

Supporting Information

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

James Armitage,[†] Ian T. Cousins,^{†*} Robert C. Buck,[‡] Konstantinos Prevedouros,[†] Mark H.

Russell,[‡] Matthew MacLeod,[§] and Stephen H. Korzeniowski[‡]

[†] Department of Applied Environmental Science, Stockholm University, SE-10691 Stockholm,
Sweden

[‡] E. I. du Pont de Nemours & Co., Inc., P.O. Box 80023, Wilmington, Delaware, U.S.A. 19805

[§] Institute for Chemical and Bioengineering, Swiss Federal Institute of Technology, ETH Zurich,
HCI G129, CH-8093 Zürich, Switzerland.

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, $\text{C}_7\text{F}_{15}\text{COOK}$, reported as 14 g L^{-1} and the solubility of the sodium salt, $\text{C}_7\text{F}_{15}\text{COONa}$, listed as approximately 275 g L^{-1} (3) and the solubility of the ammonium salt, $\text{C}_7\text{F}_{15}\text{COONH}_4$, 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 $4.1 \times 10^{-5} \text{ Pa-m}^3 \text{ mol}^{-1}$ 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 $K_{OC} = 0.41K_{OW}$ (10).

Table S1. Summary of Model Output According to Scenario.

Emission Media	Emission Level	Degradation Half-life	K _{oc}	Concentration in 2005 (pg L ⁻¹) N.Polar	N.Temp	Doubling Time (yr) N.Polar 1975 - 2005	2005 Net Flux (t yr ⁻¹) into N.Polar
Multiple Entry 31% Air 55% Water 14% Land	Max	Min	Min	69	440	9.5	10
	Max	Min	Max	60	370	9.5	9
	Max	Max	Min	81	480	9.3	11
	Max	Max	Max	71	410	9.3	10
100% Air	Min	Min	Min	36	230	8.4	19
	Min	Min	Max	32	200	8.4	17
	Min	Max	Min	43	260	8.1	21
	Min	Max	Max	37	220	8.1	19
	Max	Min	Min	76	470	9.7	21
	Max	Min	Max	71	430	9.7	19
	Max	Max	Min	89	510	9.5	22
	Max	Max	Max	83	480	9.5	21
100% Water	Min	Min	Min	40	250	8.7	11
	Min	Min	Max	38	230	8.7	10
	Min	Max	Min	47	270	8.4	12
	Min	Max	Max	44	250	8.4	11
	Max	Min	Min	65	420	9.4	19
	Max	Min	Max	57	360	9.5	16
	Max	Max	Min	78	470	9.2	21
	Max	Max	Max	67	400	9.2	18
100% Land	Min	Min	Min	35	230	8.2	10
	Min	Min	Max	30	190	8.3	9
	Min	Max	Min	41	250	8.0	11
	Min	Max	Max	35	210	8.0	10
	Max	Min	Min	64	420	9.4	19
	Max	Min	Max	47	300	9.1	14
	Max	Max	Min	76	470	9.1	21
	Max	Max	Max	57	340	8.8	16
	Min	Min	Min	34	220	8.2	10
	Min	Min	Max	25	160	7.7	8
	Min	Max	Min	40	250	7.9	11
	Min	Max	Max	30	180	7.5	9

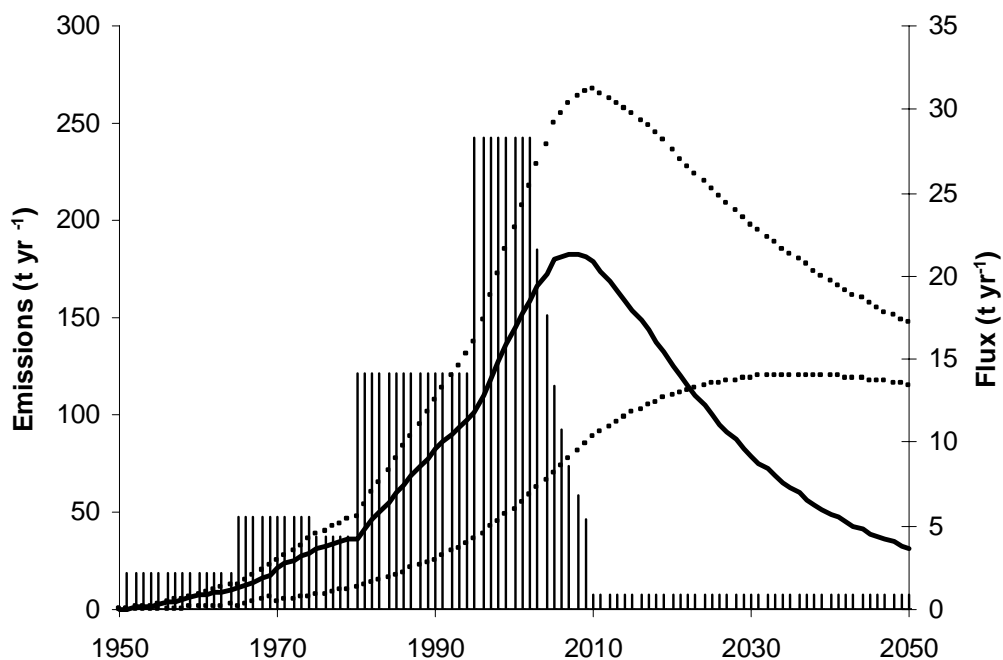


Figure S1. Illustrative time trend of modeled fluxes of PFO in and out of the Northern Polar zone in relation to emission estimates. The selected modeling scenario assumes maximum historical emission levels, a mixed mode of entry, negligible degradation (i.e. maximum half-life), and a minimum value of K_{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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