Supporting Information

Modeling Global-Scale Fate and Transport of Perfluorooctanoate Emitted from Direct Sources

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The supporting information of 7-pages provides additional details, namely: justification for selection of partitioning properties, a table including selected model outputs for all simulations (Table S1) and a figure showing time trends of fluxes to the Arctic (Figure S1).

Justification for selection of GloboPOP model inputs for K_{AW} and K_{OC}

We have estimated the solubility of PFO from solubility of the corresponding acid and its salts. The solubility of PFOA in water is reported to be 4.1 g L⁻¹ at 295 K (1) and 9.5 g L⁻¹ at 298 K (2). The solubilities of salts of PFOA are higher with the solubility of the potassium salt, $C_7F_{15}COOK$, reported as 14 g L⁻¹ and the solubility of the sodium salt, $C_7F_{15}COONa$, listed as approximately 275 g L⁻¹ (3) and the solubility of the ammonium salt, $C_7F_{15}COONH_4$, as 14 g L⁻¹.(4) Based on these data, we estimate the solubility of PFO in water to be 100 g L⁻¹.

Because it is an anion, the vapor pressure of PFO is assumed to be negligible. For purposes of estimating Henry's law constant, a low vapor pressure of 0.01 Pa is assumed, which results in negligible volatilization and vapor phase partitioning.

Assuming a solubility of 100 g L^{-1} and a negligible vapor pressure of 0.01 Pa for PFO, the Henry's law constant for this anion is 4.1 x 10^{-5} Pa-m³ mol⁻¹ or less, indicating that the anion has a negligible tendency to partition into the atmosphere from water. This value of the Henry's law constant corresponds to a dimensionless air/water partition coefficient, K_{AW} , of 1.7×10^{-8} (or log K_{AW} of -7.77) at 298 K. Because of limitations in the numerical algorithm used to solve the mass balance equations, the GloboPOP model does not accept values of log K_{AW} less than -6.5 as input. Therefore, the value used in the calculations is one order of magnitude higher than our estimate of K_{AW} ($10^{-7.77}$), however, in a recent modeling exercise with a similar multimedia model, Meyer et al. (5) noted that calculated results did not change for log K_{AW} below a value -6. Preliminary simulations using Globo-POP also indicated that raising the value of K_{AW} by an order of magnitude to $10^{-5.5}$ had a negligible effect on simulated PFO concentrations or fluxes. Because of the low sensitivity of this model input

parameter over the range considered, only one value for K_{AW} (10^{-6.5}) was included in the modeling exercise.

The sorption of fluorosurfactants at solid/liquid interfaces is strongly influenced by the characteristics of the solid surface, the liquid phase concentrations, the presence of additional electrolytes and the system pH.(6) Due to their amphiphilic nature, perfluorinated surfactants preferentially accumulate at soil/liquid interfaces. However, the conventional approach to characterizing the solid/liquid partitioning of chemicals is to evaluate the bulk phase concentrations, which are in equilibrium with each other. For modeling purposes, bulk phase equilibrium partitioning remains a useful concept and experimental evaluations of soil/water partition coefficients have been made.

Under typical environmental pH (e.g. pH 5 to 8), only a very small percentage of PFOA is in the protonated form meaning that sorption measurements in alkaline soils are essentially measurements of the sorptivity of the anion. In a study of APFO sorption in a pH 6.5 soil with 1.5% organic carbon, the resulting K_d values ranged between 0.10 to 0.38 L kg⁻¹ and K_{OC} values ranged between 7 and 25 L kg⁻¹.(7) In a more recent study, the sorption of APFO was investigated on four soils with pH values ranging from 5.4 to 7.8 and organic carbon ranging from 0.8 to 5.8%,(8) In this study, K_d values varied between 0.6 and 5.6 L kg⁻¹ and K_{OC} values ranged from 79 to 148 L kg⁻¹ (mean 104 L kg⁻¹). APFO is expected to fully dissociate to the anion in solution so these sorption studies reflect PFO behavior.

The only currently available measurements of the sorption of perfluorocarboxylic acids on sediment or soil are based on results from Higgins et al. (9). The authors report the K_{OC} value of PFO to be 100 L kg⁻¹ at neutral to slightly alkaline pH. This study agrees well with the

mean value of $104~L~kg^{-1}$ obtained from the experimental work for APFO. K_{OC} proved to be a more sensitive model input parameter than K_{AW} and it was thus decided to vary the value of K_{OC} for PFO through the full range of reported experimental values (i.e. between 7 and 150 L kg^{-1}) to determine the influence on model outputs. In order to directly enter the above K_{OC} data into GloboPOP it is necessary to input proxy K_{OW} values that provide the desired K_{OC} through the formula $K_{OC} = 0.41 K_{OW}$ (10).

Table S1. Summary of Model Output According to Scenario.

| Max Min Min Min 69 440 Max Min Max 69 440 Max Min 81 440 Max Min 81 480 Min Min 81 440 Min Min 43 260 Max Min 76 470 Max Min Min 47 270 Max Min Min 44 250 Min Min Min 47 270 Max Min Min 44 250 Min Max Min 44 250 Max Min Max 44 250 Max Min Max 44 250 Max | Emission Media | Emission Level | Degradation Half-life | Ϋ́ | Concentration in 2005 (pg L ⁻¹) | 2005 (pg L ⁻¹) | Doubling Time (vr) | 2005 Net Flux (t yr ⁻¹) |
|---|----------------|----------------|-----------------------|-----|---|----------------------------|---------------------|-------------------------------------|
| ry Max Min Min 69 440 Max Max Min 81 440 Max Max Min 410 410 Min Min 43 220 200 Min Max Min 43 220 Min Max Min 43 220 Max Min 43 220 Max Min 74 420 Max Min 44 220 Min Min 47 270 Min Max Min 47 270 Min Max Min 47 270 Min Max Min 47 270 Max Min Max 47 270 Min Max Min 47 270 Min Max Min 47 30 Min Max Min 47 30 < | | | | 3 | N.Polar | N.Temp | N.Polar 1975 - 2005 | into N.Polar |
| Max Min Max 60 370 Max Max Max 71 480 Min Min 81 480 Min Min 32 200 Min Max Min 43 260 Min Max Min 43 260 Max Min 43 260 Max Min 76 470 Max Min 43 260 Min Min 44 260 Min Max Min 47 270 Min Min Max 44 260 Min Max Min 47 260 Min Max Min 47 20 Max Min Max Min 47 20 Max Min Max Min 41 26 Min Max Min 41 20 Min <td< td=""><td>Multiple Entry</td><td>Max</td><td>Min</td><td>Min</td><td>69</td><td>440</td><td>9.5</td><td>10</td></td<> | Multiple Entry | Max | Min | Min | 69 | 440 | 9.5 | 10 |
| Max Min 81 480 Min Max 71 480 Min Min Max 71 410 Min Min Max 32 200 Min Max Min 43 260 Min Min Max 76 470 Max Min Min 40 250 Min Min Min 41 250 Min Min Min 44 250 Max Min Min 44 250 Max Min Min 44 250 Max Min Max 47 400 Min Max Max 47 400 Max Min Max 47 40 </td <td>31% Air</td> <td>Max</td> <td>Min</td> <td>Max</td> <td>09</td> <td>370</td> <td>50</td> <td>ာ</td> | 31% Air | Max | Min | Max | 09 | 370 | 50 | ာ |
| Min Min Min Min 36 250 Min Min Max 32 200 Min Max Min 43 260 Min Max Min 43 260 Max Min Min 76 470 Max Min Max 470 270 Min Min Max 88 510 Min Min Max 44 250 Min Max Min 47 270 Min Max Min 47 270 Min Max Min 47 250 Min Max Min 47 270 Min Max Min 47 270 Min Min Max 47 20 Min Max Min 47 20 Max Min Max 36 40 Max Min | 55% Water | Max | Max | Min | 81 | 480 | 9.3 | 11 |
| Min Min Min 36 230 Min Max 32 200 Min Max Min 22 200 Max Min 37 260 200 Max Min 76 470 430 Max Min Max 430 510 Min Min Min 44 250 Min Min Min 44 250 Min Min Min 44 250 Min Min Min 78 470 Min Min Min 76 470 Max Min Min 76 | 14% Land | Max | Max | Max | 71 | 410 | 9.3 | 10 |
| Min Min Min Max 32 200 Min Max Min 37 260 Max Min Min 76 470 Max Min Min 89 510 Max Min Min 40 250 Min Min Min 47 270 Min Min Min 44 250 Min Min Min 44 250 Min Min Min 44 250 Min Min Min 41 420 Max Min Min 47 400 Max Min | | Min | Min | Min | 36 | 230 | 8.4 | 19 |
| Min Max Min 43 260 Max Min Min 76 470 Max Min Max 430 420 Max Min Max 480 510 Min Min Max 480 520 Min Min Min 40 250 Min Max Min 47 270 Min Max Min 47 270 Max Min Min 47 270 Max Min Min 78 470 Max Min Min 47 250 Min Max Min 41 250 Min Min Min 41 420 Max Min Min 41 420 Max Min Min 41 420 Max Min Min 41 420 Min Min Min | | Min | Min | Max | 32 | 200 | 4.8 | 17 |
| Min Max AT 220 Max Min Max 470 470 Max Min Max 430 470 Max Min Min 44 250 Min Min Min 47 270 Min Min Min 47 270 Max Min Min 47 250 Min Min Min 47 250 Min Min Min 47 250 Min Min Min 41 40 Max Min Min 41 250 Min Min Min 41 40 Max Min Min 41 | | Min | Max | Min | 43 | 260 | 8.1 | 21 |
| Max Min Min Min 470 Max Min Max 430 Max Min Min 480 510 Min Min Min 44 250 Min Min Min 44 250 Min Min Min 44 250 Max Min Min 47 270 Max Min Min 47 250 Min Min Min 47 250 Min Min Min 47 250 Min Min Min 47 250 Max Min Min 47 260 Max Min Min 47 30 Max Min Min 47 30 Min Min Min 47 30 Min Min Min 47 30 Min Min Min 47 | | Min | Max | Max | 37 | 220 | 8.1 | 19 |
| Max Min Max 71 430 Max Max 71 430 Max Max 89 510 Min Min 480 510 Min Min 40 250 Min Max Min 47 270 Max Min 44 250 Max Min 78 420 Max Min 78 470 Min Max 67 400 Min Max 67 400 Min Max 36 190 Min Max 36 190 Max Min 41 250 Max Min Max 47 Max Min Max 47 Max Min Max 47 Max Min Max 47 Max Max 47 470 Max Max | 100% Air | Max | Min | Min | 92 | 470 | 9.7 | 21 |
| Max Min 89 510 Max Max 83 480 Min Min Min 40 250 Min Min Min 47 270 Min Min Min 47 270 Max Min Max 44 250 Max Min Max 57 360 Max Min Max 67 420 Max Min Max 67 470 Min Min Min 41 250 Min Max Min 41 250 Max Min Min 76 470 Min Min Min 47 340 Min Min Min 47 340 < | | Max | Min | Max | 71 | 430 | 9.7 | 19 |
| Min Min Min Min 40 250 Min Min Max 38 230 Min Min 47 270 Min Max 44 250 Max Min 47 270 Max Min 65 420 Max Min 78 470 Min Max 67 400 Min Min 41 250 Min Min 41 250 Min Max 35 210 Min Max 36 40 Max Min 47 30 Max Min 76 47 Max Min 76 47 Min Max 76 47 Min Max 76 47 Min Max 76 47 Min Max 77 47 Min Max | | Max | Max | Min | 89 | 510 | 9.5 | 22 |
| Min Min Min 40 250 Min Max 38 230 Min Max Min 47 270 Min Max Min 47 270 Max Min 65 420 Max Min 78 470 Min Min 78 470 Min Min 41 250 Min Min 41 250 Min Max 35 210 Max Min 41 250 Max Min 47 300 Max Min Max 47 470 Max Min Max 47 470 Min Max Min 40 250 <t< td=""><td></td><td>Max</td><td>Max</td><td>Max</td><td>83</td><td>480</td><td>9.5</td><td>21</td></t<> | | Max | Max | Max | 83 | 480 | 9.5 | 21 |
| Min Min Max 38 230 Min Max Min 47 270 Min Min Min 47 270 Max Min Min 65 420 Max Min Max 57 360 Min Min Min 400 400 Min Min Max 36 230 Min Min Max 36 210 Max Min Max 36 210 Max Min 64 420 Max Min Max 47 300 Max Min Max 57 340 Min Min Max 57 340 Min Min Max 57 340 Min Max 40 250 Min Max 36 160 Min Max 57 340 Min | | Min | Min | Min | 40 | 250 | 8.7 | 1 |
| Min Max Min 47 270 In Max Min 47 250 In Max Min 65 420 Max Min Min 78 470 Min Min Min 47 400 Min Min Min 41 250 Min Min Min 41 250 Max Min Min 47 30 Min Min Max 47 30 Min Min Max 47 470 Min Min Max 57 340 Min Max Min 40 250 Min Max Min 40 250 Min Max Min | | Min | Min | Max | 38 | 230 | 8.7 | 10 |
| r Max Max 44 250 r Max Min Min 65 420 Max Min Max 57 360 Min Max Min 78 470 Min Min Max 470 400 Min Min Min 41 250 Min Max Min 47 250 Max Min Max 47 300 Max Min Max 47 300 Min Max Max 47 340 Min Min Max 47 340 Min Min Max 47 340 Min Min Max Max 47 340 Min Max Min 47 340 360 Min Max Min 40 250 Min Max Min 40 250 | | Min | Max | Min | 47 | 270 | 8.4 | 12 |
| r Max 65 420 Max Min Max 57 360 Max Max Min 470 400 Min Min Min Min 41 230 Min Max Min 41 250 Min Max Min 47 300 Max Min Min 76 470 Max Min Min 76 470 Min Min Max 57 340 Min Min Max 57 340 Min Min Max 40 250 Min Max Min 40 250 Min Max Max 40 250 Min Max Max 40 250 | | Min | Max | Max | 4 | 250 | 8.4 | 17 |
| Max Min Max 57 360 Max Max Min 78 470 Min Min Min 470 400 Min Min Min 41 250 Min Min Min 47 250 Max Min Min 47 300 Max Min Min 76 470 Min Min Min 34 220 Min Min Min 40 250 Min Min Min 40 250 Min Max Min 40 250 Min Max Min 40 250 Min Max Max 40 250 | 100% Water | Max | Min | Min | 65 | 420 | 9.4 | 19 |
| Max Min 78 470 Min Min Min 470 Min Min Min 400 Min Min Min 41 250 Min Min Min 47 250 Max Min Min 64 420 Max Min Min 76 470 Min Min Min 34 220 Min Min Min 40 250 Min Max Min 40 250 Min Max Min 40 250 Min Max Max 180 | | Max | Min | Max | 22 | 360 | 9.5 | 16 |
| Min Min Min 35 230 Min Min Max 30 190 Min Max Min 41 250 Min Min Min 64 420 Max Min Min 76 470 Max Max Min 76 470 Min Min Min 34 220 Min Min Min 40 250 Min Max Max Max 180 | | Max | Max | Min | 78 | 470 | 9.2 | 21 |
| Min Min Min 35 230 Min Max 30 190 Min Max Min 41 250 Max Min Min 64 420 Max Min Max 47 300 Max Max Min 76 470 Min Min Min 34 220 Min Min Min 40 250 Min Max Min 40 250 | | Мах | Max | Max | 29 | 400 | 9.2 | 18 |
| Min Min Max 30 190 Min Max Min 41 250 Min Max Min 47 250 Max Min Min 47 300 Max Min 76 470 Min Min Min 34 220 Min Min Min 40 250 Min Max Min 40 250 Min Max Max 180 | | Min | Min | Min | 35 | 230 | 8.2 | 10 |
| Min Max Min 41 250 Min Max 35 210 Max Min Min 47 300 Max Min Min 76 470 Min Min Min 34 220 Min Min Min 40 250 Min Max Min 40 250 Min Max Max 180 | | Min | Min | Max | 30 | 190 | 8.3 | თ |
| Min Max Min Min 64 420 Max Min Max 47 300 Max Min 76 470 Min Min Min 34 220 Min Min Min 40 250 Min Max Max Max 180 | | Min | Max | Min | 41 | 250 | 8.0 | 11 |
| Max Min Min 64 420 Max Min Max 47 300 Max Max 76 470 Min Min Min 34 220 Min Min Max 25 160 Min Max Min 40 250 Min Max Max 180 | | Min | Max | Max | 35 | 210 | 8.0 | 10 |
| Min Max 47 300 Max Min 76 470 Max Max 57 340 Min Max 25 160 Max Max 30 180 | 100% Land | Max | Min | Min | 64 | 420 | 9.4 | 19 |
| Max Min 76 470 Max Max 57 340 Min Min 34 220 Min Max 25 160 Max Max 30 180 | | Max | Min | Max | 47 | 300 | 9.1 | 41 |
| Max Max 57 340 Min Min 34 220 Max Min 40 250 Max Max 30 180 | | Max | Max | Min | 92 | 470 | 9.1 | 21 |
| Min Min 34 220 Min Max 25 160 Max Min 40 250 Max Max 30 180 | | Мах | Max | Max | 25 | 340 | 8.8 | 16 |
| Min Max 25 160 Max Min 40 250 Max Max 30 180 | | Min | Min | Min | 34 | 220 | 8.2 | 10 |
| Max Min 40 250 Max Max 30 180 | | Min | Min | Max | 25 | 160 | 7.7 | ω |
| Max 30 180 | | Min | Max | Min | 40 | 250 | 7.9 | 11 |
| | | Min | Max | Max | 30 | 180 | 7.5 | 0 |

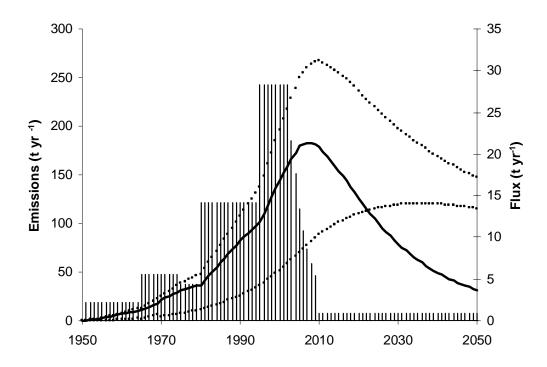


Figure S1. Illustrative time trend of modeled fluxes of PFO in and out of the Northern Polar zone in relation to emission estimates. The selected modeling scenario assumes maximum historical emission levels, a mixed mode of entry, negligible degradation (i.e. maximum half-life), and a minimum value of $K_{\rm OC}$. Vertical bars represent annual emissions, the solid line represents the net annual flux to the Northern Polar zone and dotted lines represent annual fluxes in and out of the Northern Polar zone.

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