

MODELING THE LONG-TERM FATE AND TRANSPORT OF PFO(A) EMITTED FROM DIRECT SOURCES USING A TWO-DIMENSIONAL GLOBAL-SCALE MODEL

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Introduction

Perfluorocarboxylates (PFCAs) are widely distributed in the global environment and are currently of significant scientific and regulatory interest. Besides direct emissions of these substances from their production and use (“direct sources”)¹, it is now well-established that precursor compounds such as fluorotelomer alcohols (FTOHs) and POSF-based chemicals (e.g. perfluorooctyl sulfonamidoethanols (FOSEs)) degrade in the environment to yield appreciable quantities of PFCAs across a range of chain-lengths (“indirect sources”)². While atmospheric transport and degradation of precursor substances provides a rapid mechanism for distributing PFCAs to remote locations, the contribution of oceanic transport to the contamination of marine environments in remote areas (e.g. the Arctic) is often underappreciated.

The eight-carbon homologue, PFO(A), is the most frequently detected PFCA in the abiotic environment and is therefore an appropriate compound to model since comparisons between predictions and observations can be made more readily than for other PFCAs. In this study, the long-term fate (1950 – 2010) of PFO(A) was simulated using a spatially-resolved multimedia environmental fate model and then the results were evaluated against available data.

Materials and methods

All simulations were conducted using BETR-Global, a two-dimensional environmental fate model which divides the globe into 288 boxes based on a 15 x 15° grid (see Figure 1). Emission estimates from 1950 – 2010 were based on Prevedouros et al.¹ and considered emissions from fluoropolymer (FP) manufacturing facilities and APFO manufacturing facilities only. The locations of these facilities were based on Prevedouros et al.¹ and Will et al.³ and correspond to zones 78 – 80, 60 – 62, 64, 85, 92 – 94 and 114 – 116 (see Figure 1). Emissions from FP facilities were assumed to occur 65% to freshwater, 23% to air and 12% to land while emissions from APFO facilities were assumed to occur 95% to freshwater and 5% to air. Total emissions of PFO(A) over the simulation period (1950 – 2010) were estimated to be approximately 2600 – 5100 metric tons (min/max). The main simulations were conducted under the assumption that the behaviour of this compound in the environment can be described using the physical-chemical properties of the anionic form only. Additional simulations were conducted using a multi-species version of the model (accounts for both neutral and ionized form) assuming pK_a values of 3.5, 1.5 and -0.5. Physical-chemical property values for both the neutral and anionic form of this compound are summarized in Table 1. As in Armitage et al.⁴, the anionic form (PFO⁻) was assigned a negligible value for log K_{AW} (representing a non-volatile compound) and a log K_{OW} that yielded a log K_{OC} consistent with reported measurements through the algorithm relating K_{OW} to K_{OC} (i.e. K_{OC} = 0.41 K_{OW}).

Results and discussion

Predicted concentrations in global surface oceans for the year 2005 are presented in Figure 2 while a comparison between predicted and observed values^{5,6} is provided in Table 2. Qualitatively, the observations and predictions are in good agreement. For example, the limited dispersion of this compound to the Southern Hemisphere is well-represented. Concentrations in the Pacific Ocean close to Asia (e.g. offshore Japan, South China Sea) are substantially higher than concentrations in the Pacific Ocean close to the western US (at least at the latitudes sampled^{5,6}). Interestingly, the model predicts that high concentrations of PFO(A) are present in the northern Pacific (above 45 °N). Unfortunately, no sampling has been conducted in this area despite the obvious importance of these ocean waters in terms of transport into the Arctic via the Bering Strait. Quantitatively, the predicted values are acceptable and do not

systematically over- or underpredict the observations presented here. There is good agreement overall between predictions and observations in the North Atlantic which suggests that the predicted distribution of PFO(A) into the Arctic zone from this region is reasonable.

Predicted concentrations in the surface ocean compartments were relatively insensitive to assumptions regarding pKa in the multi-species model simulations (considering the pKa range spans 4 orders of magnitude). Concentrations in the Arctic zones (1 – 24) are approximately 1.3 – 1.6 times higher (on average) when assuming pKa of 3.5 in comparison to pKa of -0.5. The main reason for the higher concentrations when pKa = 3.5 is that atmospheric long-range transport of PFO(A) adds a significant gross deposition flux to the Arctic zones (3000 kg yr⁻¹ to zones 1 – 24 in 2005). However, with a pKa of 3.5, over 99% of the mass of PFO(A) in the atmosphere is in the gaseous phase (as neutral PFOA, not associated with aerosols) and deposition is dominated by gaseous absorption (as opposed to precipitation or dry deposition). This behaviour profile seems unlikely, given available monitoring data which suggests that PFO(A) is almost exclusively aerosol-bound in the environment⁷. Another confounding factor is the observation⁸ that other highly fluorinated compounds (e.g. FTOHs and FOSEs) appear to exhibit far more extensive sorption to aerosols than would be predicted from the standard algorithm based on K_{OA} (which is utilized by BETR-Global). If this enhanced sorption behaviour is also true of neutral PFOA then the BETR-Global models need to be modified to better account for this discrepancy. Although ocean-transport of PFO(A) emitted from direct sources is still the main pathway for the dispersion of this compound in the marine environment regardless, the multi-species simulations suggest a substantial atmospheric transport potential, given certain assumptions regarding pKa and aerosol-air partitioning. It is therefore critical to have reliable measurements of both of these properties before making any further conclusions regarding the behaviour of this compound in the environment.

Acknowledgements

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References

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Table 1. Physical-chemical properties adopted for simulations.

Property	PFOA	PFO-
log K _{OW}	4.3	(2.6)
log K _{AW}	-2.4	(neg)
log K _{OC}	3.5	2.2
Degradation rate constant	(neg)	(neg)

Table 2. Comparison of measured^{4,5} and predicted concentrations in surface ocean compartment

Sampling Location (as defined in study)	Year	Measured (pg L ⁻¹)	ZONE (see Fig.1)	Predicted (pg L ⁻¹)
North Atlantic	2003	52 - 338	57	80
			58 - 60	105 - 130
Mid-Atlantic	2002	67 - 439	129 - 131	15 - 30
			104	75
Offshore US East Coast	2002	-	79 - 80	285 - 370
Offshore Japan	2002	137 - 1060	92 - 94	140 - 310
Central to Western Pacific	2002	136 - 142 15 - 62	97 - 100	25 - 50
			121 - 125	10 - 20
			150 - 151	0.3 - 0.6
			171 - 175	0.1 - 0.7
South Pacific Ocean	2004	< 20	217	1
			264	0.5
South China Sea	2004	160 - 420	116 - 117	65 - 100
			140 - 141	20 - 40
Indian Ocean	2006	< 20	188	26
			236	0.5
Offshore Angola	2004	< 20	157	2

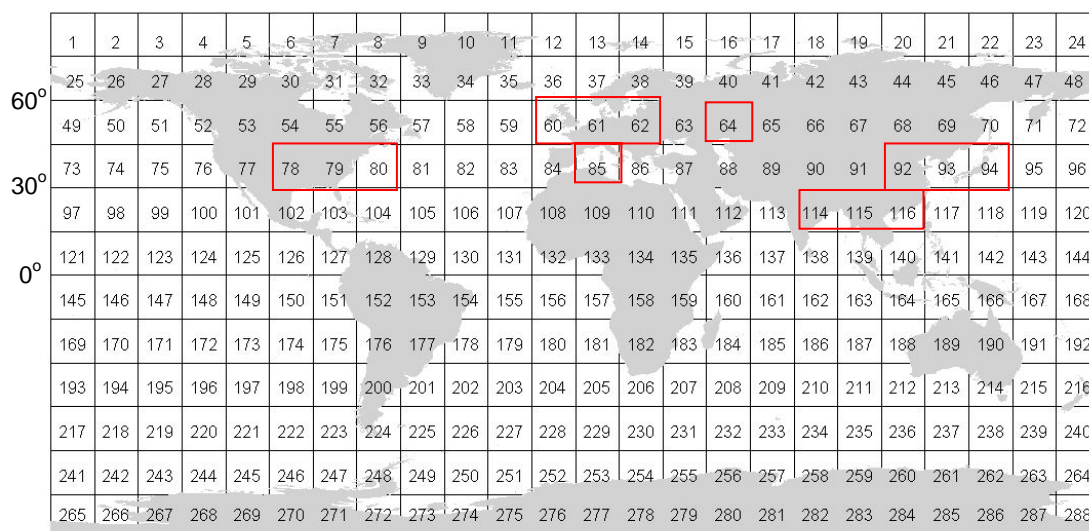


Figure 1. BETR-Global spatial resolution (288 zones, 15 x 15°). Zones with direct sources are indicated by red.

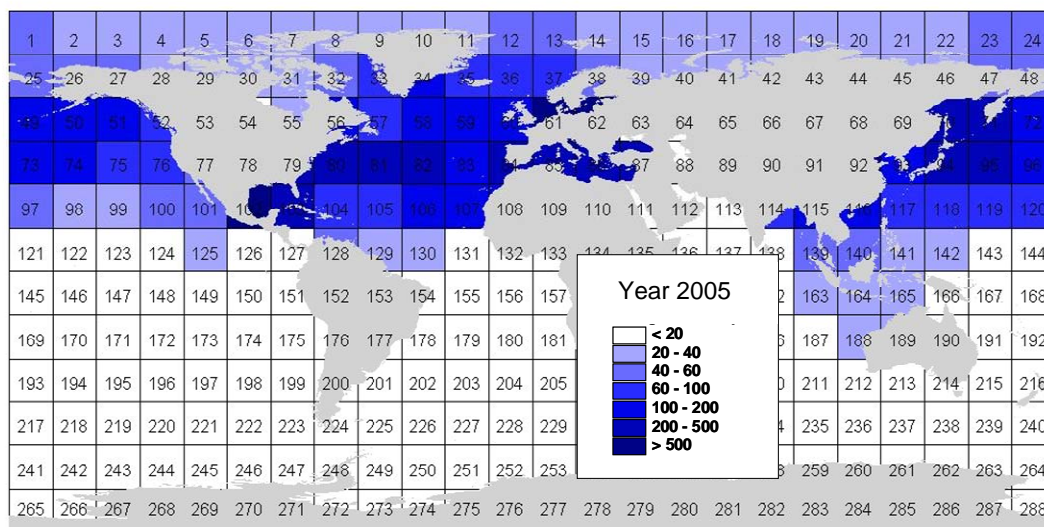


Figure 2. Predicted concentrations (pg L^{-1}) in 2005 assuming maximum emission scenario. Predicted concentrations assuming minimum emission scenario are approximately two times lower.