

## Mass balance investigation of Perfluorooctanoic Acid (PFOA) environmental levels, emissions and sinks in the Northern Hemisphere

Ian T Cousins<sup>1</sup>, Konstantinos Prevedouros<sup>1</sup>, Robert C Buck<sup>2</sup>, Stephen H Korzeniowski<sup>2</sup>

<sup>1</sup>Stockholm University

<sup>2</sup>DuPont Chemical Solutions Enterprise

### Introduction

Perfluoroalkyl sulfonic acids (PFASs), perfluoroalkyl carboxylic acids (PFCAs) and their potential precursors are of increasing scientific and regulatory interest because they have been found to occur globally in a wide array of environmental samples including biota<sup>1-3</sup>. Both PFAS and PFCAs are considered to be highly persistent with no known degradation mechanisms, whilst some homologues possess bioaccumulation potential<sup>4,5</sup>. As a result, perfluorooctyl sulfonyl (POSF) products were recently phased out by their largest global producer. In addition, perfluorooctanoic acid (PFOA) is the subject of preliminary risk assessment by the US Environmental Protection Agency<sup>6,7</sup>.

PFCAs have been used for over fifty years as processing aids in the manufacture of fluoropolymers; various PFASs and fluorotelomer products have been used in metal plating and cleaning, coating formulations, fire-fighting foams, inks, vinyl polymerization, lubricants, gasoline, and as oil and water repellents for leather, paper and textiles<sup>8</sup>. To date, neither the sources of PFOA in the environment nor its overall fate and transport properties are well understood or described. This paper provides the first detailed account of direct and indirect sources of PFOA in the environment. Further, an estimation of the continental production, use and emissions from 1950-2000 will be reported. A mass balance investigation between sources and amounts currently residing in the Northern Hemisphere environment has been performed as well as an estimation of the magnitude of historical removal processes. Finally, future areas of research are proposed and inferences on different pathways of long-range chemical transport are given.

### Materials and methods

Throughout the calculations that follow, it was hypothesized that the overwhelming majority of historical PFOA production, use and emissions occurred in the Northern Hemisphere. This assumption is deemed valid since only minor uses (e.g. mining) occurred in the Southern Hemisphere and atmospheric and aquatic mass exchange between the two Hemispheres is generally considered limited. The first part of the study involved the estimation of production, use and emissions of PFOA from a variety of direct (manufacturing, industrial and consumer uses) and indirect sources. Indirect sources refer to the chemical being present as reaction impurity or where a different substance/mixture may degrade to give PFOA. Figure 1 presents the PFCA/PFOA sources for which a comprehensive examination has been undertaken. Production and emissions were calculated from a number of previously unpublished as well as published chemical industry data that have very recently become available. All estimated values were provided as ranges to account for the uncertainty in production, use and emission values over time.

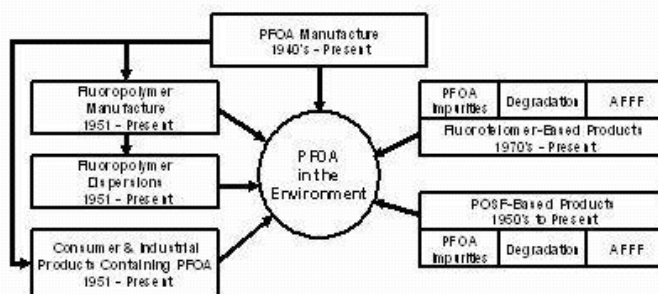


Figure 1. Potential PFOA sources into the Northern Hemisphere environment

Secondly, a mass balance computation was performed, following similar approaches to those of Axelman and Broman and Jönsson et al. who attempted an environmental accounting of polychlorinated biphenyl (PCB) distribution in the Northern Hemisphere environment and global shelf sediments, respectively<sup>9,10</sup>. The current investigation will compare estimated historical PFOA emissions with existing environmental levels and historical losses. A comprehensive literature search was performed to estimate representative PFOA levels in sediments, water (fresh-, coastal-, open ocean- ground- tap- and rain-) and biota. 10% and 90% concentration percentiles were calculated in order to account for the uncertainty/variability in environmental levels. Historical losses through degradation were assumed minimal, whilst the influence of sedimentation to deep sea, physical mixing of surface with deep ocean water, burial in soils and burial in freshwater and continental shelf sediments was comprehensively addressed. These loss processes were evaluated by knowledge of continental inventories, compartmental residence times and physical parameters such as sedimentation rates, particle deposition fluxes, sediment mixing depths, etc. In all cases, maximum and minimum ranges were quantified, whilst an average of 50 years was assumed to represent the historical use period.

## Results and discussion

The following table presents the results of the mass balance study. It was estimated that approximately 3,000-10,000 tonnes of PFOA have historically been released to the Northern Hemisphere environment as a result of the direct and indirect sources described above. Table 1 also reveals that 75-90% of the current PFOA environmental inventory is predicted to reside in the water, with an additional 10-25% bound to sediments. The influence of soils and biota as a sink/reservoir of this chemical was shown to be very small and was excluded from further calculations. The mass balance investigation also highlights close agreement between estimated sources and sinks of PFOA.

**Table 1. Estimated PFOA emissions, environmental distribution and sinks**

	MIN	MAX	Distribution Range
<b>Estimated emissions (t)</b>	3000	10000	
<b>Environmental presence (t)</b>			
Marine environment	250	12000	45-60%
Freshwater environment	150	5500	25-30%
Marine sediments	130	1400	5-25%%
Freshwater sediments	10	70	1-2%
<b>Historical losses (t)</b>			
Environmental degradation	0	0	
Physical sedimentation	70	600	
Physical water mixing	10	1200	
Sediment burial	70	2300	
<b>TOTAL PRESENT (t)</b>	<b>700</b>	<b>23000</b>	

Considering PFOA has been emitted for more than 50 years and has been shown to mainly reside in water, chemical transport through the horizontal movement of water from temporal latitudes to remote environments may be very important and previously underestimated. For this reason, travel distances in river and open ocean waters were calculated using estimated sediment and water residence times, sediment inventory and average water flows. PFOA travel distances were calculated to be on the order of  $10^5$  to  $10^6$  km. Furthermore, the chemical amount that can be aquatically transported was computed as the result of a mean open ocean concentration and the total flow of water entering the Arctic surface ocean<sup>11,12</sup>. This amount was approximately 30-50 tonnes per year that is significantly higher to the respective number that may be delivered to the Arctic from Northern Hemisphere fluorotelomer alcohol degradation and subsequent atmospheric deposition<sup>13</sup>. This implies that atmospheric transport of (only one of the many possible) PFCA atmospheric precursor chemicals may be smaller than physical, aquatic transport.

## Conclusions

The vast majority of PFCAs, including PFOA, are released to the environment from fluoropolymer manufacture; indirect sources of PFOA are minor compared to emissions from fluoropolymers. There are still large uncertainties associated with the estimates of indirect emissions especially those originating from product impurities or degradation of products to form PFOA. A large proportion of PFOA was estimated to be emitted direct to water (>70%) with smaller amounts emitted to land and air. The mass balance study also confirmed the importance of the surface water compartments for PFOA storage and advocated more measurements in a vertical gradient within the water-mixing layer but also in deeper ocean depths. Important sink processes included physical mixing and sedimentation to the deep oceans and sediment burial. It is encouraging that the max/min ranges of the sum of the total environmental inventory and historical sink processes overlap the max/min ranges of the emission estimates. These inventory and mass balance estimates are subject to large uncertainties, but as more measurements are published these uncertainties may diminish. Finally, a quantitative comparison of the atmospheric transport of PFOA precursors and the aquatic transport of the substance itself suggest that ocean transport is the most important transport route.

## Acknowledgements

The authors would like to thank PERFORCE, a research project funded by the European Union, for support of this work.

**References**

1. Giesy J.P. and Kannan K. (2001) *Environ. Sci. Technol.* 35: 1339-1342.
2. Kallenborn R., Berger U., Järnberg U., Dam M., Glesne O., Hedlund B., Hirvi J.-P., Lundgren A., Mogensen B.B. and Sigurdsson A.S. (2004) *Nordic screening project report*.
3. De Silva A.O. and Mabury S.A. (2004). *Environ. Sci. Technol.* 38: 6538-6545.
4. Ellis D.A., Martin J.W., De Silva A.O., Mabury S.A., Hurley M.D., Sulbaek Andersen M.P. and Wallington T.J. (2004) *Environ. Sci. Technol.* 38: 3316-3321.
5. Martin J.W., Mabury S.A., Solomon K.R. and Muir D.C.G. (2003) *Environ. Toxicol. Chem.* 22: 196-204.
6. Renner, R. (2004) *Environ. Sci. Technol.* 38: 11A-12A.
7. United States Environmental Protection Agency Preliminary (2003) Office of Pollution Prevention and Toxics, Risk Assessment Division.
8. Holzapfel W. (1966) *Fette, Seifen, Anstrichmittel* 68: 837-842.
9. Axelman J. and Broman D. (2001) *Tellus* 53B: 235-259.
10. Jönsson A., Gustafsson Ö. Axelman, J. and Sundberg H. (2003) *Environ. Sci. Technol.* 37: 245-255.
11. Macdonald R.W., Barrie L.A., Bidleman T.F., Diamond M.L., Gregor D.J., Semkin R.G., Strachan W.M.J., Li Y.F., Wania F., Alaee M., Alexeeva L.B., Backus S.M., Bailey R., Bowers J.M., Gobeil C., Halsall C.J., Harner T., Hoff J.T., Jantunen L.M.M., Lockhart W.L., Mackay D., Muir D.C.G., Pudykiewicz J., Reimer K.J., Smith J.N., Stern G.A., Schroeder W.H., Wagemann R., Yunker M.B. (2000) *Sci. Total Environ.* 254: 93-234.
12. Aagaard K. and Carmack E.C. (1989). *J. Geophys. Res.* 94, 14485-14498 Freshwater to the Arctic
13. Ellis D.A., Martin J.W., De Silva A.O., Mabury S.A., Hurley M.D., Sulbaek Andersen M.P., Wallington T.J. (2004) *Environ. Sci. Technol.* 38: 3316-3321.