

## Bench Test of the Dual Membrane Passive Diffusion Sampler for Per & Polyfluoroalkyl Substances (PFAS)

### Purpose:

Controlled laboratory tests were conducted to validate that samples acquired using the Dual Membrane Passive Diffusion Sampler (DMPDB) represent the concentrations of PFAS in the water surrounding the sampler after a designated residence time. Eight PFAS compounds were studied, including; short-chain, medium-chain, and long-chain, to provide a representation across the range of PFAS.

### Test Method:

1. The sampling tests were conducted in a controlled environment using a PVC test chamber filled with approximately 67 Liters of water and the spiked with eight lab certified PFAS, representing long, medium and short chain PFAS.
2. The chamber water was intermittently mixed using a low volume peristaltic lab pump and allowed to stabilize for 6 days after spiking.
3. 6 days after spiking, 9 DMPDB samplers were filled with 500ml each of DI water and installed in the chamber using EON's polypropylene suspension tether assemblies. The samplers were left in place for the specified residence times to allow for the concentration gradient to cause PFAS to diffuse from the chamber fluid, through the membranes and into the samplers. The total water volume for the samplers and the chamber was approximately 71.5 Liters. The water in the samplers comprised about 6.3% of the total water volume.
4. At 21 days after sampler installation, a control sample of the chamber water was obtained through a port midway along the height of the chamber, and decanted into lab supplied HDPE bottles. 3 DMPDB samplers were then removed from the chamber and the contents decanted into lab supplied HDPE bottles. After the 3 samplers were removed and sampled, a second control sample was taken of the chamber water and decanted into lab supplied HDPE bottles. The remaining 6 samplers were left in place.
5. The samples above were sent to Test America and analyzed for the 8 spiked PFAS using method 537M.
6. At 41 days after sampler installation, a control sample was taken from the port in the chamber and decanted into lab supplied HDPE bottles. The remaining 6 DMPDB samplers were then removed from the chamber and the contents decanted into lab supplied HDPE bottles. After the 6 samplers were removed and sampled, another control sample was taken of the chamber water and decanted into lab supplied HDPE bottles.
7. The samples were sent to Test America for analysis of 8 PFAS using method 537M. These first samples were tested at a TestAmerica facility in Sacramento, Ca and the second set were tested at the TestAmerica facility in Lancaster, PA because of the laboratory's PFAS backlog.

### Discussion & Notes:

- Since the test objective was to determine if the sampler concentrations match the concentrations of the chamber water at a point in time, pre-test concentrations of PFAS in the chamber were not collected. Changes that may have occurred in the PFAS concentrations in the chamber were deemed irrelevant as long as the sampler results were similar to the chamber concentrations at each sample event.
- An initial stabilization period was allowed after spiking the chamber water to ensure the PFAS mixing and so that any potentially significant reaction of PFAS with the chamber, would be minimized before adding the samplers.
- Two control samples were acquired at each sample event, one immediately before and one immediately after the samplers were removed from the chamber and sampled. This provided a way to gage repeatability and set a reference for test variability outside of the samplers.

- The control samples were acquired from a port midway along the height of the chamber in such a way that the control samples did not come in contact with any materials other than the test chamber and the HDPE sample bottles.
- The laboratory results from the two control samples taken at each sampler removal can be compared to the results from the sampler contents from that test to determine if the sampler produces results equivalent to the water surrounding the samplers.
- Three of the nine samplers were removed from the chamber and contents tested after 21 days and then the remaining nine samplers were removed and tested after 41 days so that it could be determined whether concentration equilibration between the sampler contents and the chamber water could be achieved in 21 days or if a longer residence was required, and are there any negative effects from a longer residence time within these residence time parameters.
- The data suggests that 21 days residence is adequate to produce a representative PFAS sample. A lower limit has not been established. Additional time may be required in slow recharge wells to accommodate the well returning to “normal” conditions after being disturbed when the samplers are added, however that time is not related to membrane diffusion time.
- There was a slight concentration decrease between the time the first samplers were removed and the second samplers were removed from the chamber. It is significant and positive that the controls and the samplers each tracked similar decreases. The cause for the decrease is unknown but possibilities include; variances in lab processing as the first set of samples were directed to one TestAmerica facility and the second set to another, or disturbing the chamber contents during two rounds of sampling caused a decrease for unknown reasons.
- Some current publications express concern over adsorption of PFAS compounds onto sampling equipment such as bailers and tubing, causing a reduction in the PFAS concentrations in the water samples after the sample is removed from the well. It is hypothesized that the longer residence time required for diffusion sampling allows PFAS in the groundwater to equilibrate with the sampler materials before the sampler is removed from the well, negating the effect of adsorption that may otherwise occur with short contact times experienced by pumping and bailing. The high degree of correlation between sampler results and the controls suggest that adsorption is not affecting DMPDB sample results because of the extended sampler residence time required for passive diffusion sampling.
- The test concentrations in the range of about 20 ng/L to 30ng/L are about half of the EPA threshold of 70 parts per trillion (ppt) (ng/L).
- A second round of sampling, following a similar procedure, was conducted at spiked concentrations from about 1 ng/L to 10 ng/L and showed similar correlations between the controls and the sampler contents, further demonstrating the effectiveness of the DMPDB for sampling PFAS, even at concentrations below 10ng/l.

## Dual Membrane PDB (DMPDB) PFAS Test Data

Compare the DMPDB Sample results to the Control Sample results for each PFAS

Table 1: 20-30 ng/L PFAS

Method: 537 (modified) - Fluorinated Alkyl Substances			Residence Time 21 Days				
PFAS	Laboratory (ng/L)		Control Samples (ng/L)		DMPDB Samples (ng/L)		
Sample ID>	RL	MDI	4MC-16	4MC-26	4M4-16	4M5-16	4U5-16
6:2-Fts	1.75	0.87	29	30	28	30	28
Perfluoro-Octanesulfonate	1.75	0.35	18	20	20	21	19
Perfluorobutanesulfonic Acid	0.87	0.26	36	36	34	33	34
Perfluoroheptanoic acid	0.87	0.35	27	28	29	30	26
Perfluorohexanesulfonic Acid	1.75	0.35	29	27	24	27	26
Perfluorohexanoic acid	1.75	0.35	30	31	31	31	30
Perfluorooctanoic acid	0.87	0.26	37	35	33	35	36
Perfluoropentanoic acid	5.3	1.8	30	30	30	29	29

Table 2: 20-30 ng/L PFAS

Method: 537 (modified) - Fluorinated Alkyl Substances			Residence Time 41 Days							
PFAS	Laboratory (ng/L)		Control Samples (ng/L)		DMPDB Samples (ng/L)					
Sample ID>	RL	MDI	4MC-36	4MC-46	4M5-16	4L5-26	4U4-16	4MR-16	4L4-16	4M5-26
6:2-Fts	1.75	0.87	25	23	23	21	20	22	21	21
Perfluoro-Octanesulfonate	1.75	0.35	18	17	18	20	17	18	17	16
Perfluorobutanesulfonic Acid	0.87	0.26	30	28	29	29	28	28	29	26
Perfluoroheptanoic acid	0.87	0.35	24	23	23	21	22	22	22	23
Perfluorohexanesulfonic Acid	1.75	0.35	23	23	25	23	23	22	25	23
Perfluorohexanoic acid	1.75	0.35	29	29	27	27	29	26	26	28
Perfluorooctanoic acid	0.87	0.26	32	33	32	32	29	33	29	31
Perfluoropentanoic acid	5.3	1.8	25	25	24	24	23	24	24	25

**Table 3: 1-10 ng/L PFAS**

Method: 537 (modified) - Fluorinated Alkyl Substances			Residence Time: 21 Days										
PFAS	Laboratory (ng/L)		Control Samples (ng/L)		DMPDB Samples (ng/L)								
Sample ID>	RL	MDL	5MC-16	5MC-26	5U4-16	5U5-16	5U5-26	5L4-16	5L5-16	5L5-26	5M4-16	5M5-16	5M5-26
Perfluorobutanoic acid (PFBA)	1.9	0.33	1.3	1.0	1.4	1.2	1.3	1.3	1.4	1.2	1.1	1.4	1.3
qualifier			J B	J B	J B	J B	J B	J B	J B	J B	J B	J B	J B
Perfluorooctanoic acid (PFOA)	1.9	0.81	10	10	9.8	9.8	11	9.8	10	11	9.7	10	9.9
Perfluorooctanesulfonic acid (PFOS)	1.9	0.51	6.5	5.9	5.9	14	6.3	5.8	8.3	6.1	7.3	6.1	6.0
Perfluoropentanoic acid (PFPeA)	1.9	0.47	7.5	7.4	7.6	6.7	7.3	6.9	7.7	7.9	6.7	8.1	7.3
Perfluorohexanoic acid (PFHxA)	1.9	0.55	8.6	8.2	9.1	9.2	8.9	8.5	8.8	8.6	9.0	8.8	8.4
Perfluoroheptanoic acid (PFHpA)	1.9	0.24	7.4	7.0	7.0	7.0	7.0	7.0	7.2	7.0	7.4	6.6	7.1
Perfluorobutanesulfonic acid (PFBS)	1.9	0.19	8.8	8.9	8.2	10	8.9	8.5	9.1	9.3	8.9	8.8	9.5
Perfluorohexanesulfonic acid (PFHxS)	1.9	0.16	7.3	7.5	7.2	7.3	7.0	7.3	7.5	7.3	7.5	7.3	7.2
qualifier			B	B	B	B	B	B	B	B	B	B	B
6:2 FTS	19	1.9	7.2	6.6	7.3	7.1	6.4	6.7	7.1	7.1	6.7	6.1	6.3
qualifier			J	J	J	J	J	J	J	J	J	J	J

**Table 4: Lab Qualifiers and Method Blank for Table 3**

Qualifier	Qualifier Description				
B	Compound was found in the blank and sample.				
J	Result is less than the RL but greater than or equal to the MDL and the concentration is an approximate value.				
QC Method Blank	Result	Qualifier	RL	MDL	Unit
Perfluorobutanoic acid (PFBA)	0.476	J	2.0	0.35	ng/L
Perfluorohexanesulfonic acid (PFHxS)	0.357	J	2.0	0.17	ng/L