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

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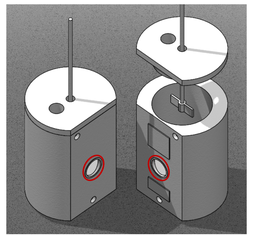
## Introduction

Diffusive gradients in thin-films (DGT) passive sampling devices (PSDs) are kinetic samplers in which target analytes (e.g., PFAS) in the bulk water accumulate in a binding layer following diffusion through (1) a diffusive boundary layer (DBL) of thickness, $\delta_{DBL}$, that can be determined in-situ and (2) a gel layer of known thickness, $\delta_{Gel}$. Following a deployment time, $t_D$, which ranges from several days to a few weeks, PFAS are extracted from the binding layer. The time-weighted average bulk water concentration of each PFAS, $C_{bulk}$ should equal $C_{DGT}$, which is calculated from the extracted PFAS concentration adjusted for extraction efficiency and the PFAS diffusion coefficient in the gel layer, $D_{Gel}$. For 24 target PFAS, we present $D_{Gel}$ values as a function of pH and temperature, binding layer extraction efficiencies from two resins, and comparisons of grab samples to DGT-PSD box tests with $t_D$ of 2-, 6-, and 11-days.

## 1. PFAS Diffusion Coefficients: Two-Compartment Diffusion Cell Tests



**Scheme 1.** A two-compartment diffusion cell showing source and sink compartments with porthole (redlined) for gel layer.

**Objective:** Determine PFAS $D_{Gel}$ values as a function of PFAS chain length, temperature, and pH.

**Background:** The diffusive gel restricts PFAS mass transport between the bulk water and the binding layer to molecular diffusion; therefore, $D_{Gel}$ is needed to determine $C_{DGT}$ for each PFAS.

**Experimental Method:** Diffusion cell tests were conducted to measure PFAS concentration profiles in the source and sink compartments. PFAS diffused across the gel where $\delta_{Gel}$ = 0.08-, 0.12-, 0.16-, 0.20 cm. $D_{Gel}$ was determined using a finite difference model formulated from Fick's first two laws.

1. pH 7 ✦ 22ºC (n = 3)
2. pH 7 ✦ 5ºC (n = 1)
3. pH 5 ✦ 22ºC (n = 1)
4. pH 9 ✦ 22ºC (n = 1)

**Results:**


Increasing chain length
- $D_{Gel}$ about halved from C4 to C10

Decreasing temperature
- $D_{Gel}$ about halved from 25 to 5 °C

C4–C10 PFCAs and C4–C9 PFSAs

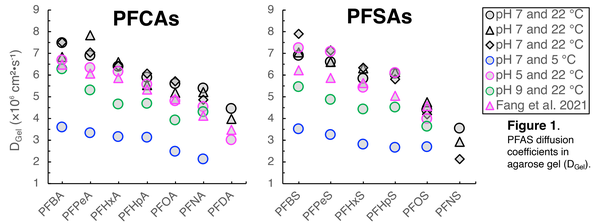



**Figure 1.** PFAS diffusion coefficients in agarose gel ($D_{Gel}$).

## 2a. PFAS Extraction Efficiencies from SBA Resin

**Objective:** Determine PFAS extraction efficiencies from SBA Resin.

**Experimental Conditions:** See section 2b. Utilized strong base anion (SBA) resin.

**Results:**
- SBA resin had low PFAS extraction efficiencies compared to WAX resin (see section 2b)
- SBA resin was not utilized in further tests

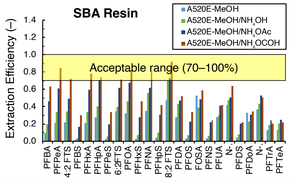



**Figure 2.** PFAS extraction efficiencies from SBA resin.

## 2b. PFAS Extraction Efficiencies from WAX Resin

**Objective:** Determine PFAS extraction efficiencies from WAX resin and identify extraction solvents to achieve ≧ 70 % recovery of at least 12 PFAS.

**Experimental Method:** Utilized weak anion exchange (WAX) resin and four methanol (MeOH) based extraction solvents: (1) **MeOH only**, (2) **MeOH + 50 µM $NH_4OH$**, (3) **MeOH + 50 µM $NH_4OAc$**, and (4) **MeOH + 50 µM $NH_4OCOH$**.

**Results:**
- **MeOH only** produced PFAS extraction efficiencies between 15–65 %
- Salt addition improved PFAS recoveries, with **$NH_4OH$ chosen for Box Tests**

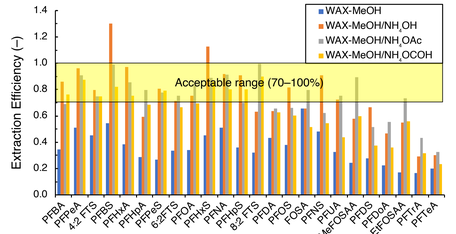
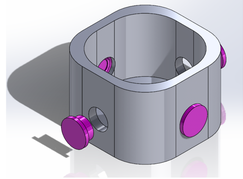



**Figure 3.** PFAS extraction efficiencies from WAX resin. PFAS spiked at 1,000 ng•L$^{-1}$ for 24 hours.

## 3. Assess DGT-PSDs for Determining PFAS Concentrations in Box Tests



**Scheme 2.** Box fabricated of ultrahigh molecular weight polyethylene with working liquid volume of 750 mL. Circular cutouts in wall faces allow for installation of DGT-PSD (magenta).

**Objective:** Demonstrate $C_{DGT}$ within 40% of time weighted average $C_{bulk}$ for at least 12 of 24 target PFAS compounds.

**Experimental Method:** Three box experiments spiked with 24 target PFAS at 5,000 ng•L$^{-1}$. PFAS extracted using using MeOH + 50 µM $NH_4OH$. All tests completed with four DGT-PSDs ($\delta_{Gel}$ = 0.12 cm) and deployment times, $t_D$, of **2-**, **6-**, and **11-days**.

**Results:** Validated test (± 40%)
- $C_{DGT}$ within 40 % of $C_{bulk}$ at:
  - $t_D$ = **2-days**, 5 PFCAs and 5 PFSAs
  - $t_D$ = **6-days**, 4 PFCAs and 4 PFSAs
  - $t_D$ = **11-days**, 4 PFCAs and 4 PFSAs
- Proof-of-concept for quantifying PFAS with DGT-PSDs

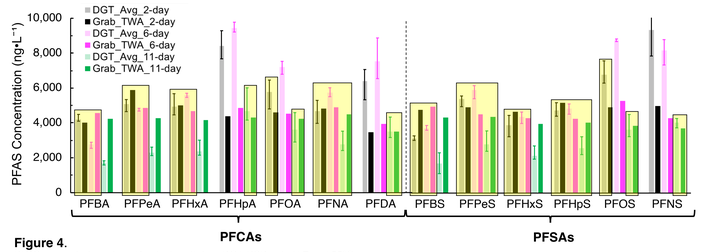



**Figure 4.** PFAS concentrations from Box tests with four DGT-PSDs at pH 7 and 22ºC.

## Future Work

- Diffusion cell tests to assess the impact of conductivity on analyte mass transport through agarose gel
- Extraction efficiency tests to quantify PFAS uptake and recovery with WAX resin and determine associated uncertainty
- Box experiments with lower initial PFAS concentrations (100–500 ng•L$^{-1}$ ) to assess WAX binding layers

**Reference:** Fang et al., *Environ. Sci. Technol.*, 2021, 55, 14, 9548-9556.

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