

Development of a Diffusive Gradients in Thin-Films Passive Sampling Device for PFAS (ER20-1363)

Samuel D. Hodges, Huong T. Pham, and Julian L. Fairey (University of Arkansas)

Introduction:

Diffusive gradients in thin-films (DGT) passive sampling devices (PSDs) are kinetic samplers in which analytes sorb in a binding layer following diffusion through (1) a stagnant diffusive boundary layer (DBL), the thickness of which, δ_{DBL} , varies with local hydrodynamics, and (2) a hydrogel of known thickness, δ_{Gel} . The hydrogel restricts mass transport to molecular diffusion and, therefore, diffusion coefficients in hydrogels, D_{gel} , are needed to determine time-weighted average PFAS concentrations. Here, a two-compartment diffusion cell (2Comp-DCell) was used to measure PFAS concentration profiles across hydrogels as a function of pH and temperature. A finite-difference model (FDM) was used to determine $D_{PFAS-Gel}$ informed by 2Comp-DCell tests with nitrate in which δ_{DBL} was determined as a function of mixing speed in the Source and Sink compartments.

Finite-Difference Model for the Two-Compartment Diffusion Cell:

D_{gel} determinations from 2Comp-DCell tests typically rely on four assumptions: (I) Analyte diffusion in the gel is indistinguishable from that in the water, $D_{gel} = D_{water}$, (II) the source compartment concentration is constant over the experiment duration, $C_{Source} = \text{constant}$, (III) the sink compartment concentration increases linearly in time and its maximum is negligible compared to the source concentration, $C_{Max-Sink} \ll C_{Source}$, and (IV) the δ_{DBL} is negligible, such that $\delta_{DBL} \ll \delta_{Gel}$.

At environmentally relevant PFAS concentrations, 2Comp-DCell experiments span 3–5 days and violate assumptions II and III. The FDM developed in Task 1 eliminates the need for these assumptions through implementation of a stepwise regression procedure. The handling of assumptions I and IV is described next.

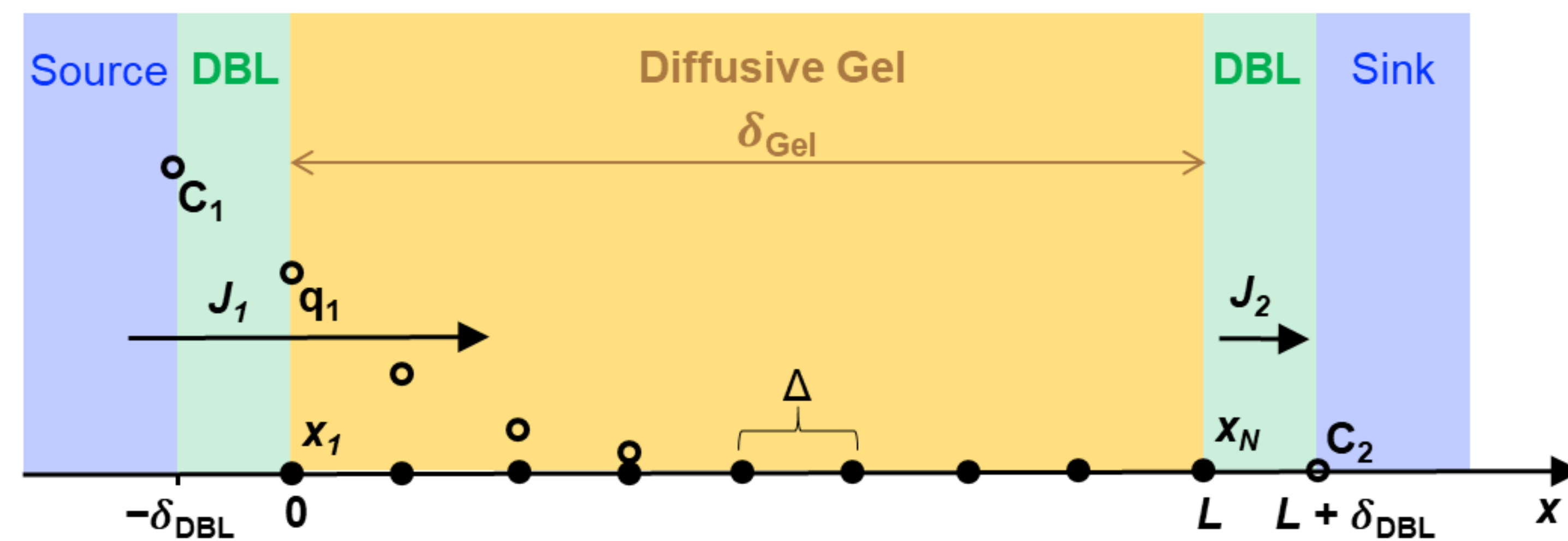


Figure 1. (left)

Schematic of one-dimensional diffusion problem in the two-compartment diffusion cell tests used in the formulation of the finite-difference model.



Figure 2. (above)
Digital rendering of a 2Comp-DCell Compartment

$$\text{Source Side: } \frac{\partial q_1}{\partial t} = \frac{D_{gel}}{\Delta^2} [q_0 - 2q_1 + q_2] = \frac{D_{gel}}{\Delta^2} \left[\frac{2\Delta J_1}{D_g} + q_2 - 2q_1 + q_2 \right] = \frac{2D_{gel}}{\Delta^2} [q_2 - q_1] + \frac{2J_1}{\Delta}$$

$$\text{Sink Side: } \frac{\partial q_N}{\partial t} = \frac{2D_{gel}}{\Delta^2} [q_{N-1} - q_N] - \frac{2J_2}{\Delta}$$

Diffusion Boundary Layer Thickness:

Assumption I is only necessary if $\delta_{DBL} \ll \delta_{Gel}$. If assumption IV is true, δ_{DBL} can be ignored and both assumptions are unnecessary. Assumption IV is dependent on the hydrodynamic properties in the diffusion cell. To investigate the 2Comp-DCell hydrodynamics, tests with nitrate were completed as a function of δ_{Gel} (0.08, 0.12, 0.16, 0.20 cm), gel type (agarose and agarose cross-linked polyacrylamide (APA)), and stir rate (100, 200, and 500 RPM). This array of 60 tests was analyzed with the FDM to determine δ_{DBL} in the 2Comp-DCell.

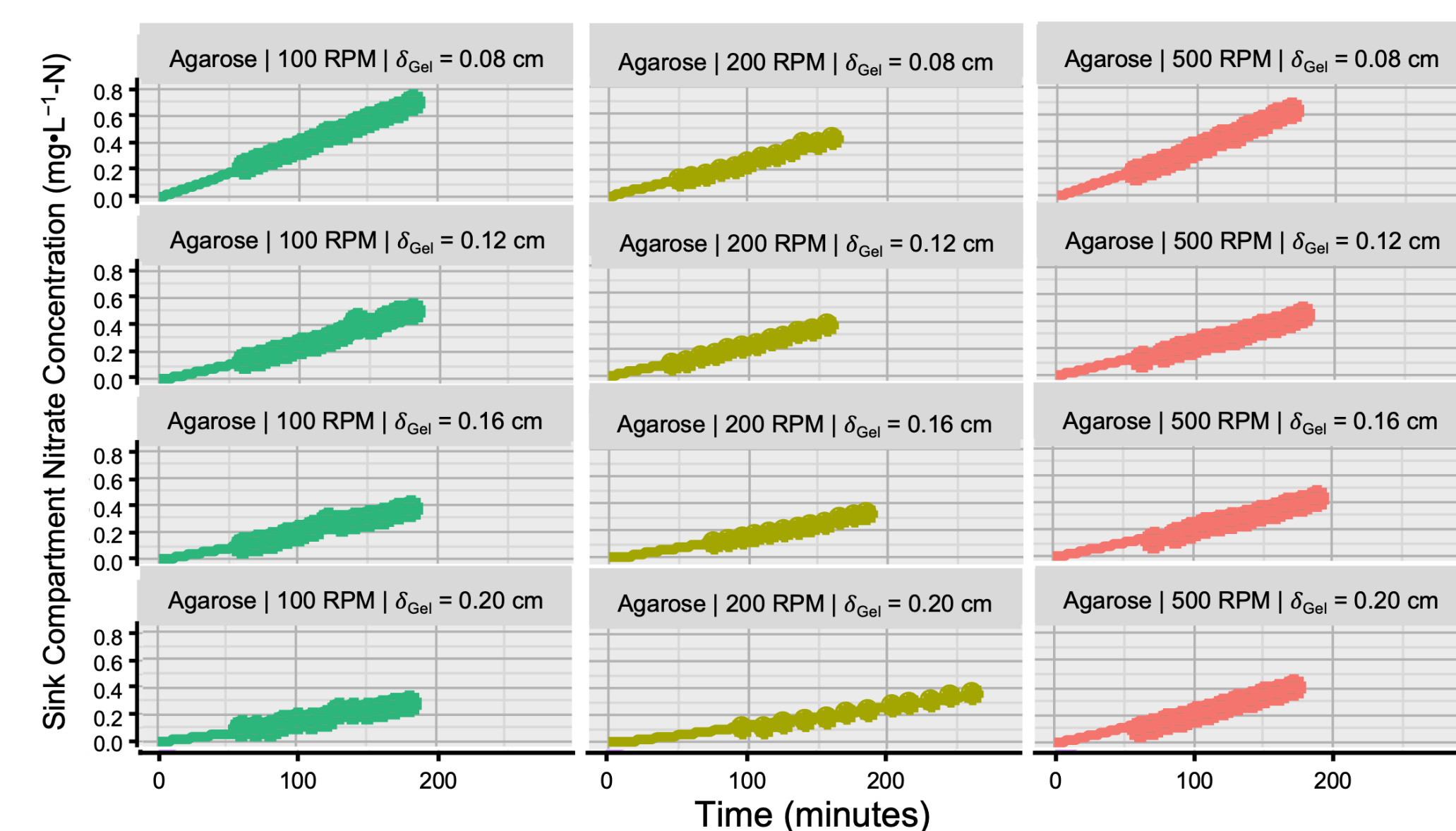


Figure 3. (above)

Sink compartment nitrate concentration profiles from 2Comp-DCell tests with agarose gel. The points are measured nitrate concentrations and lines are FDM-simulated profiles.

- $D_{Gel-APA} < D_{Gel-agarose} \rightarrow$ used agarose gel for PFAS
- $D_{Gel-APA} = 14.0 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$
- $D_{Gel-agarose} = 15.7 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$
- At 100 RPM, $\delta_{DBL} = 80 \mu\text{m}$, total DBL distance = 160 μm
- At 200 RPM, $\delta_{DBL} = 50 \mu\text{m}$, total DBL distance = 100 μm
- At 500 RPM, $\delta_{DBL} \approx 0$, used for PFAS 2Comp-DCell tests

Two-Compartment Diffusion Cell Tests with Mixture of 24 Target PFAS:

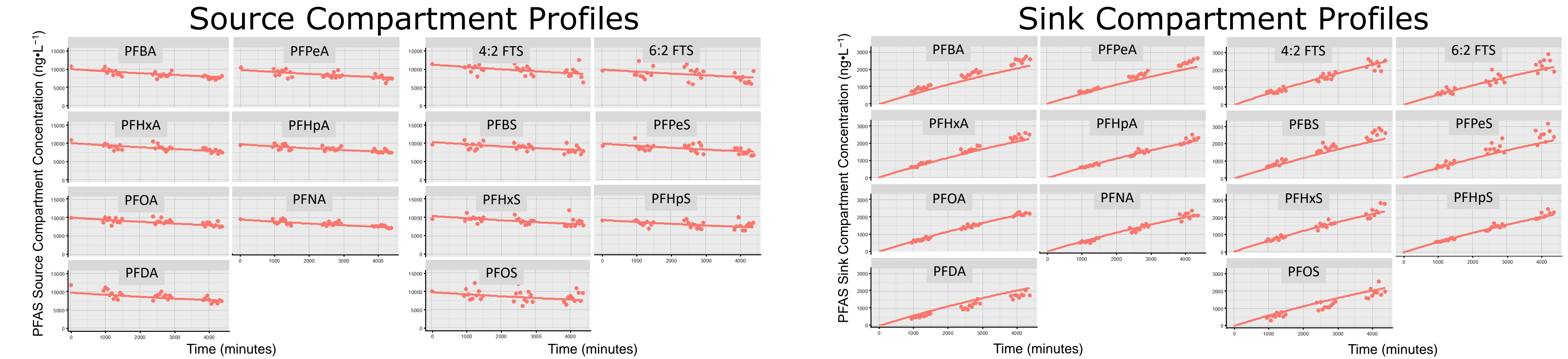


Figure 4. (above)

Source and sink compartment PFAS concentration profiles from 2Comp-DCell tests. The points are measured PFAS concentrations and lines are FDM simulated profiles. Tests were completed at room temperature (22 °C) and pH 7 with a gel thickness, δ_{Gel} , of 0.12 cm, and compartment mixing speed of 500 RPM.

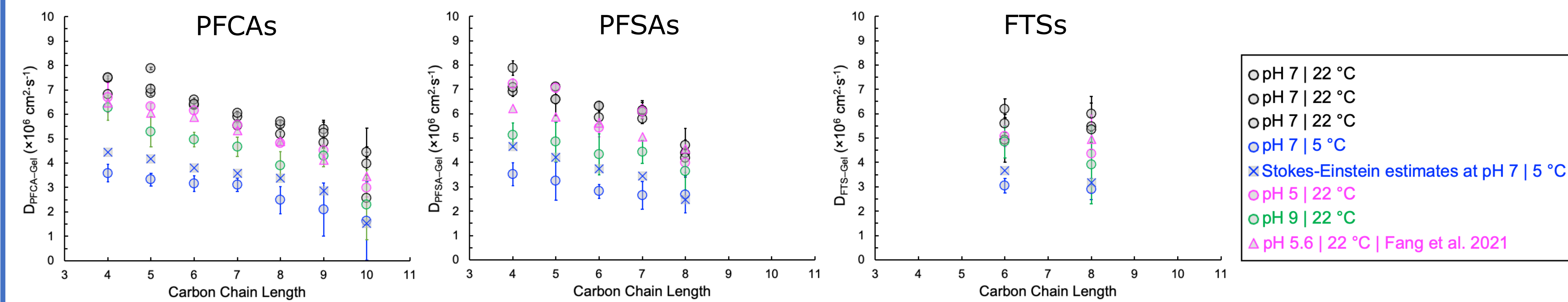


Figure 5. (above)

Diffusion coefficients in agarose gel ($D_{PFAS-Gel}$) for the (a) C4–C10 PFCAs, (b) C4–C8 PFSAs, and (c) 4:2- and 6:2 FTSs. The source compartment was spiked with a mixture of the 24 target PFAS at 10,000 $\text{ng} \cdot \text{L}^{-1}$. Three experiments (black circles) were completed at pH 7.0 and room temperature (22 °C) and one experiment was completed at (i) pH 7.0 and 5 °C (blue circles), (ii) pH 5.0 and 22 °C (magenta circles), and (iii) pH 9.0 and 22 °C (green circles). Error bars are the weighted residual sum of squares (WRSS) between the model fit and experimental data. The Stokes-Einstein equation was used to predict $D_{PFAS-Gel}$ at 5 °C (blue crosses) based on their respective values at 22 °C and pH 7. $D_{PFAS-Gel}$ from Fang et al. 2021¹ at pH 5.6, room temperature, and source compartment PFAS spiked at 2,500,000 $\text{ng} \cdot \text{L}^{-1}$ (magenta triangles).

- $D_{PFAS-Gel}$ decreased with increasing carbon chain length for the C4–C10 PFCAs and C4–C8 PFSAs
- pH 5 (n=1) \approx pH 7 (n=3) < pH 9 (n=1) \rightarrow negative charge on Agarose may retard PFAS diffusion
- Dropping temperature from 22 to 5 °C decreased $D_{PFAS-Gel}$ by about one-half
- Estimates of $D_{PFAS-Gel}$ by Stokes-Einstein equation overpredicted $D_{PFAS-Gel}$ by 15–30 %
- Decreased temperature may produce additional restrictions of gel pore spaces

Future Work:

- 2Comp-DCell tests with C11–C14 PFCAs, C9–C11 PFSAs, 8:2 FTS, PFOSA, N-MeFOSAA, and N-EtFOSAA
- 2Comp-DCell tests with nitrate to assess impact of pH and conductivity on mass transport through Agarose
- DGT-PSD binding layer selection (strong base anion and/or weak-base anion resins)
- Laboratory-scale deployments of DGT-PSDs to assess accuracy for PFAS mixtures and determine method detection limits vs. deployment time for the 24 target PFAS

Acknowledgements:

The authors thank David G. Wahman (USEPA, Cincinnati, Ohio) who is a technical advisor on ER20-1363 and Levi M. Hauptert (USEPA, Cincinnati, Ohio) for help with the numerical modeling.