# UNDERSTANDING THE TRANSPORT OF ANTHROPOGENIC FLUORINATED COMPOUNDS IN THE ENVIRONMENT

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## Introduction

Short-chain (4-13 carbon) fluorinated molecules are of increasing scientific and regulatory interest since they have been found globally in the environment and in human blood serum[1-10]. In order to understand why these compounds are found in such diverse places, it is important to determine their physicochemical properties and to demonstrate what mechanisms might be important to exposure and long-range transport.

Fluorinated compounds have properties that are quite different from their hydrocarbon counterparts due to the extremely high strength of the C-F bond. Perfluorinated compounds are both hydrophobic and oleophobic, that is, they are neither miscible in aqueous or hydrocarbon solvents. Perfluoroalkanes are more hydrophobic than hydrocarbons. For example, octane and perfluorooctane are not miscible since octane is too polar. Perfluorinated compounds might be better considered as a third class of compounds (hydrophobic, oleophobic, perfluoro). On the solvatochromic $\Pi^*$ scale, an index of solvent dipolarity/polarizability, water is 1.09, cyclohexane is 0.00, and perfluorooctane is –0.41.[11] Placing perfluorinated compounds in a separate class requires our rethinking the analogies that compare perfluorocompounds (especially) to hydrocarbons and will help to rationalize better their “unusual” and often unexpected properties.

Vapor pressure and solubility measurements are presented for a variety of fluorinated compounds. Experiments demonstrating the potential for atmospheric transport of undissociated acids and fluorotelomer alcohols are also described.

## Materials and Methods

### Physical properties

Solubility measurements of several perfluorocarboxylic acids were determined in ultrapure water (17.6 x $10^6$ $\Omega\cdot$cm) at 22°C following OECD Guideline 105.[12] The pH of each saturated acid solution was also measured. The vapor pressure of the 7-2 secondary fluorotelomer alcohol was determined via headspace gas chromatography mass spectrometry.[13] Vapor pressures of the 8-2 fluorotelomer acid, the 8-2 fluorotelomer unsaturated acid, and perfluorotridecanoic acid were determined via the Scott boiler method.[14] Solubility in water of ammonium perfluorooctanoate and sodium perfluorooctanoate was determined via cloud point.

### Transport studies

**Sublimation.** In order to determine if sublimation is a pathway for transport of fluorotelomer intermediates such as fluorotelomer olefins or alcohols, 16.8 g of the 8-2 fluorotelomer alcohol was placed in a 20 mL uncapped scintillation vial at approximately 21°C. Over a 37-day period, the mass in the vial was monitored.

**Quiescent water transport.** To determine if a perfluoroacids could be transported from an aqueous solution to air in an acid-rain environment, a 182.7-ppm solution of perfluorooctanoic acid was placed in a three-neck 250-mL round-bottom flask. Nitrogen was delivered using a calibrated rotometer to measure the flow across the surface of the liquid. The solutions were buffered at pH 4 (to simulate acid rain) (potassium hydrogen phthalate) and pH 7 (neutral solution) (sodium and potassium phosphate). A magnetic stirring bar was used to mix the liquid slowly but without turbulence. Three solid phase C18 extraction cartridges were placed in-line to capture the acid vapors.

**Foam fractionation.** To determine the potential of aerosol transport[15] from the organic microlayer film on the surface of bodies of water, foam fractionation experiments were carried out. In the first experiment 51 mL of a 100 mg/L solution of perfluorooctanoic acid was placed in a 100 mL glass tube. The tube was 25 cm high with takeoff ports at 10 cm, 15 cm, and 21 cm from the bottom of the tube. Filtered air was introduced into the bottom of the tube through a fritted bubbler. Air flow from 0.62L/min to 1.00 L/min was measured using a calibrated rotometer. At various times samples of foam and suspended liquid were collected from the appropriate port into a 10-mL graduated cylinder. The concentration of perfluorooctanoate was measured before and after the foam collection and from the foam samples via liquid chromatography tandem mass spectrometry.[16]

## Results

Transport Studies

**Figure 1.** Sublimation of 8-2 Solid Fluorotelomer Alcohol at Ambient Temperature

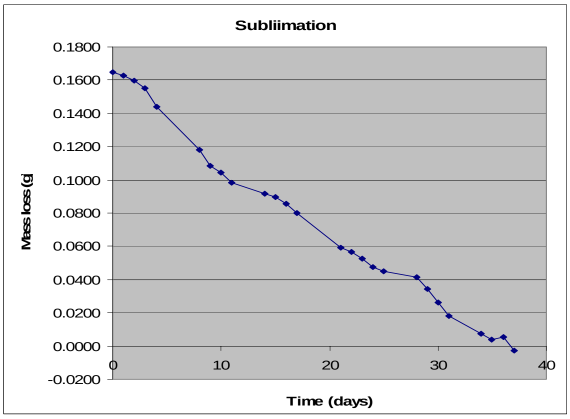

Figure 2. Quiescent Water Transport, Perfluorooctanoic Acid Buffered at pH 4.

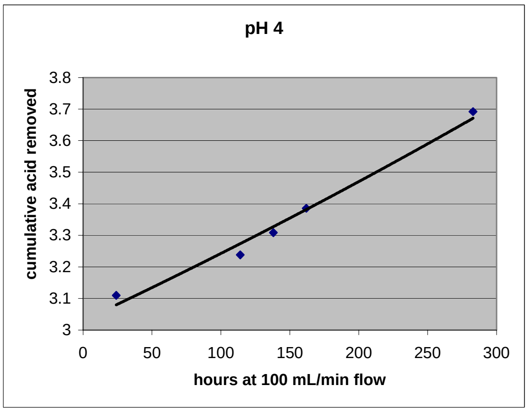

**Table 1.** Physical Properties

| Compound | Aqueous Solubility (mg/L)* | Temperature (C) for solubility | pH of saturated solution | Vapor pressure,kPa / Temperature, C) | Melting point (C) |
|---|---|---|---|---|---|
| Perfluoroheptanoic acid | 118,000 | 21.6 | 2.00 | | |
| Perfluorooctanoic acid | 4,340 | 24.1 | 2.52 | 0.128 (59.25)# | |
| Perfluorononanoic acid | | | 2.45 | 1.12 (99.63)# | |
| Perfluorodecanoic acid | 260 | 22.4 | 2.98 | 3.129 (129.56)# | |
| Perfluoroundecanoic acid | 92.3 | 21.9 | 2.82 | 0.616 (112.04)# | |
| Perfluorododecanoic acid | | | 3.89 | 0.856 (127.58)# | |
| Perfluorotridecanoic acid | | | 2.96 | 1.228 (141.50) | |
| 8-2 fluorotelomer acid | | | | 0.187 (99.57) | 87.8 |
| 8-2 flurotelomer unsaturated acid | | | | 0.390 (108.0) | 106.6 |
| 7-3 fluorotelomer acid | | | | 0.528 (116.30) | 86.7 |
| 7-2 secondary fluorotelomer alcohol | | | | 0.227 ((50.0) | |
| 8-2 fluorotelomer alcohol | 137 ug/L# | 25 | | 0.029 (45.0)# | |
| 1-H perfluoroheptane | | | | 3.9 (45.0)# | |
| ammonium perfluorooctanoate | 37.10% | 22 | | | 275 |
| sodium perfluorooctanoate | 16.90% | 22 | | | 164 |
| | | | | | |
| *except as noted | | | | | |
| #published data | | | | | |

Table 2. Foam Fractionation: PFOA

| Description | Sample Mean | Concentration (ppm) Std Dev |
|---|---|---|
| bulk liquid at t = 3 min | 112.4 | 2 |
| bulk liquid at t = 10 min | 78.8 | 0.6 |
| bulk liquid at t = 16.5 min | 47.1 | 0.5 |
| bulk liquid at t = 21.5 min | 41.6 | 0.7 |
| | | |
| foam collected at t = 8-10 min | 97.4 | 0.4 |
| foam collected at t = 15-16.5 min | 151.2 | 0.1 |
| foam collected at t = 21.5-22.5min | 58.3 | 0.3 |

Table 3. Foam fractionation, PFOA with Sodium Dodecyl Sulfate Co-surfactant

| Sample | Pot conc. (ppm) | Fraction conc. (ppm) |
|---|---|---|
| P-1 | 19.2 | |
| F-1 | | 26.9 |
| P-2 | 17.5 | |
| F-2 | | 22.8 |
| P-3 | 15.1 | |
| F-3 | | 31.1 |
| P-4 | 8.4 | |

P = Pot
F = Fraction

## Discussion

The aqueous solubility of the perfluorocarboxylic acids diminishes with increasing chain length (Table 1). In general the vapor pressure of fluorinated compounds is higher than expected when compared to their hydrocarbon counterparts. In the absence of a solution or adsorbed state, solid 8-2 fluorotelomer alcohol sublimes rapidly at ambient temperature (Figure 1). Given its low solubility in water (150 ppb), and high sorptivity to organic solvent or sorbent, only under conditions where no sorptive medium is present would the 8-2 fluorotelomer alcohol be expected to partition to the air compartment.

The quiescent water transport results at pH 4 (Figure 2) indicate that at a pH were equilibrium exists between dissociated and undissociated acid, the undissociated acid is likely escaping into the headspace and is being removed with the air. The foam fractionation experiments summarized in Table 2 and Table 3 indicate that perfluorooctanoate is concentrated in the surface foam whether alone in an aqueous solution or with another co-surfactant. This result suggests that foam (marine aerosol) transport should be considered an important transport mechanism.

**References**

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