0.13 | 99.92 |
| 12 | 0.01 | 0.08 | 100 |
| 13 | 0.00 | 0.00 | 100 |
| 14 | 0.00 | 0.00 | 100 |

**Table S8**. Concentrations of PFAS in gull chest muscle, clamworm, bivalve, shrimp and sediment sample.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| ng/g ww | Gull chest muscle(n=8) | Clamworm(n=5) | Bivalve(n=5) | Shrimp(n=6) | Sediment(n=9) | LOD | LOQ |
| Mean±SD | Median(range) | Mean±SD | Median(range) | Mean±SD | Median(range) | Mean±SD | Median(range) | Mean±SD | Median(range) |
| PFOA | 177.89±216.92 | 163.97(11.82-677.44) | 71.86±39.10 | 82.59(30.97-117.04) | 22.42±11.25 | 21.60(8.2-37.25) | 1.91±1.61 | 1.11(0.47-4.23) | 0.92±0.00 | 0.34(0.05-4.84) | 0.02 | 0.06 |
| PFBA | 171.52±184.48 | 127.40(nd-517.70) | 20.09±18.24 | 13.24(4.14-46.05) | 1.83±2.46 | 0.53(nd-5.68) | 0.85±1.43 | 0.21(nd-3.65) | 0.27±0.04 | 0.22(0-0.79) | 0.01 | 0.03 |
| PFUNDA | 32.31±48.33 | 6.09(nd-134.75) | 0.35±0.57 | 0.09(nd-1.34) | 0.61±0.37 | 0.51(0.50-1.20) | 1.86±1.02 | 2.31(nd-2.73) | nd | nd | 0.03 | 0.09 |
| PFDA | 19.55±29.42 | 4.33(nd-82.32) | 0.38±0.65 | nd(nd-1.5) | 0.80±0.62 | 0.74(nd-1.47) | 0.62±0.28 | 0.67(0.09-0.89) | nd | nd(nd-0.01) | 0.01 | 0.03 |
| PFNA | 10.96±12.35 | 5.52(1.08-34.17) | 1.39±0.93 | 1.98(0.2-2.18) | 1.15±0.92 | 1.50(nd-2.21) | 1.54±0.73 | 1.64(0.42-2.41) | nd | nd(nd-0.05) | 0.03 | 0.1 |
| PFDODA | 9.80±11.86 | 5.94(nd-31.60) | nd | nd(nd-0.12) | nd | nd | 0.38±0.24 | 0.45(0-0.64) | nd | nd(nd-0.08) | 0.04 | 0.12 |
| PFHPA | 6.06±9.16 | 0.81(nd-25.33) | 1.69±2.02 | 0.83(nd-5.14) | 0.13±0.11 | 0.10(nd-0.27) | nd | nd | nd | nd | 0.02 | 0.06 |
| PETeDA | 2.13±3.22 | 0.82(0-9.43) | nd | nd | nd | nd | nd | nd | nd | nd | 0.04 | 0.12 |
| PFPeA | 1.21±2.84 | 0(0-8.10) | 3.18±2.46 | 1.82(1.31-7.16) | nd | nd | nd | nd | nd | nd | 0.03 | 0.1 |
| PFHxA | 0.68±1.91 | 0(0-5.41) | 2.35±3.28 | nd(nd-6.77) | nd | nd | nd | nd | nd | nd(nd-0.18) | 0.03 | 0.1 |
| **∑PFCAs** | **432.10±334.13** | **313.89(66.69-1086.21)** | **101.32±62.53** | **100.68(36.94-184.34)** | **26.94±10.61** | **26.40(14.28-41.77)** | **7.15±0.97** | **7.35(6.04-8.39)** | **1.22±0.03** | **0.82(0.05-5.12)** |  |  |
| PFOS | 159.34±252.65 | 33.94(0.62-57.78) | 0.87±0.33 | 0.84(0.58-1.42) | 0.51±0.40 | 0.25(0.21-1.02) | 1.90±0.70 | 1.86(0.87-2.81) | 0.44±0.00 | nd(nd-3.98) | 0.05 | 0.15 |
| PFHxS | 2.28±2.48 | 1.83(0-6.64) | 1.03±1.02 | 0.525(nd-2.14) | 0.04±0.07 | 0.02(nd-0.16) | 0.31±0.27 | 0.29(nd-0.77) | nd | nd | 0.01 | 0.03 |
| PFBS | nd | nd | 0.01±0.02 | nd(nd-0.05) | nd | nd | 0.06±0.12 | nd(nd-0.31) | nd | nd | 0.01 | 0.03 |
| PFDS | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd(nd-0.08) | 0.02 | 0.06 |
| **∑PFSAs** | **161.62±251.72** | **37.67(0.62-274.54)** | **1.91±1.01** | **1.42(1.01-3.02)** | **0.56±0.38** | **0.37(0.24-1.02)** | **2.27±0.91** | **2.41(0.87-3.21)** | **0.45±1.32** | nd**(**nd**-3.97)** |  |  |
| **∑PFAS** | **593.72±392.95** | **486.79(67.31-1278.07)** | **103.23±62.18** | **103.71(39.92-185.76)** | **27.49±10.84** | **37.50(14.64-42.79)** | **9.42±1.33** | **10.17(7.64-10.87)** | **1.67±2.82** | **0.82(0.05-9.10)** |  |  |

“nd” means not detected.

**Table S9** Summary of studies reporting the exposure to PFAS in seabirds muscle worldwide.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Species** | **Tissue** | **PFOS** | **PFOA** | **PFAS** | **Concentration(ng/g)** | **Reference** | **Region** |
| Brown pellcan (*Pelecanus occidentalis*) | muscle | 0.8 |  | PFHxS, PFOS, PFOA, FOSA | <1.00-2.7 | Olivero-Verbel et al., (2006) | Colombia |
| Black guillemot (*Cepphus grylle*)Glaucous gull (*Larus hyperboreus*) | Liver,muscle | 13.565.8 | nd | PFHxS, PFOS, PFHxA, PFOA, PFNA, PFDcA, PFBS, PFDcS, PFUnA, PFDoA, PFTeA | n.d.-65.8 | Haukås et al., (2007) | Barents Sea east of Svalbard |
| Black-footed albatross (*Phoebastria nigripes*) | muscle | 3.92 | 0.12 | PFBS, PFHxS, PFOS, PFDS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrDA, PFTeDA, PFHxDA, PFODA, PFEtCHxS | n.d.-6.93 | Chu et al., (2015) | North Pacific Ocean |
| Black-tailed gull *(Larus Crassirostris*) | muscle | 1.37 | - | PFOS | 1.37 | Chen et al., (2018) | China |
| Herring gull (*Larus argentatus*)Great shearwater (*Puffinus gravis*) | muscle | 24.74 | - | PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrDA, PFTeDA, 4:2 & 6:2 & 8:2 FTS, FOSA, N–Me-FOSAA, N–Et-FOSAA, PFEtCHxS, PMPA, PFO2HxA, PEPA, PFO3OA, HFPO-DA, PFO4DA, PFO5DoDA, Nafion BP4, Nafion BP2, Nafion BP1, NVHOS | n.d.-64.1 | Robuck et al., (2021) | United States |