Modeling the Global Fate and Transport of Perfluoroalkylated Substances (PFAS)

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Abstract

Perfluoroalkylated substances (PFAS) are persistent contaminants that are widely distributed in the global environment. Despite the fact that these chemicals have been manufactured and used for over 50 years, there has been little scientific and regulatory interest until very recently. An important research priority over the past decade has been to gain a better understanding of the mechanisms and pathways explaining the presence of these compounds in remote regions. One explanation is related to the use and release of volatile precursor compounds which undergo atmospheric transport and are also susceptible to degradation to PFAS through gas phase reactions with radical species. The main purpose of this doctoral thesis was to investigate an alternative explanation, namely the long-range transport (LRT) of PFAS themselves, which have been released into the environment in substantial quantities during manufacturing and product use. **Papers I – III** explore the LRT potential of perfluorocarboxylic acids and perfluorocarboxylates and demonstrate that both oceanic and atmospheric transport are efficient pathways of dispersion from source to remote regions of the Northern Hemisphere. Oceanic transport of perfluorooctane sulfonate (PFOS) was shown to be an important process in **Paper IV** as well. The role of precursor transport and degradation to PFOS was also examined in this paper. The most interesting aspect of the fate and transport of PFOS precursors is the rapid response in ambient concentrations exhibited by these compounds in the model simulations following production phase-out. Since precursor compounds are known to degrade to PFOS *in vivo*, the modeling results demonstrate that this exposure pathway is a plausible explanation for the declining trends in PFOS concentrations reported for marine mammals in some remote environments.

Table of Contents

Abbreviations

ACP	Arctic Contamination Potential
AFFF	Aqueous fire-fighting foam
APFN	Ammonium perfluorononanoate
APFO	Ammonium perfluorooctanoate
BCF	Bioconcentration factor
BAF	Bioaccumulation factor
C8 – C13	Refers to the number of carbon atoms of perfluorocarboxylates
DDT	Dichloro-diphenyl-trichloroethane
ECF	Electrochemical fluorination
FP	Fluoropolymer
FTOH	Fluorotelomer alcohol
H	Henry's Law constant
K_{AW}	Air-water partition coefficient
K_{OA}	Octanol-air partition coefficient
K_{OC}	Organic carbon-water partition coefficient
K_{OW}	Octanol-water partition coefficient
K_{QA}	Aerosol-air partition coefficient
LFER	Linear free energy relationship
LRT	Long-range transport
OC	Organic carbon
PCB	Polychlorinated biphenyls
PCDD/F	Polychlorinated dibenzo-dioxins and furans
PFAS	Perfluoroalkylated substances
PFC	Perfluorocarboxylate (dissociated form)
PFCA	Perfluorocarboxylic acid (neutral form)
PFC(A)	Collective term, perfluorocarboxylic acid & perfluorocarboxylate
PFO	Perfluorooctanoate
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctyl sulfonate
pK_a	Acid dissociation constant
POSF	Perfluorooctanesulfonyl fluoride
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
R	Ideal gas constant
SVOC	Semi-volatile organic compound
US EPA	United States Environmental Protection Agency
VF	Volume fraction
xFOSA	Perfluorooctane sulfonamides (N-methyl, N-ethyl)
xFOSE	Perfluorooctane sulfonamidoethanols (N-methyl, N-ethyl)

List of Papers

This thesis is based upon the following papers, referred to in the following text by their Roman numerals.

I **Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sources**

Armitage, J.; Cousins, I.T.; Buck, R.C.; Prevedouros, K.; Russell, M.H.; MacLeod, M.; Korzeniowski, S.H. *Environ Sci. Technol.* **2006**, 40, 6969 – 6975.

II **Modeling the global fate and transport of perfluorooctanoic acid (PFOA) and perfluorooctanoate (PFO) emitted from direct sources using a multispecies mass balance model**

Armitage, J.M.; MacLeod, M.; Cousins, I.T. *Environ. Sci. Technol.* **2009**, 43, 1134 – 1140.

III **Comparative assessment of the global fate and transport pathways of long-chain perfluorocarboxylic acids (PFCAs) and perfluorocarboxylates (PFCs) emitted from direct dources**

Armitage, J.M.; MacLeod, M.; Cousins, I.T. *Environ. Sci. Technol.* (submitted)

IV **Modeling the global fate and transport of perfluorooctane sulfonate (PFOS) and precursor compounds in relation to temporal trends in wildlife biomonitoring data**

Armitage, J.M.; Schenker, U.; Scheringer, M.; Martin, J.W.; MacLeod, M.; Cousins, I.T. (manuscript)

Statement

I, James M. Armitage, made the following contributions to the papers presented here:

Paper I
I contributed to the development of model scenarios, conducted all model simulations, analyzed model output and took the lead role in authoring the paper.

Paper II
I was responsible for deriving the updated version of the surface ocean exchange matrix used for these simulations (using drift buoy data), contributed to the development of model scenarios, conducted all model simulations, analyzed model output and took the lead role in authoring the paper.

Paper III
I was responsible for deriving the spatially-explicit emission estimates for the compounds simulated here, contributed to the development of model scenarios, conducted all model simulations, analyzed model output and took the lead role in authoring the paper.

Paper IV
I contributed to the development of model scenarios used to assess the exposure hypotheses, analyzed model output and took a lead role in authoring the paper. All model simulations were conducted by Urs Schenker (ETH Zurich).

Objectives

The overall objectives of this thesis were to apply multimedia environmental fate models to perfluoroalkylated substances (PFAS) in order to i) test current hypotheses explaining the ubiquitous presence of these compounds in the global environment ii) help identify and prioritize the major uncertainties in our current understanding of the behaviour of these compounds in the environment and iii) help identify and prioritize monitoring data gaps and research questions that would provide important insights into the fate and transport of these compounds

The specific objectives of Papers I – IV were as follows:

Paper I
The main purpose of this paper was to test the hypothesis that oceanic long-range transport of perfluorooctanoate (PFO) emitted from direct sources (i.e. related to manufacturing and use) can explain the presence of this compound in the Arctic Ocean. The fate and transport of the neutral form of this compound, PFOA, was not explicitly considered here.

Paper II
The main purpose of this paper was to explore the fate and transport of perfluorooctanoatic acid (PFOA) and perfluorooctanoate (PFO) emitted from direct sources under various assumptions about the emission mode of entry, aerosol-air partitioning and acid dissociation constant (pK_a). The simulations were conducted using a model with greater spatial resolution, which allowed more explicit representation of surface ocean circulation patterns.

Paper III
The main purpose of this paper was to compare the fate and transport of perfluorocarboxylic acids (PFCAs) and perfluorocarboyxlates (PFCs) emitted from direct sources under various assumptions about emission mode of entry and pK_a. We focused on the relative behaviour of specific homologue pairs (C8 and C9, C10 and C11, C12 and C13) typically used to gain insight into the potential contribution of different exposure sources (i.e. direct versus indirect sources)

Paper IV
The main purpose of this paper was to investigate how divergent temporal trends in PFOS concentrations in marine wildlife from remote regions of the world are related to a major production phase-out which occurred over the period 2000–2002. Emission inventories for PFOS and important precursor compounds were derived and used as input to a global-scale fate and transport model. The modeled temporal trends in ambient concentrations were then compared and contrasted in the context of different exposure pathways driving PFOS body burdens in wildlife before and after the production phase-out.

Introduction

Perfluoroalkylated substance (PFAS) is the term used to describe a wide range of chemicals containing fully fluorinated carbon atoms of varying chain length (i.e. $CF_3[CF_2]_n-$) . Perfluorocarboxylic acids (PFCA; $C_nF_{2n+1}COOH$) and perfluorooctane sulfonate (PFOS; $C_8F_{17}SO_3^-$) are perhaps the most widely known examples of PFAS due to the fact that they have been measured widely in the global environment and are present at detectable concentrations in wildlife and humans in both industrialized and source regions (1–3). Although once considered biologically inactive, a range of toxicological effects have been attributed to these compounds based on recent studies using a variety of laboratory animals (4) Volatile precursor compounds such as fluorotelomer alcohols (FTOHs) and perfluorooctane sulfonyl fluoride (POSF)-based substances including perfluorosulfonamides (xFOSA) and perfluorosulfonamidoethanols (xFOSE) are also of great interest as they are known to degrade to PFCAs and PFOS under environmentally relevant conditions (5–7).

Although PFAS have been manufactured and used commercially for over five decades, scientific and regulatory interest was quite low until recently. Now that the ubiquitous presence of these compounds is recognized, researchers have been attempting to understand how PFAS have become so widely distributed in the global environment. Transport and degradation of volatile precursor compounds in the atmosphere has been suggested as the most likely explanation for the presence of PFAS in biota in remote areas such as the Arctic (e.g. see *ref* 5, 8, 9). However, the publication of a global source inventory for the perfluorocarboxylates in 2006 (10) first pointed to the potential importance of direct sources, primarily from the manufacture and use of perfluorocarboxylates (PFCs) as processing aids in the manufacture of fluoropolymers such as polytetrafluoroethene (PTFE) and polyvinylidene fluoride (PVDF). It seemed plausible that given the relatively high water solubility of PFCs, their persistence and their release to surface waters for over 50 years that long-range ocean transport could be a possible alternative transport pathway to remote marine environments like the Arctic Ocean.

Application of mass balance modeling approaches to gain further insights into the fate and transport of PFCs in the global environment became more feasible following the publication of the historic emission estimates (10). These research tools allow key fate and transport processes to be simulated in a systematic and transparent manner. Model outputs can be used to test different hypotheses regarding mechanisms and pathways driving the global dispersion of these compounds. Perhaps more importantly, major uncertainties and knowledge gaps can be identified, leading to recommendations regarding research and sampling campaigns that are most likely to yield high value data. This thesis work is comprised of four modeling studies, three regarding the fate and transport of PFC(A)s (**Paper I – III**) and one regarding the fate and transport of PFOS and its precursors (**Paper IV**). The model simulations in **Papers I – III** assess the oceanic and atmospheric LRT potential of PFC(A)s and discuss the findings in relation to relevant monitoring data. The model simulations in **Paper IV** were conducted primarily to explore the historic and future trends in PFOS exposure in the global marine environment following a major production phase-out by the largest manufacturer which occurred in 2000–2002. A brief summary of the methods and main results is presented in the following sections.

Methods

Fugacity-based Multimedia Environmental Fate Modeling. The concept of fugacity was first introduced as a criterion of equilibrium by G.N. Lewis in 1901 (11). It is based on the understanding that chemicals present in a system containing different phases (e.g. air, water, soil) will tend to be distributed such that the chemical potential is equal in all phases (i.e. the system achieves minimal Gibbs free energy). Whereas chemical potential is logarithmically related to concentration, fugacity is logarithmically related to chemical potential and thus linearly (or near linearly) related to concentration. For this reason, fugacity is much more practical for modeling the behaviour of contaminants in the environment. Fugacity is estimated as follows (12, 13).

$$f_i = \frac{C_i}{Z_i} \tag{1}$$

where f_i is the fugacity (Pa) of the chemical in phase i, C_i is the concentration (mol m^{-3}) of the chemical in phase i and Z_i is the proportionality constant, known as the fugacity capacity (mol m^{-3} Pa^{-1}) of phase i. Fugacity is often described as the 'escaping' tendency of the chemical in a given phase whereas fugacity capacity essentially represents the partitioning capacity of the phase. The net diffusive flux between two phases will always be from phases with higher fugacity to phases with lower fugacity until equifugacity is achieved and phases with high fugacity capacities will achieve a higher concentration than a phase with low fugacity capacity, given the same fugacity (since $C = fZ$). Multimedia environmental models based on the fugacity approach were first proposed by Mackay (12, 13). Typically, the environment is divided into bulk compartments representing the atmosphere (gas phase + aerosols), water (water + suspended solids + dissolved organic carbon), sediments (solids + water) and soil (solids + water + air); vegetation may also be included as an additional compartment (see Figure 1). One key assumption of fugacity-based models is that the phases within a compartment are at equifugacity. Depending on the application, the model may represent the entire system of interest as one large 'box' or subdivide it into multiple boxes, each further divided into the various compartments. Once the volume fractions (VF) of each phase in a compartment are estimated, the bulk compartment fugacity capacity is calculated as a function of the fugacity capacity of each constituent multiplied by its VF.

By definition, the fugacity capacity of pure air is calculated as:

$$Z_A = \frac{1}{RT} \tag{2}$$

where R is the ideal gas constant ($\sim$ 8.314 Pa m^3 mol^{-1}) and T is the absolute temperature in Kelvin (K). Since the ratios of fugacity capacities are equivalent to partition coefficients, e.g. the air-water partition coefficient $K_{AW} = Z_A / Z_W$, fugacity capacities for other phases can be estimated using these data. For example,

$$Z_W = \frac{Z_W}{Z_A} Z_A = \frac{Z_A}{K_{AW}} = \frac{1}{K_{AW}(RT)} = \frac{1}{H} \tag{3}$$

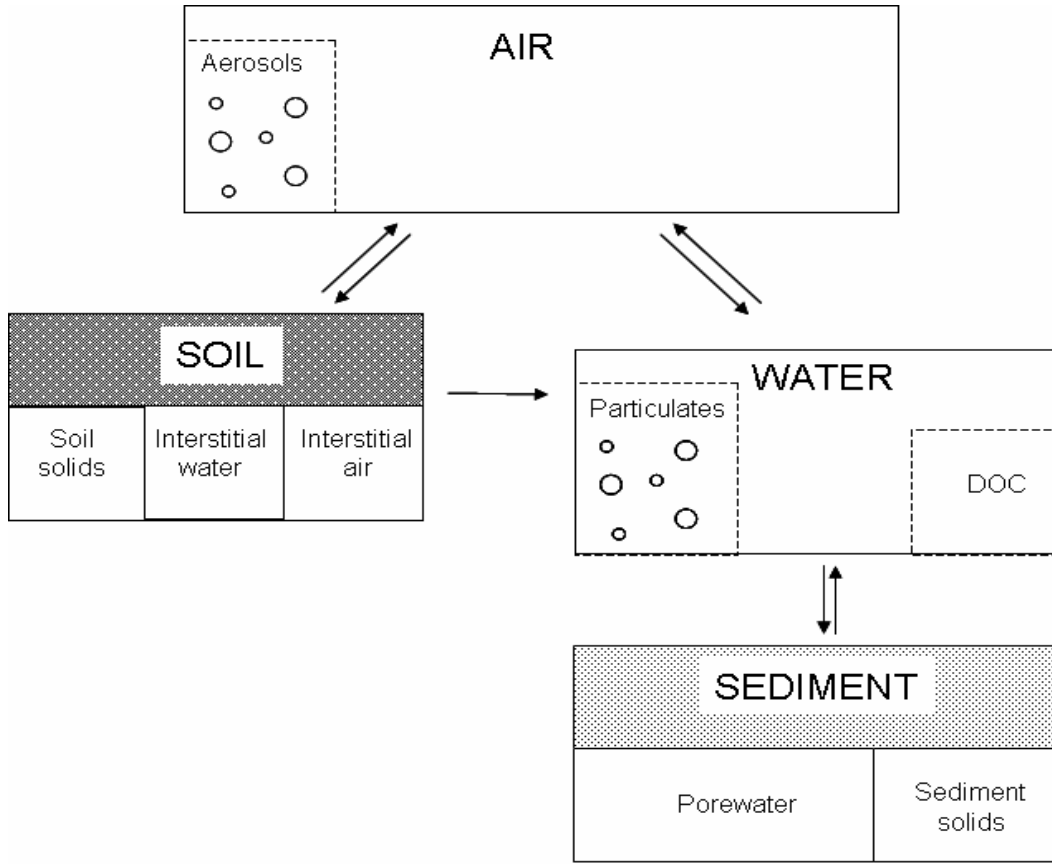where H is the Henry's Law constant (Pa m^3 mol^{-1}).

Figure 1. Typical compartmentalization of the abiotic environment assumed in fugacity-based fate models

The fugacity capacity of sediment solids (Z_S) can be estimated as:

$$Z_S = \frac{Z_S}{Z_W} Z_W = \rho_S K_{SW} Z_W = \frac{\rho_S K_{SW}}{H} \tag{4}$$

where K_{SW} is sediment solids-water partition coefficient (L kg^{-1}) and ρ_S is the density of the solids (kg L^{-1}). When available, empirical measurements of environmental partition coefficients may be used. In the absence of such data, partition coefficients for environmental phases are often estimated from the octanol-water partition coefficient (K_{OW}) or octanol-air partition coefficient (K_{OA}), since *n*-octanol has been shown to be a reasonable surrogate for both organic carbon (OC) and lipids for many organic contaminants of concern and in most cases, organic carbon and lipids are expected to be the dominant 'environmental solvent'. In the case of sediment solids, for example, K_{SW} can be estimated as:

$$K_{SW} = \delta_{OC} K_{OC} = \delta_{OC} \varphi K_{OW} \qquad (5)$$

where δ_{OC} is the average organic carbon content of the sediment solid, K_{OC} is the organic carbon-water partition coefficient, here estimated from K_{OW} and φ, a proportionality constant representing the ratio of the sorptive capacity of organic carbon to *n*-octanol. Values of φ can be quite variable but it is typically assumed to be 0.35 or 0.41 for most model applications, following *ref* 14 or *ref* 15 respectively. More recently, the limitations of this approach (a single parameter linear free energy relationship or sLFER) have been highlighted and the application of polyparameter linear free energy relationships (pp-LFERs) has been recommended (16), particularly for more polar compounds.

Having established the properties of the compartments included in the model, the remaining task is to represent processes controlling the fate of the chemical in the environment i.e. intermedia transport and degradation. Some examples of key fate processes included in these models are listed in Table 1. Both diffusive and nondiffusive transport processes are included in fugacity-based models, estimated by D values (mol Pa^{-1} h^{-1}). D values are also used to represent degradation processes and pseudo-elimination processes such as growth dilution. For diffusive processes across interfaces, D values are estimated following the two-resistance concept (17–19) and require estimated mass transfer coefficients characterizing diffusivity and then the area of exchange and the fugacity capacities of the phases considered. For example, the transport D-value for air-water diffusive exchange (D$_V$) is estimated as:

$$D_V = (\frac{1}{k_{VA} A_E Z_A} + \frac{1}{k_{VW} A_E Z_W})^{-1} \qquad (6)$$

where k$_{VA}$ is the air-side mass transfer coefficient (m h^{-1}), A$_E$ is the area of exchange (m^2) and k$_{VW}$ is the water-side mass transfer coefficient (m h^{-1}). The gross flux of chemical (N$_{i-j}$, mol h^{-1}) is then estimated by multiplying the transport D value by the appropriate fugacity. For example, air-to-water exchange is

$$N_{A-W} = D_V f_A \qquad (7)$$

whereas water-to-air exchange is

$$N_{W-A} = D_V f_W \qquad (8)$$

Table 1. Examples of intermedia exchange and major sink processes included in fugacity-based models

Intermedia Exchange	Process	Brief Description
Air - surface (air, soil)	Diffusion	Transport based on molecular diffusivity (across boundary layer)
	Rain dissolution	Gas phase chemical equilibrates with rainwater (may also adsorb to surface)
	Wet deposition	Aerosols scavenged by raindrops during precipitation events
	Dry deposition	Aerosols that are deposited via gravitational settling, impaction etc
Soil - water	Soil run-off	Transport of contaminants with eroding soil particles
	Water run-off	Transport of contaminants in surface water run-off
Sediment - water	Diffusion	Transport based on molecular diffusivity
	Deposition	Suspended solids deposited to sediment surface
	Resuspension	Sediment solids resuspended into the water column

Major Sinks	Process	Brief Description
All compartments	Degradation	Transformation of the parent compound to metabolites
Sediment	Sediment burial	Transport of particle-bound contaminant out of the active sediment layer (only the active sediment layer has significant chemical exchange with the overlying water)
Soil	Vertical mixing	Transport of particle-bound contaminant to more inaccessible/deeper soil layers through soil convection
	Leaching (vertical)	Transport of contaminants to more inaccessible/deeper soil layers through water percolation
Surface ocean water	Particle settling	Transport of particle-bound contaminant to deep ocean (outside model domain)
	Deep-water formation	Transport of surface waters to deep ocean (density-driven)

* Adapted from *ref* 13

Nondiffusive exchange processes (e.g. advection, particle deposition) are often based directly on volumetric flows ($m^3 h^{-1}$). For example, the transport D value for advective outflow is:

$$D_{AO} = G_{AO} Z_{Bi} \qquad (9)$$

where G_{AO} is the volume of air (or water) leaving the model domain per unit time ($m^3 h^{-1}$) and Z_{Bi} is the bulk compartment fugacity capacity. However, for other processes (e.g. particle deposition), the flow rates can also be estimated from mass transfer coefficients (i.e. settling velocity, $m h^{-1}$) and area of exchange (m^2).

Degradation processes in a phase are typically assumed to be first-order (or pseudo first-order) and can therefore be estimated from degradation rate constants (k_{Ri}, h^{-1}) and the volume of the compartment (V_i, m^3) i.e.

$$D_{Di} = k_{Ri} V_i Z_i \qquad (10)$$

where Z_i is the fugacity capacity of the phase being considered. Pseudo first-order kinetics are most commonly applied to represent reactions in the gas phase e.g. OH radical reactions. In such cases, it is assumed that the concentration of other reactant i.e. OH radicals is not significantly influenced by reactions with the compound of interest and hence is effectively constant; seasonally-variable OH radical concentrations can easily be represented in the model parameterization however.

Applying Fate & Transport Models to PFAS. Fugacity-based chemical fate models have been applied predominantly to neutral organic compounds, particularly semi-volatile organic compounds (SVOCs) such as polychlorinated biphenyls (PCBs), DDT, and dioxins/furans (PCDD/Fs). In fact, model parameterization is often guided by insights gained through empirical studies of environmental fate processes using these substances. Applying these models to ionizing compounds such as PFAS is somewhat problematic because if it is assumed that the anion has zero (or negligible) vapour pressure, it has no (or an indeterminable) Henry's Law constant (H). It is therefore impossible to calculate the fugacity capacity of water (Z_W) or any other phase. The practical solution is to assign an arbitrary but negligible K_{AW} to the anion, which ensures that the substance behaves as desired (i.e. highly water soluble, non-volatile) and allows

16

other Z-values to be calculated (13). Using this approach, the relative concentrations in all compartments other than the atmosphere are representative and can be compared directly to measured values. The 'error' associated with this model strategy is insignificant in the broader context of the current model applications; the overall behaviour of the chemical can be represented accurately and the models produce useful results. For the multispecies model applications (**Paper II** and **III**), the issue is no longer of concern since surface-air exchange is dominated by the behaviour of the neutral form anyway (i.e. Z_A is meaningful and can be used to calculated Z_W).

The more substantial factor complicating the application of fugacity-based models to PFAS is the uncertainty in key physical-chemical property data. For SVOCs, it is often uncertainties in the degradation rate constants that are the most problematic whereas partition coefficients (e.g. K_{OW}, K_{OC}, K_{AW}) are relatively well-known or can be estimated reasonably well using property estimation software (e.g. EPI-SUITE, SPARC). For the PFAS considered here, the opposite problem is encountered; they are stable under environmentally-relevant conditions (meaning uncertainties in degradation rate constants are not relevant) but accurate physical-chemical property values are difficult to determine experimentally. First and foremost, there are substantial discrepancies between estimates of the acid dissociation constant (pK_a) measured directly (3.8 ± 0.1; *ref* 20), indirectly (1.3; *ref* 21, 22) and generated using property estimation software (-0.1 to 0.7; *ref* 23). These uncertainties primarily influence the extent to which the neutral species impact the overall fate and transport of PFC(A)s. This is an important consideration because only the neutral form has an appreciable vapour pressure and can volatilize from surface compartments into the atmosphere. In other words, while modeling approaches exist to simulate speciating compounds (e.g. using distribution ratios, see *ref* 16), there is large uncertainty regarding the proportion of each species estimated to be present in each compartment of the model environment.

Other key environmental fate properties typically available for persistent organic pollutants (POPs) are also of questionable applicability and/or reliability. For example, perfluorooctanoate (PFO) is an anionic surfactant that tends to be present at the interface

between water and octanol in typical experimental set-ups, rendering any measured K_{OW} value unreliable (10). The neutral form of this compound, PFOA, is also challenging to work with due to its low water solubility and high surface activity. Arp et al. (24) also recently characterized a sampling artefact when using glass fibre filters in active air sampling equipment, related to irreversible adsorption to the surface of the filter. Consequently, empirical data on aerosol-air partitioning (K_{QA}) for these compounds may be misleading. Some environmental partitioning data are available however. For example, empirical data on sorption of PFAS to sediment solids were recently published (25) and were used directly in the model simulations conducted in **Papers I – IV**. Physical-chemical properties for neutral PFCAs and POSF-based precursor compounds are also available, selected here based on the compilation of physical-chemical properties generated using different property estimation software presented in *ref* 26. Strategies to address these model uncertainties are discussed for each model application in the Methods section of **Papers I – IV**.

Overview of Selected Models. The following global-scale fate and transport models were applied: GloboPOP (27), BETR Global (28) and CliMoChem (29). All three models are conceptually similar (fugacity-based, Eulerian coordinate system) and the most important differences relate to spatial resolution. GloboPOP (**Paper I**) and CliMoChem (**Paper IV)** are latitudinally-resolved models that are primarily designed to simulate transport in the north-south direction whereas BETR Global (**Paper II, III**) divides the globe into 288 regions (based on a 15 x 15° grid) and can therefore explicitly represent transport in the east-west direction. The greater spatial resolution in BETR Global is particularly important when considering ocean transport. Ocean transport (north-south) in GloboPOP and CliMoChem is parameterized according to estimates of bulk eddy diffusivity and residence times of conservative tracers (e.g. radionuclides) in surface ocean waters. Modeled concentrations in each latitudinal zone represent global averages and do not distinguish between different oceans (e.g. Pacific versus Atlantic). The greater spatial resolution in BETR Global allows ocean transport to be represented more realistically and since all major oceans are distinct, regional differences in concentrations related to the location of major emission sources can be identified.

18

Further information on each model is presented in **Papers I – IV**; model development undertaken to update BETR Global (new surface ocean exchange matrix, introduction of multispecies algorithms) is described in the Supporting Information of **Paper II**.

Emission Estimation Methodology. Prevedouros et al. (10) distinguish between two main emission types, direct and indirect sources. Direct sources refer to emissions of PFAS during the manufacturing process and the use of commercial products that *intentionally* contain these compounds. Examples of PFAS-containing products include aqueous fire-fighting foams (AFFFs) and acid mist suppressing agents used in the metal plating industry. Indirect sources refer to emissions of PFAS which are related to i) degradation of precursor compounds or ii) the *unintentional* presence of PFAS in commercial products as residual impurities. This terminology is adhered to for this work.

Papers I – III consider emissions of PFC(A)s only from direct sources (e.g. manufacturing and use) whereas **Paper IV** considers emissions related to direct and indirect sources (e.g. precursor degradation) of PFOS. Emission estimates attributable to direct sources of PFC(A)s were published in *ref* 10 in 2006. Manufacturing of commercial surfactant products (APFO, APFN) and fluoropolymer (FP) products were estimated to be the dominant direct emission sources (> 80%) (10). Since the majority of emission emanate from point sources (i.e. industrial complexes), it is relatively straightforward to assign emissions to the appropriate model regions. Total emission estimates were then divided among the model regions according to estimated production capacity (30). Complete details of the emission estimation methodologies employed for PFC(A)s are presented in **Papers I – III** and the accompanying Supporting Information. Paul et al. (31) recently published an emission inventory for PFOS, based primarily on submissions to the United States Environmental Protection Agency (US EPA) made by the major manufacturer (3M Company). However, this emission inventory does not include precursor substances despite ample evidence that these substances degrade to PFOS through atmospheric degradation and biotransformation (6, 7, 32, 33). It was therefore necessary to re-derive emission estimates for PFOS and its precursor substances. All of these substances are manufactured from the same primary

intermediate, POSF. The basic approach to derive emission estimates was to estimate emission rates for PFOS and the major precursors as a function of POSF-based production (e.g. kg PFOS emitted per kg POSF produced) and then scale emissions to historic POSF production volumes. Emission rates and geographical distribution of emissions were based on information from publicly available sources including submissions to the US EPA (34–39) and Stockholm Convention Secretariat (40, 41). Complete details of the emission estimation methodology and calculations are provided in the Supporting Information accompanying **Paper IV**.

Modeling Strategies. One of the main goals of the work in **Papers I – III** was to assess and compare the long-range transport (LRT) potential of PFAS emitted from direct sources in industrialized regions to other sources. LRT potential was characterized by emissions-dependent model outputs such as gross atmospheric deposition fluxes and oceanic inflows (kg yr^{-1}) and an emissions-independent metric termed Arctic Contamination Potential (ACP). ACP, described in *ref* 42, is particularly useful because it provides a way to compare chemicals in terms of transport efficiency, which is primarily a function of physical-chemical properties (although emission mode of entry and geographical distribution of emissions can have an influence). In **Paper IV**, both direct and indirect sources of PFOS were explicitly considered in the model simulations. To assess the relative contribution of different sources to modeled concentrations of PFOS in source and remote regions, mass balances in each compartment and key model outputs related to direct and indirect sources of PFOS were tracked separately.

In each paper, a default model parameterization (i.e. emission scenario & physical-chemical properties) was established as a baseline scenario. The influence of the uncertainty in emission estimates and physical-chemical property estimates was assessed by conducting a series of simulations with different parameter sets. The effect of the uncertainty in emission estimates on model outputs is most immediately clear because all model processes are described in terms of first- or pseudo first-order rate constants. Therefore, all model outputs scale directly to the magnitude of emissions i.e. if emissions are three times higher, so are all modeled concentrations and deposition fluxes. The

20

influence of physical-chemical properties or environmental partition coefficients was assessed by conducting simulations across a range of values, either based on empirical data or covering the spectrum of possible behaviour (e.g. varying the % of particle-associated chemical in the atmosphere from <1 to >99%).

Summary of Main Results

Fate and Transport of PFC(A)s. The model results in **Paper I** and **II** provide evidence to support the hypothesis that ocean transport of C8 emitted from direct sources is an important pathway for distributing this compound in the marine environment. The contribution of indirect sources was not explicitly assessed in these modeling studies. The preferred approach was to compare mass fluxes generated as model output in **Paper I** and **II** to independent estimates of mass fluxes either based on modeling (43, 44) or monitoring studies (8). Based on these comparisons, mass fluxes associated with ocean transport are greatly in excess of estimated atmospheric deposition fluxes related to indirect sources. There was also good agreement between modeled concentrations and available monitoring data in surface ocean waters of the Northern Hemisphere, suggesting that the emission estimates for this homologue are accurate. The model results characterizing oceanic LRT potential were found to be insensitive to model assumptions regarding physical-chemical properties (e.g. pK_a, K_{OC}) and mode of entry and thus the conclusions can be considered robust.

The atmospheric LRT potential of C8 emitted from direct sources was assessed in **Paper II** and **III**. Model results characterizing this transport pathway were sensitive to model assumptions, particularly pK_a. Mode of entry, more specifically, the treatment of stack emissions from manufacturing facilities also has an important influence. These uncertainties are most relevant when considering the potential for C8 emitted from direct sources to contribute to contaminant loading in remote terrestrial environments (e.g. alpine and High Arctic lakes) as oceanic transport of C8 dominates the modeled concentrations in the marine environment in both source and remote regions regardless. Considering all model output characterizing atmospheric LRT potential, it is reasonable

to conclude that this pathway is a plausible mechanism for global dispersion of direct emissions and that PFO(A) detected in precipitation cannot be attributed solely to indirect sources. However, it is vital to constrain the estimated values of pK_a before further quantitative comparisons can be made.

Outputs characterizing the relative fate and transport of C8 – C13 were presented in **Paper III**. The trends in overall LRT potential, as characterized by ACP, were sensitive to pK_a and mode of entry. Interestingly, ocean transport of higher chain length is not limited so much by processes occurring in surface ocean waters (e.g. particle settling, deep-water formation) as by the processes which determine the mass of contaminant transferred from the terrestrial to marine environment (e.g. surface run-off, sediment burial, soil convection). Once in the marine environment (pH = 8.1), the mass of all homologues is dominated by the anionic form (PFC), which is predominantly in the aqueous phase as opposed to associated with particulate matter. Hence, ocean transport remains relatively efficient for all PFC(A)s. Volatilization of neutral PFCAs from terrestrial surfaces was determined to be a key important process, particularly as chain length increases. The explanation for this model behaviour lies with the assumed trends in air-water (K_{AW}) and organic-carbon water (K_{OC}) partitioning with chain length assumed for neutral PFCAs. Higher homologues have a greater tendency to sorb to solids (K_{OC}) but also a greater preference for the gas phase compared to aqueous phases (K_{AW}). Overall transport potential is determined by the balance between processes that limit mobilization of PFCA from terrestrial compartments (K_{OC}) and processes that liberate PFCAs from terrestrial compartments (K_{AW}). Consequently, overall LRT potential is increased under assumptions of elevated pK_a and if the mode of entry includes emissions to air. On the basis of these results, it is possible to conclude that C9 – C13 emitted from direct sources have an inherent potential for both oceanic and atmospheric LRT.

Realistic emission estimates of C9 – C13 were also derived for **Paper III**, based on the emission estimation methodology applied in **Paper II**. Although monitoring data are limited, comparisons to model output suggest that the emission estimates for C9 are also reasonable and that it is plausible that measured concentrations of C8 and C9 in wildlife

22

inhabiting industrialized and remote regions are strongly influenced by direct emissions, particularly in the marine environment. These homologues also have the potential to impact remote terrestrial system but it is difficult to constrain quantitative estimates of e.g. atmospheric deposition fluxes due to the uncertainty in pK_a and to a lesser extent aerosol-air partitioning. Direct emissions of C11 and C13 are high in comparison to emissions of C10 and C12, which are approximately 50 times lower than C11 and C13 respectively. While all of these homologues are transported with sufficient efficiency to impact remote regions, the modeled C11**:**C10 concentration ratios in the abiotic environment are difficult to reconcile with measured concentration ratios of these homologue pairs in biota (insufficient data available for C13:C12). The uncertainty in relative bioaccumulation potential through complex food webs is one of the main factors limiting a more definitive assessment for all homologues considered.

Fate and Transport of PFOS and Its Precursors. The fate and transport of PFOS and its precursor compounds was investigated in **Paper IV** in the context of divergent trends in measured concentrations in marine biota in remote regions (decreases in Canadian Arctic Archipelago, Alaskan Coast; increases in East & West Greenland) following a major production phase-out of PFOS and its precursors. Three distinct exposure hypotheses were considered here: 1.) uptake of PFOS emitted into the environment related to its manufacture and use dominates 2.) uptake of PFOS formed in the environment through degradation of POSF-based precursor compounds dominates and 3.) uptake of POSF-based precursor compounds followed by transformation to PFOS *in vivo* dominates.

Model output for the period following the major production phase-out for ambient concentrations characterizing Exposure Hypothesis 1 and 2 were found to be qualitatively similar. PFOS concentrations in surface ocean waters of the Arctic region (65–90 $^\mathrm{o}$N) continue to increase following the production phase-out. This model behaviour indicates that oceanic transport of PFOS from temperate regions (i.e. source zones) is sufficient to maintain a positive net flux into the Arctic region. The continued dispersion of PFOS in surface ocean waters is facilitated by the relatively long residence time in this

compartment (i.e. loss processes are inefficient). Hence, it is not possible to reconcile observed declines in measured PFOS concentration in remote regions assuming that Exposure Hypothesis 1 or 2 dominate. However, the behaviour of POSF-based precursor is in sharp contrast to PFOS. Oceanic concentrations of precursor compounds follow atmospheric concentrations and decline sharply in both source and remote regions once emissions are reduced. The sudden decline in atmospheric ∑Precursor concentrations following production phase-out, due to atmospheric degradation, results in rapid volatilization of precursors from the ocean in order to approach a new equilibrium between these two compartments (i.e. the two compartments remain tightly coupled). Degradation of precursors transferred from the ocean continues of course, reducing the total mass of the parent compounds in the global environment over a short period of time. Given this model output, a rapid response in marine organisms is plausible if the major exposure route in marine food webs is uptake and metabolism of precursor compounds to PFOS *in vivo*. Observed trends in biomonitoring data may diverge in different locations due to the relative inputs of the various compounds driving exposure. For example, it is possible that marine mammals in the certain regions continue to be predominantly exposed to PFOS in surface ocean waters (and hence show no response to the production phase-out) whereas marine mammals elsewhere were exposed predominantly to precursor sources (and hence exhibit declining PFOS concentrations). Further research into the bioaccumulation potential of precursor compounds as well as degradation pathways *in vivo* are required to strengthen this hypothesis further. Continued monitoring of precursor compounds in the atmosphere and surface ocean waters may also provide important insights.

Conclusions

This doctoral thesis has demonstrated the value of applying mass balance model approaches to better understand the fate and transport of PFAS in the global environment. With respect to PFC(A)s, the potential of direct emissions of the C8–C13 homologues to impact remote regions has been better characterized and research priorities have been identified (see below). **Papers I – III** provide evidence that the LRT potential of PFC(A)s emitted from direct sources is not negligible, as has been and continues to be

suggested. These chemicals do not have the same properties as typical POPs and hence there is no reason to assume that the fate and transport behaviour is similar (i.e. atmospheric transport alone controls global dispersion). Oceanic transport of PFCs is relatively efficient and can explain the presence of these compounds in remote marine environments. The influence of direct emissions of PFC(A)s on remote terrestrial environments through atmospheric LRT is admittedly far more uncertain. However, model output presented in **Papers II** and **III** provides evidence of the potential importance of this transport pathway. The modeling simulations of PFOS and its precursor compounds conducted in **Paper IV** have also provided very useful insights. Most importantly, a plausible explanation for why PFOS concentrations in wildlife can be decreasing in some remote regions while increasing in others has been elucidated.

Future Perspectives

From the model outputs generated for this work, it is clear that one of the most important research priorities for PFAS is basic research into physical-chemical properties and partitioning beheviour. For the PFC(A)s, the most important task is to arrive at a scientific consensus regarding the acid dissociation constant (pK_a). Model assessments of atmospheric LRT potential and interpretation of atmospheric monitoring data will remain greatly hindered otherwise. For PFOS and its precursors, the most interesting research questions are related to the biological uptake and metabolic processing of precursor compounds. For example, it would be interesting to determine i) tissue distribution patterns exhibited by neutral PFAS and ii) if existing mechanistic bioaccumulation models can be applied to these compounds (including estimates of whole body biotransformation rate constants). Additional studies confirming and expanding the understanding of degradation pathways and kinetics for neutral PFAS both *in vivo* and in the atmosphere will also be of high value.

In the broader context, it is interesting to note that the intense scientific and public scrutiny of PFAS has already led to a series of voluntary measures on the part of industry to reduce emissions from manufacturing and use of many PFAS. However, a related

trend to be aware of is the shift towards shorter chain homologues as replacement products. For example, although it seems likely that PFOS will be completely phased out in the near future, the use of the 4 carbon homologue, perfluorobutane sulfonate (PFBS), is likely to increase substantially. The rationale for favouring this replacement chemical is based on data showing that bioconcentration factors (BCF) and bioaccumulation factors (BAF) decline substantially with chain length, particularly for PFAS with 7 or less carbons. Regardless, this behaviour does not mean biological exposure will be negligible in source or remote regions and it is misleading to suggest otherwise. Indeed, the LRT potential is likely to be quite similar or in excess of the longer chain homologues because these replacement compounds exhibit lower sorption to the terrestrial solids shown to limit transport in **Paper III**. As these substances are also highly persistent and bioavailable, it is inevitable that wildlife and humans will be exposed to PFBS and shorter chain PFCA homologues. Given the faster elimination kinetics of shorter chain PFAS, however, one would expect lower levels of these compounds in biological tissues for a unit exposure compared to longer chain perfluorinated compounds. Nevertheless, all potential replacements should be subject to a high level of scrutiny, regardless of chain length. In particular, assessments should include bioaccumulation studies using air-breathing as well as aquatic organisms, since it is already understood that uptake and elimination kinetics in fish cannot be used to accurately predict chemical behaviour in mammals and birds in all cases (45, 46). Given the fact that controlling emissions, especially from use of consumer products, is difficult to say the least, caution is clearly warranted.

Acknowledgements

I gratefully acknowledge the important contributions of my co-authors to Papers I – IV. Thank you for your patience and helpful suggestions. I particularly wish to thank Ian T. Cousins (main supervisor) and Matthew MacLeod, who have been instrumental to the successful completion of this work. I have also had many inspiring and/or reassuring conversations with Michael McLachlan related to this thesis work and 'scientific life' in general. I also extend my thanks to the ITM Education Committee for their comments on the thesis document.

I would also like to take this opportunity to thank everyone at ITM for creating such a wonderful work environment, both socially and scientifically. Karin Nyström, Administrative Officer of ITMx, deserves a special mention since she has been looking out for me from the very first day I got here. She is also a big fan of partition coefficients. Tack tack, tusen tack!

Special thanks also to former and current members of my research group (Konstantinos Prevedouros, Erick Nfon, Robin Vestergren).

Parents. School is out! Thanks for all the love and support.

Finally….Thanks and love to Phase I (2004 – 2006) and Phase II (2008 – present) friends in Sweden. Lots of great memories and funny stories! Regarding my epic Midsummer showdown in Dalarna: Those hillbillies sure know how to drink – rematch in Valhalla! (I'll have all the time I need)

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