Aerosol Enrichment of the Surfactant PFO and Mediation of the Water – Air Transport of Gaseous PFOA

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Experimental Details

**Sample Collection.** River water was collected from Lock 20 on Little Lake in the City of Peterborough, Ontario (44°18' N, 78°19' W) and from the Otonabee River near Trent University, Peterborough, Ontario (44°21' N 78°17' W). Lake water was collected from Lake Ontario near Victoria Park Beach in Cobourg, Ontario (43°57' N, 78°10' W). All lake and river water samples were collected at near-shore locations in collapsible 20 L polypropylene (PP) carboys on June 15, 2006. Samples of Atlantic Ocean water were collected from Prince Edward Island National Park, PEI (46°30.3’ N 63°24.6’ W) on June 10th, 2006. Ocean water samples were collected near-shore in 25L high density polyethylene (HDPE) canisters. All water samples were stored at 4°C prior to use.

**Experimental Set-up.** The bulk chamber was assembled using an 18 L polycarbonate container with an air inlet and outlet in the top of the chamber. The bulk chamber contained 6 L of water spiked with PFOA and stirred continuously. The aerosol generator was centrally suspended in the bulk chamber below the water surface. A collection vessel and aerosol breakthrough vessel were connected in series to the bulk chamber using vacuum tubing with a vacuum flow rate of 50 – 100 mL/min. The vessels were cooled in ice baths to condense the aerosols from the air stream.

![Figure S1: Experimental set-up.](image)
Detection of Gas Phase PFOA. Three separate methods were used to detect the presence of gas phase PFOA.

In the first method the experimental apparatus used was the same as that described for investigating the enrichment of PFO in aerosols. Subsequent to the collection vessels a further two 250 mL HDPE gas-washing bottles were inserted. These contained approximately 100 mL of the 50 mM KOH solution, and samples were collected upon completion of the 12 hour experiment. Samples of the KOH trap solutions were neutralized to pH ~7 with 2M HCl prior to LC-MS/MS analyses.

The second method utilized Orbo™ 609 Amberlite® XAD®-2 adsorption tubes (400/200mg, Supelco, Bellefonte, PA) in place of the KOH traps to detect the presence of gas phase PFOA in the system. The XAD tubes were inserted into lengths of PVC tubing, sealed tightly with metal hose clamps, and connected to the apparatus in-line preceding the vacuum source. A control XAD tube was used to check for background PFOA by vacuuming ambient air through it for the 12 hour duration of the experiment. A blank XAD cartridge was also analyzed.

In the third method the outflow from the bulk chamber was directed through a glass tap to control the removal of the aerosol, followed by a large 50 cm water-jacketed condenser mounted above the bulk chamber. The outflow of the condenser was connected in-line to the primary and secondary collection vessels in the same manner as described above. Following the secondary collection flask, the outflow was directed through primary and secondary XAD tubes. The in-line XAD tubes were changed at various intervals throughout the experiment. With the glass tap closed, aerosols were generated for 1 hour. After 1 hour, the aerosol generator was turned off, and the aerosols were given residence times in the headspace ranging from 0 – 90 s and then removed from the headspace using a positive flow of air (10 – 50 mL/min) introduced at the top of the bulk chamber headspace. Aerosols produced in the bulk chamber headspace were transported through the outflow and into the condenser, where they were
condensed and allowed to drip back into the bulk chamber. Here, only gas phase PFOA was thought to be transported beyond the condenser and collection vessels.

Upon completion of the experiments, all XAD cartridges were sealed and stored at 4°C until elution. The primary and secondary beds of the XAD cartridges were eluted separately with 50 – 100 mL of HPLC grade methanol. Samples were prepared directly from the XAD eluent without further dilution, and were analyzed by LC-MS/MS using matrix-matched standards.

**Behavior and Fate of PFO in Aerosols.** The apparatus used to observe the behavior of PFO in the aerosol droplets was the same as that described above for the investigation of enrichment of PFO in aerosols. The main modification was that the collection of aerosols was not continuous. A one-way glass tap between the bulk chamber and the primary collection vessel was closed and the aerosol generator was run for one hour periods. After approximately one hour, the aerosol generator was shut off and the aerosols were allowed to equilibrate in the headspace for up to 120s. The glass tap was opened and the headspace was evacuated through a ice-cooled primary and secondary collection vessels for approximately 5 minutes. The condensed aerosol was collected and removed from the system after each repetition of the procedure.
Aerosol-Mediated Removal Model

The experimental rate of chemical loss from bulk water due to the formation of aerosols was examined using a mathematical model. The experimental system was modeled as a two-compartment system of bulk water and aerosols. The chemical, perfluorooctanoate (PFO), is assumed to be uniformly distributed in each of the compartments. The air and the container walls are not explicitly included in the model but are implicitly included as the destination of the PFO lost from the aerosols and water.

Transport and loss of chemical is described by the rate constants (s$^{-1}$) $k_{aq}$ and $k_{qw}$ for aerosol generation and condensate return respectively, $k_{qa}$ for loss from the aerosols, and $k_{Lw}$ for loss from the water, as shown in Figure S3 ($C_{aq}(t)$ and $C_{w}(t)$ are the concentrations of PFO in aerosols and bulk water respectively as a function of time).
Aerosols with an approximate diameter of 50 µm were produced by an ultrasonic aerosol generator. The rate of aerosol generation in the experimental system was determined to be $2.6 \times 10^{-6}$ s$^{-1}$ by the collection of aerosols over a 15 hour period. In a closed system, such as that modeled here, the rate at which aerosols condense and return to the water must be equal to their generation rate, thus $k_{wq} = k_{qw}$.

When aerosols were not generated, PFO was lost from the bulk water at a rate of 0.4% per hour. This loss process, likely a direct partitioning to either the air as PFOA and/or the container walls, since PFO does not degrade appreciably, is represented by the rate constant $k_{Lw}$ and is 0.004 h$^{-1}$ or $1.1 \times 10^{-6}$ s$^{-1}$.
The half-life of PFO in the aerosols was experimentally determined to be 7.2 s; a rate constant, \( k_{qa} \) of 0.096 s\(^{-1}\). This rapid loss from the aerosols was defined as gas phase partitioning of PFOA. Furthermore, this was considered to be a loss process in which no PFOA re-partitioned to the water droplets in the head space of the system.

The rate of change of the concentration (ppb/s) of PFO in the water and aerosol compartments of the experiment outlined above, with respect to time, is defined by the following system of differential equations:

\[
\begin{align*}
\frac{dC_w(t)}{dt} &= k_{qw} C_q(t) - (k_{wa} + k_{Lw}) C_w(t) \\
\frac{dC_q(t)}{dt} &= k_{qw} C_w(t) - (k_{qa} + k_{qw}) C_q(t)
\end{align*}
\]

(1)

For an initial water concentration of 255 ppb and aerosol concentration of 0 ppb, and subject to the parameters described above as shown in Figure S3, the solution of Equations (1) is:

\[
\begin{align*}
C_w(t) &= 255e^{-3.7\times10^{-6}t} + 1.85\times10^{-7}e^{-0.096t} \\
C_q(t) &= 0.0069e^{-3.7\times10^{-6}t} - 0.0069e^{-0.096t}
\end{align*}
\]

(2)

Using the equations in (2) the model predicts the half-life of PFO in the bulk water to be 52 hours as shown in Figure S3. This is in excellent agreement with the experimentally determined half-life of 60±13 hours.
Figure S4: Modeled results for the concentration of PFO in the bulk water (ppb) over time (h).

It should be noted that this model does not predict the concentrations measured in the aerosols. By assuming only a two-compartment system, the surfactant property of PFO was ignored. Experimentally, and indeed in the environment, aerosols are produced from the surface water which is highly enriched in PFO, possibly by many orders of magnitude. If the extent of this enrichment was accurately known, the concentration of the surface layer could have been used to calculate the concentration in the aerosols and the aerosol-to-bulk water enrichment factor measured experimentally could have been compared to model results. However, this discrepancy between modeled and measured concentrations does not affect the rate of loss since all rate constants were experimentally determined.