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

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Introduction:

Diffusive gradients in thin-films (DGT) passive samplers are kinetic samplers in which analytes sorb to a binding layer following diffusion through a (1) stagnant diffusive boundary layer (DBL), the thickness of which, δ_{DBL}, varies with local hydrodynamics and (2) 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 (TWA) PFAS concentrations.

Two-compartment Diffusion Cell (D-Cell):

- Well-mixed source and sink compartments bridged by diffusive gel
- Source compartment spiked with analytes and measure in source and sink over time
- Sized for DGT Research® commercial gels
- Used to determine DGel ± 95% confidence interval (CI) for each analyte

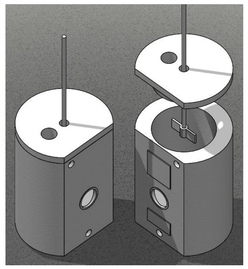

Figure 1: Digital rendering of a two-compartment diffusion cell (D-Cell)

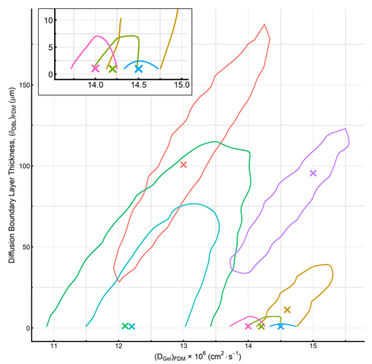

Figure 2: Two parameter error contours of D_{Gel} for nitrate vs. δ_{DBL} indicates 500 RPM mixing speed minimizes DBL

D-Cell Validation[1]:

- Non-steady state diffusive flux required development of a finite difference model (FDM)
- Minimized diffusive boundary layer thickness (δ_{DBL}) at 500 RPM mixing speed

Validated D-Cell and FDM used to Measure D_{Gel} ± 95% CI for 20+ PFAS

- D-Cell tests spiked at C_{Source} of 10,000 ng•L^{-1}
  - C_{Source} decreased 10–30% over 72 hours
  - Non-steady-state flux required FDM
  - 500 RPM mixing speed
  - δ_{DBL} negligible

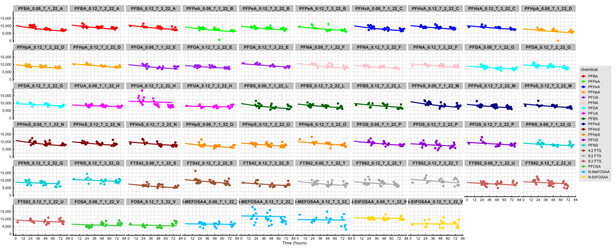

Figure 3: Source D-Cell temporal profiles with FDM fits shows C_{Source} decreases 10-30% over 72 hour test indicating non-steady-state flux.

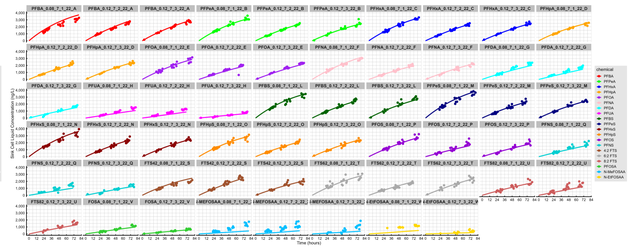

Figure 4: Sink D-Cell temporal profiles with FDM fits shows C_{Sink} increases over 72 hour test with shorter chain PFAS diffusing faster as expected.

- C_{Source} and C_{Sink} used to determine D_{Gel} ± 95% CI for 20+ PFAS with the FDM

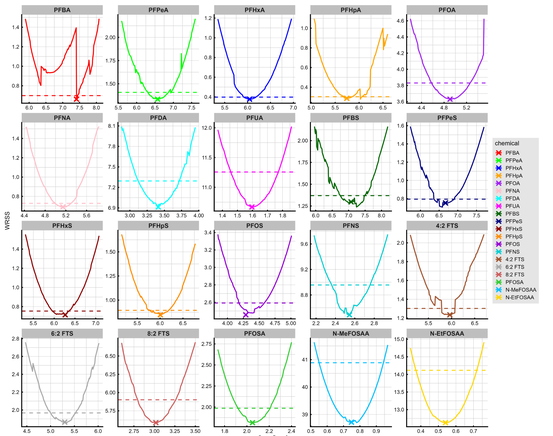

Figure 5: Weighted residual sum of squares (WRSS) error between experimental and simulated PFAS concentration profiles vs. D_{Gel}. Minimum WRSS was best fit D_{Gel} and intersection of error space parabola with horizontal line indicates ± 95% CI for 20 PFAS.

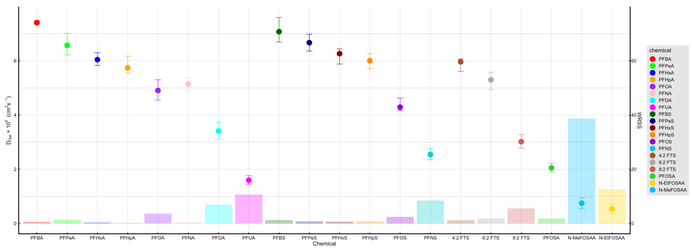

Figure 6: D_{Gel} (circles) ± 95% CIs and WRSS error (bars) for 20+ PFAS

- 20+ PFAS
  - D_{Gel} decreased with increasing chain-length from 7.4 to 0.30 x 10^{-6} cm^2•s^{-1}
  - Larger WRSS indicates poorer FDM fits
- C4–C11 PFCAs
  - 95% CIs ranged from 0.070–0.79 x 10^{-6} cm^2•s^{-1}
- C4–C9 PFSAs
  - 95% CIs ranged from 0.41–0.91 x 10^{-6} cm^2•s^{-1}
- X:2 FTSs, PFOSA, FOSAAs
  - 95% CIs ranged from 0.32–0.64 x 10^{-6} cm^2•s^{-1}

Box Tests with Mixture of 20+ PFAS:

- Batch experiments with four DGT passive samplers
- Aqueous phase sampled at beginning, mid-point, step-change, and end of test to determine time-weighted-average (TWA) PFAS concentrations.
- DGT binding layers extracted at end of test, adjusted for extraction efficiency, and averaged.
  - Errors propogated from binding layer extraction and D_{Gel} to determine DGT 95% CIs

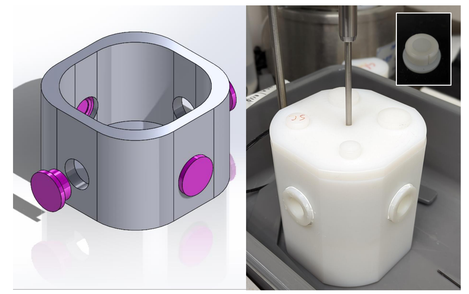

Figure 7: Digital rendering of a DGT Box (left), photo of a box experiment (right), and an assembled DGT passive sampler (inset).

DGT Box test with C_{in} step-change:

- C_{in} initially 500 ng•L^{-1} and step increased to about 3,700 ng•L^{-1} at 96 hours (Figure 8a & 8b).
- Aqueous phase sampled at beginning, step-change, and end of test to determine time-weighted-average (TWA) PFAS concentrations (TWA, Figure 8c & 8d).
- DGT binding layers extracted after 138 hours (DGT, Figure 8c & 8d).
- 10 of 20 PFAS had C_{DGT} ± 30% of C_{TWA} as indicated by the asterisk (Figure 8c & 8d)
  - DGTs captured TWA of C_{in} step-change
- 14 of 20 PFAS have complete mass balances as indicated by total mass recovered of 100% ± 30% (Figure 8e & 8f)
  - Long-chain and hydrophobic PFAS losses attributed to sorption to Box walls

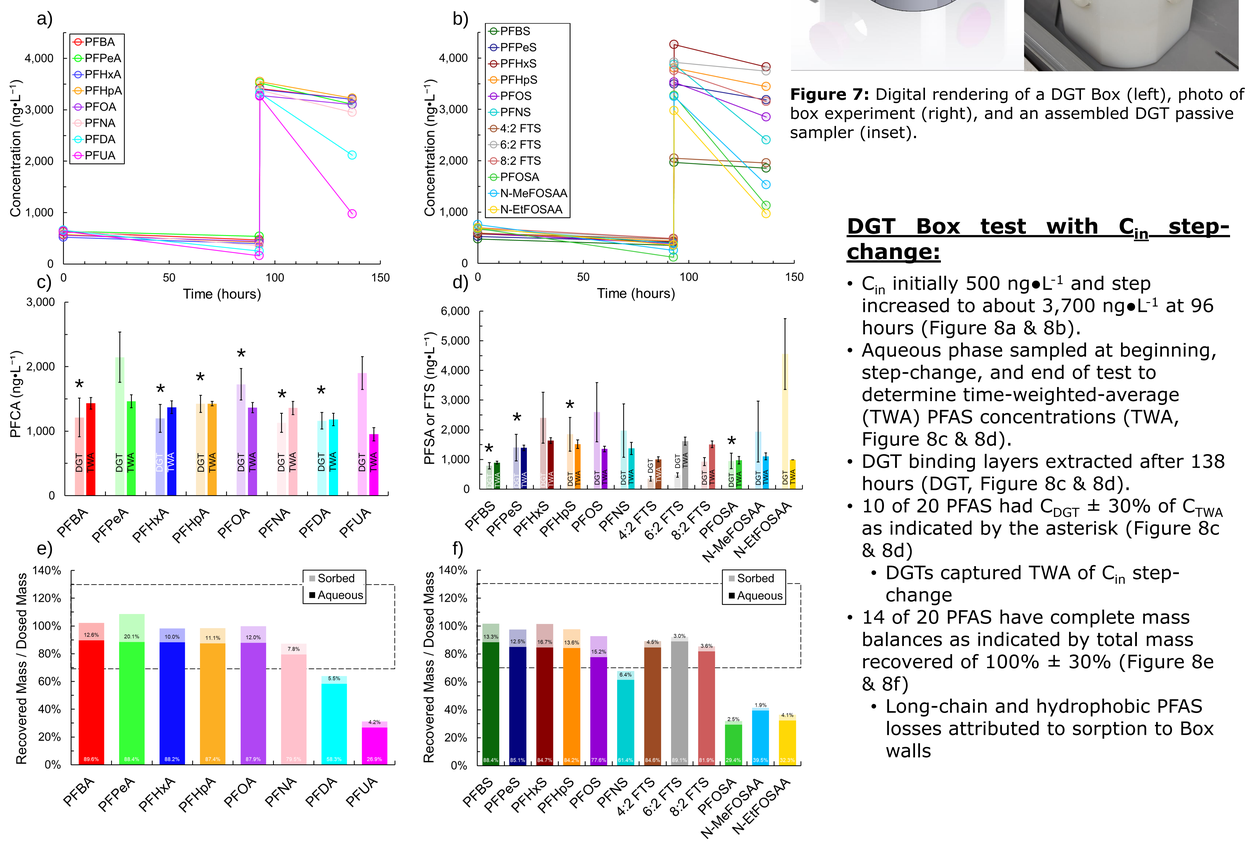

Figure 8: DGT Box test for a step-change at 96 hours. (**a & b**) Aqueous phase PFAS concentrations, (**c & d**) time-weighted-average (TWA) aqueous phase concentrations with 95% CIs and the average of four DGT passive sampler concentrations adjusted for extraction efficiencies (not shown) with 95% CIs which includes errors propogated from D_{Gel} and DGT binding layer extraction, and (**e & f**) mass balances of 20 PFAS with the dashed box indicating ± 30% threshold for completion.

Ongoing Work:

- D-Cell lining with stainless steel to decrease sorption of long-chain and hydrophobic PFAS
- Reducing uncertainty in DGT binding layer extraction efficiencies using mass-labeled PFAS
- Continuous flow box tests to assess hydrodynamics and measure method detection limits (MDLs)

Acknowledgements:

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Reference: [1] Hodges et al., *Environ. Sci. Technol.*, 2023, 57, 26, 9793-9801 | **Contact**: Julian Fairey, julianf@uark.edu