

SUPPORTING INFORMATION

A graphene-based hydrogel monolith with tailored surface chemistry for PFAS passive sampling

*Jitka Becanova, Zachary Saleeba, Aidan Stone, Robert H. Hurt, Anna R. Robuck,
Rainer Lohmann*

List of Tables:

Table SI 1 Perfluorinated compounds analyzed using LC-MS/MS method.

Table SI 2 Gradient Mobile Phase Program

Table SI 3 Mass spectrometer (MS) instrumental parameters:

Table SI 4 MS/MS Parameters of target PFAS

Table SI 5 Equilibrium time

Table SI 6 Elution profile

Table SI 7 Mass balance

Table SI 8 Partition coefficient

Table SI 9 PFAS concentration in graphene monolith deployed in Delaware River

Table SI 10 PFAS concentration in grab water samples (Delaware River)

Table SI 11 Method detection limits

List of Figures:

Figure SI 1 Equilibrium time

Figure SI 2 Elution profile

Figure SI 3 TGA analysis of graphene monolith

Figure SI 4 Monolith outer surface morphology

Figure SI 5 XPS characterization of GO precursor

Figure SI 6 High resolution XPS characterization of GO precursor and graphene monolith

Figure SI 7 Field deployment

Liquid chromatography mass spectrometry (LC-MS/MS) analysis

Prior to running a batch of samples, the overall performance of LC-MS instrument was tested by running 3 instrumental blanks (the 600 μL of 4 mM ammonium acetate in LC-MS grade water spiked with 50 μL of surrogate standard and mixed with 350 μL of 4 mM ammonium acetate in LC-MS grade methanol) together with QA/QC instrumental performance check (concentration of native compounds 2 $\text{ng}\cdot\text{mL}^{-1}$). Every batch of samples consisted of 8 samples followed by QA/QC instrumental performance check and instrumental blank. At the end of the day, the calibration curve together with sets of instrumental blanks was analyzed.

PFAS concentration calculation was based on the isotope dilution method of quantitation and was performed by automated data system (Analyst). A list of both, native PFASs as well as their isotope labelled analogues included in the method are presented in Table SI 1.

Method detection limits (MDL) were calculated as the average concentration at which the sample signal:noise ratio is 3 (dilution coefficient applied). If the concentration in the sample was below MDL than $\frac{1}{2}$ of MDL was taken for further calculations. If any samples exceeded the top calibration level, then the sample was diluted and reanalyzed.

Table SI 1 Perfluorinated compounds analyzed using LC-MS/MS method.

Compound Name	Native Abbreviation	Isotope Labeled Abbrev.
Perfluorinated Carboxylates		
Perfluorobutanoate	PFBA	MPFBA
Perfluoropentanoate	PFPeA	M5PFPeA
Perfluorohexanoate	PFHxA	M5PFHxA
Perfluoroheptanoate	PFHpA	M4PFHpA
Perfluorooctanoate	PFOA	M8PFOA
Perfluorononanoate	PFNA	M9PFNA
Perfluorodecanoate	PFDA	M6PFDA
Perfluoroundecanoate	PFUnDA	M7PFUdA
Perfluorododecanoate	PFDoDA	MPFDoA
Perfluorotridecanoate	PFTriDA	
Perfluorotetradecanoate	PFTeDA	M2PFTeDA
Perfluorinated Sulfonates		
Perfluorobutane sulfonate	PFBS	M3PFBS
Perfluorohexane sulfonate	PFHxS	M3PFHxS
Perfluoroheptane sulfonate	PFHpS	
Perfluorooctane sulfonate	PFOS	M8PFOS
Perfluoroalkyl Sulfonamides		
Perfluorobutane sulfonamide	FBSA	
Perfluorooctane sulfonamide	FOSA	M8FOSA
N-methylperfluoro-1-octanesulfonamid	N-MeFOSA	d-N-MeFOSA
N-ethylperfluoro-1-octanesulfonamid	N-EtFOSA	d-N-EtFOSA

Fluorotelomer Sulfonates		
4:2 fluorotelomer sulfonate	4:2 FtS	M2-4:2 FtS
6:2 fluorotelomer sulfonate	6:2 FtS	M2-6:2 FtS
8:2 fluorotelomer sulfonate	8:2 FtS	M2-8:2 FtS
PFOA Replacement		
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid	HFPO-DA	M3HFPO-DA

LC Conditions

For the analysis, 40 μ L of water or sampler extract was injected on the LC column (45°C) and target compounds were eluted with mobile phase gradient (Table 2) consisted of 2 mM ammonium acetate in water and methanol (flow rate 0.2 mL/min).

Table SI 2 Gradient Mobile Phase Program

mobile phase / time (min)	A (%) - 2mM ammonium acetate in water	B (%) - 2mM ammonium acetate in methanol
0.0	60	40
0.5	60	40
3.5	45	55
10.0	15	85
13.0	15	85
13.1	60	40
16.0	60	40

MS/MS Conditions

The triple quadrupole tandem mass spectrometer was operated in multiple reaction monitoring (MRM) mode using negative electrospray ionization (ESI-). Instrument parameters are shown in Table SI 3 and compound specific MS/MS parameters are summarized in Table SI 4.

Table SI 3 Mass spectrometer (MS) instrumental parameters:

Curtain Gas (CUR)	30
Collision Gas (CAD)	medium
IonSpray Voltage (IS)	-4500 V
Temperature (TEM)	400°C
Ion Source Gas 1 (GS1)	30
Ion Source Gas 2 (GS2)	30

Table SI 4 MS/MS Parameters of target PFAS

Analyte	Type	Internal	MRM transitions	Declasteration	Collision
---------	------	----------	-----------------	----------------	-----------

		Standard		potential (V)	Energy (V)
PFBA	Target	MPFBA	213 → 169; -	-20	-12; -
PFPeA	Target	M5PFPeA	263 → 219; -	-40	-10; -
PFHxA	Target	M5PFHxA	313 → 269; 119	-35	-13; -26
PFHpA	Target	M4PFHpA	363 → 319; 169	-55	-15; -24
PFOA	Target	M8PFOA	413 → 369; 169	-45	-17; -24
PFNA	Target	M9PFNA	463 → 419; 219	-40	-15; -24
PFDA	Target	M6PFDA	513 → 469; 219	-50	-18; -26
PFUnDA	Target	M7PFUnDA	563 → 519; 269	-45	-20; -26
PFDoDA	Target	M2PFDoA	613 → 569; 319	-45	-22; -26
PFTTrDA	Target	M2PFDoA	663 → 619; 169	-50	-19; -36
PFTeDA	Target	MPFTeDA	713 → 669; 169	-65	-22; -34
PFBS	Target	M3PFBS	299 → 80; 99	-45	-70; -40
PFHxS	Target	M3PFHxS	399 → 80; 99	-55	-60; -45
PFHpS	Target	M3PFHxS	449 → 80; 99	-50	-100; -85
PFOS	Target	M8PFOS	499 → 80; 99	-55	-120; -90
FBSA	Target	MFOSA	298 → 78; 64	-40	-50; -90
FOSA	Target	MFOSA	498 → 78; 64	-105	-84; -130
MeFOSA	Target	d-N-MeFOSA	512 → 169; 219	-95	-36; -34
EtFOSA	Target	d-N-EtFOSA	526 → 169; 219	-90	-36; -34
4:2 FTS	Target	M2-4:2FTS	327 → 307; 81	-50	-28; -40
6:2 FTS	Target	M2-6:2FTS	427 → 407; 80	-50	-32; -42
8:2 FTS	Target	M2-8:2FTS	527 → 507; 71	-50	-40; -46
HFPO-DA	Target	M3HFPO-DA	329 → 169; 285	-45	-12; -20

Water extraction method:

Water extracts were prepared following a modified protocol after Taniyasu et al. 2005 using a PFAS-Free Thermo Scientific Dionex AutoTrace 280. 500 ml of surface water was spiked with 10 ng of isotopically-labelled surrogate using a mix incorporating the Wellington MPFAC-24ES with added HFPO-DA. Spiked samples were loaded onto 150 mg/6cc Oasis WAX SPE cartridges at a flow rate of 5 mL/min. Cartridges were dried for 15 min and rinsed with 4mL of 0.1% ammonium acetate. Sample extracts were eluted with 4mL methanol followed by 4 mL of basic methanol (0.1% NH₄OH in methanol). Combined extracts were evaporated to 1mL, and an aliquot diluted in 2.5mM ammonium acetate buffer for a final sample makeup of 3:1 aqueous:organic. Samples were characterized for legacy and novel PFAS using a Thermo-Fisher Orbitrap Fusion with a heated electrospray ionization source in negative mode.

Table SI 5 Equilibrium time: amount of individual PFAS in graphene monoliths (n=7) exposed to PFAS in water for various time (0-48 hrs.)

	PFAS amount ng/sampler						
	Exposure time (hour)						
	0	1	2	8	12	24	48
PFBA	0.226	0.869	1.31	1.78	2.59	2.32	2.57
PFPeA	0.085	0.408	0.559	1.15	1.41	1.27	1.21
PFHxA	0.011	0.727	0.838	0.933	1.58	1.42	1.50
PFHpA	0.063	1.08	1.25	1.74	2.97	2.85	3.16
PFOA	0.011	2.69	3.25	3.81	6.78	6.05	6.71
PFNA	0.060	7.59	7.38	14.5	16.4	15.2	15.8
PFDA	<MDL	8.12	11.2	11.6	19.3	21.7	21.1
PFUnDA	<MDL	5.59	12.6	11.1	15.9	14.6	16.2
PFDoDA	<MDL	1.84	7.68	13.9	13.5	12.14	13.4
PFTTrDA	<MDL	0.496	6.90	10.1	8.1	7.70	8.53
FOSA	0.018	7.80	5.84	16.3	32.4	30.2	31.5
HFPO-DA	0.098	0.557	0.894	1.27	1.78	1.76	1.95
PFBS	0.023	0.714	0.973	1.34	1.78	1.70	1.89
PFHxS	0.016	1.65	2.91	3.59	4.03	3.88	4.30
PFOS	0.070	8.83	10.1	16.8	22	21.6	21.0
6:2 FTS	0.024	4.32	8.16	9.87	10.2	9.58	10.6

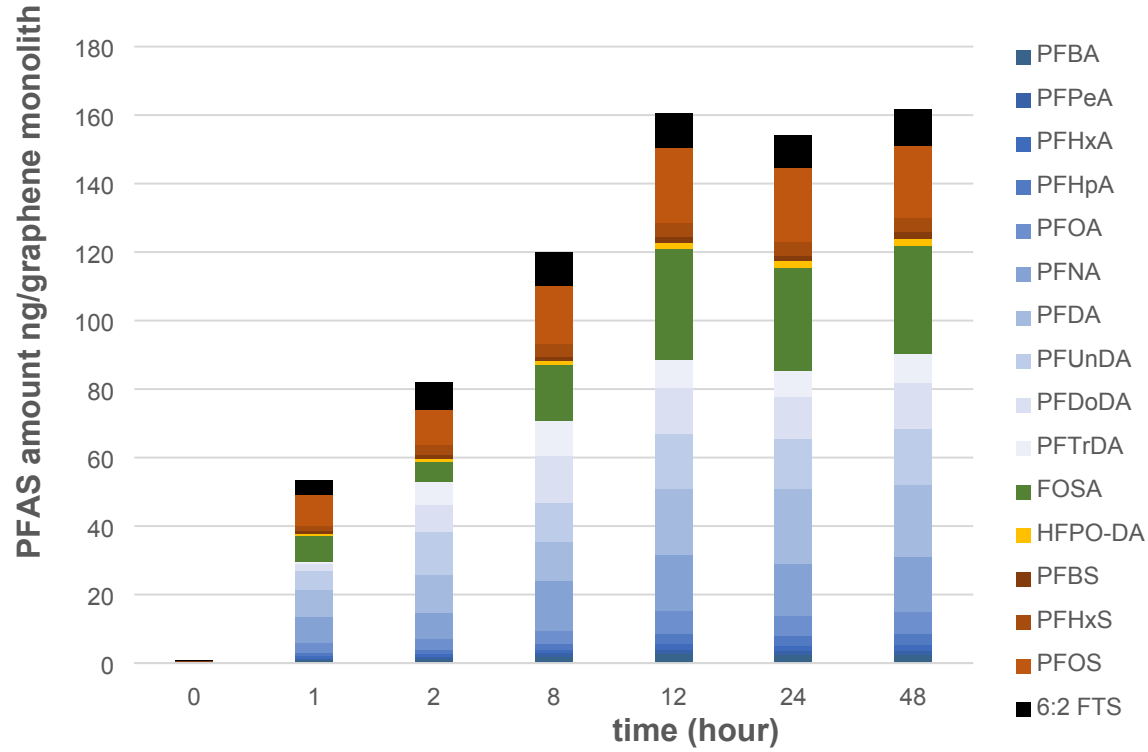


Figure SI 1 Equilibrium time: amount of individual PFAS in 7 graphene monoliths exposed to PFAS in water for various time (0-48 hrs.)

Table SI 6 Elution profile: concentration of individual PFAS in three methanolic fraction (1st, 2nd & 3rd) – each fraction constitutes of 2mL of methanol; extraction time 1hour.

	PFAS concentration ng/extract								
	GH sampler #6			GH sampler #7			GH sampler #8		
	1 st	2 nd	3 rd	1 st	2 nd	3 rd	1 st	2 nd	3 rd
PFBA	0.869	1.78	0.074	1.38	1.31	0.131	2.59	0.226	0.144
PFPeA	0.808	1.15	<MDL	0.818	0.559	0.089	1.41	<MDL	<MDL
PFHxA	0.727	0.933	<MDL	0.936	0.838	0.168	1.58	0.011	<MDL
PFHpA	1.38	1.74	0.034	1.37	1.25	0.06	2.97	<MDL	<MDL
PFOA	2.69	3.81	0.019	3.03	3.25	0.213	6.78	<MDL	<MDL
PFNA	7.59	14.5	0.261	9.81	7.38	0.401	16.4	<MDL	<MDL
PFDA	11.2	11.6	0.122	9.19	8.12	0.189	22.3	<MDL	<MDL
PFUnDA	16.6	11.1	0.062	14.4	5.59	0.102	15.9	<MDL	<MDL
PFDoDA	21.8	3.99	0.513	21.4	1.84	0.576	13.5	<MDL	<MDL
PFTTrDA	22.9	1.08	0.16	9.44	0.496	0.526	8.1	<MDL	<MDL
FOSA	27.8	16.3	0.322	25.1	5.84	0.638	32.4	0.018	<MDL
HFPO-DA	0.557	1.27	0.027	1.09	0.894	0.047	1.78	0.098	<MDL
PFBS	0.714	1.34	0.034	1.16	0.973	0.053	1.78	0.023	<MDL
PFHxS	2.65	3.59	0.047	2.87	2.91	0.159	4.03	0.016	<MDL
PFOS	8.83	16.8	0.207	7.08	10.1	0.253	22	<MDL	<MDL
6:2 FTS	4.32	9.87	0.279	5.14	8.16	0.142	10.2	0.024	0.036

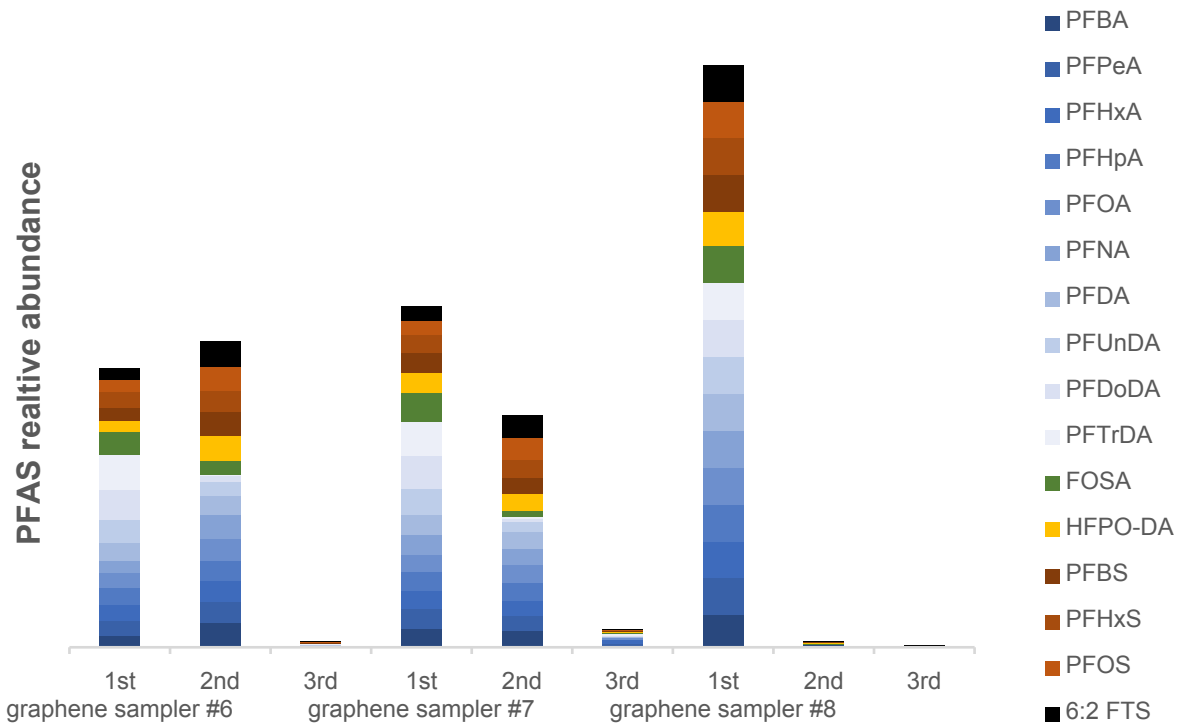


Figure SI 2 Elution profile: relative abundance of individual PFAS in 3 methanolic fraction – each fraction constitutes of 2mL of methanol; extraction time 1hour.

Table SI 7 Mass balance: Amount of individual PFAS in both fraction in µg (water - W) and ng (graphene hydrogel sampler - S) in equilibrium; both phases combined (W+S); fraction (%) of spiked amount calculated.

	units	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTTrDA	PFTeDA
GH # 11_W	µg	16.7	6.60	6.45	7.16	5.36	8.09	4.91	5.12	4.17	1.56	1.33
GH # 12_W	µg	11.8	6.75	6.50	5.60	6.06	5.83	8.40	5.43	5.45	2.22	1.99
GH # 13_W	µg	13.2	6.10	6.25	6.25	6.21	4.77	5.21	5.19	4.25	1.66	2.36
Average_W	µg	13.9	6.49	6.40	6.34	5.88	6.23	6.17	5.25	4.62	1.81	1.89
GH # 11_S	ng	5.51	2.45	3.41	5.53	10.4	40.5	73.8	124	147	98.3	27.7
GH # 12_S	ng	4.68	2.85	2.2	3.81	9.28	26.4	50.3	83.8	104	85.3	36.4
GH # 13_S	ng	5.07	2.51	2.67	4.01	9.48	21.9	56.0	93.1	140	110	35.7
Average_S	ng	5.1	2.6	2.8	4.5	9.7	29.6	60.0	100	130	98.0	33.3
W + S	ug	13.91	6.49	6.41	6.34	5.89	6.26	6.23	5.35	4.75	1.91	1.93
spiked	ug	11.69	8.44	8.26	9.88	5.56	8.94	9.01	8.77	8.09	6.26	4.17
fraction	%	119	77	78	64	106	70	69	61	59	31	46

	units	FOSA	MeFOSA	EtFOSA	HFPO-DA	PFBS	PFHxS	PFOS
GH # 11_W	µg	3.26	3.19	1.06	6.25	6.00	4.92	4.02
GH # 12_W	µg	5.40	1.83	1.74	8.45	4.42	5.01	3.19
GH # 13_W	µg	3.44	1.06	0.72	6.95	4.14	4.31	4.25
Average_W	µg	4.03	2.01	1.18	7.22	4.85	4.74	3.82
GH # 11_S	ng	88.6	12.9	11.5	2.33	2.97	10.2	37.7
GH # 12_S	ng	103	40.3	52.5	2.37	2.52	5.84	24.2
GH # 13_S	ng	105	55.7	51.2	2.63	2.15	8.6	15.5
Average_S	ng	98.9	36.3	38.4	2.4	2.5	8.2	25.8
W + S	ug	4.13	2.06	1.21	7.22	4.86	4.75	3.85
spiked	ug	5.30	5.30	3.15	5.82	5.08	4.77	5.09
fraction	%	78	39	38	124	96	100	76

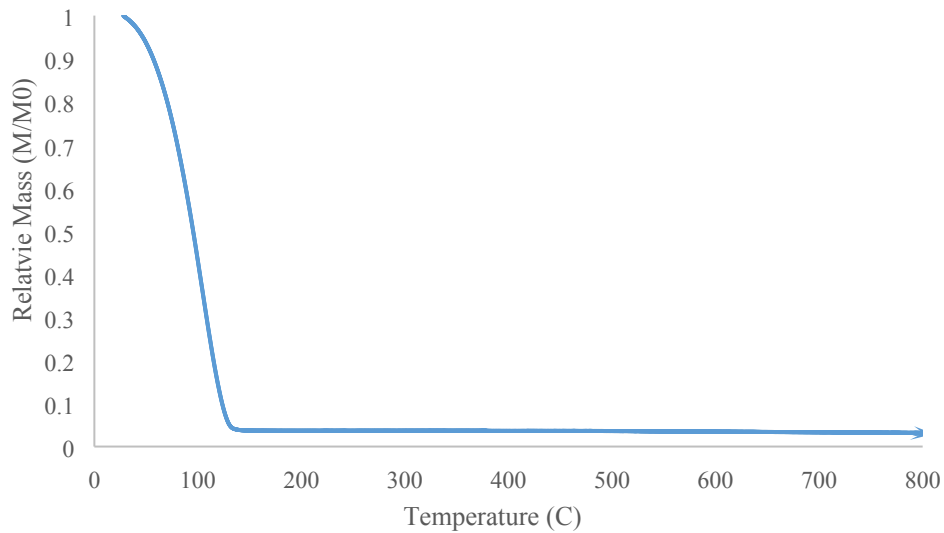


Figure SI 3: TGA analysis of graphene monolith. Thermogravimetric profile of as-produced graphene hydrogel monolith in N_2 flow showing ~96% mass decrease associated with evaporative water loss.

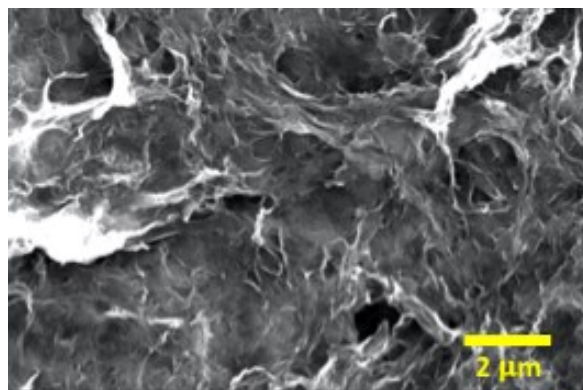


Figure SI 4: Monolith outer surface morphology. Scanning electron micrograph of the side surface of a graphene monolith device showing a skin-like layer of higher density than the highly porous interior.

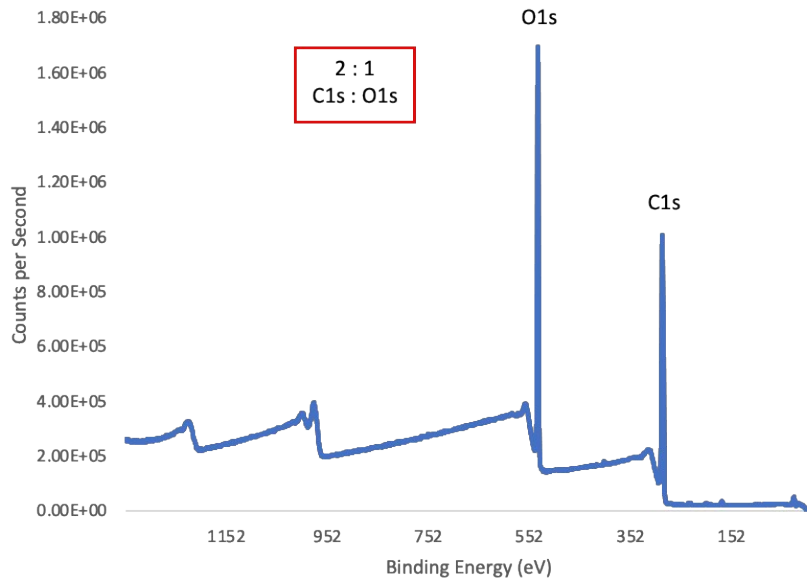


Figure SI 5: XPS characterization of GO precursor. X-ray photoelectron spectrum of graphene oxide nanosheet precursor (measured on a drop cast film) used to estimate starting C:O atomic ratio.

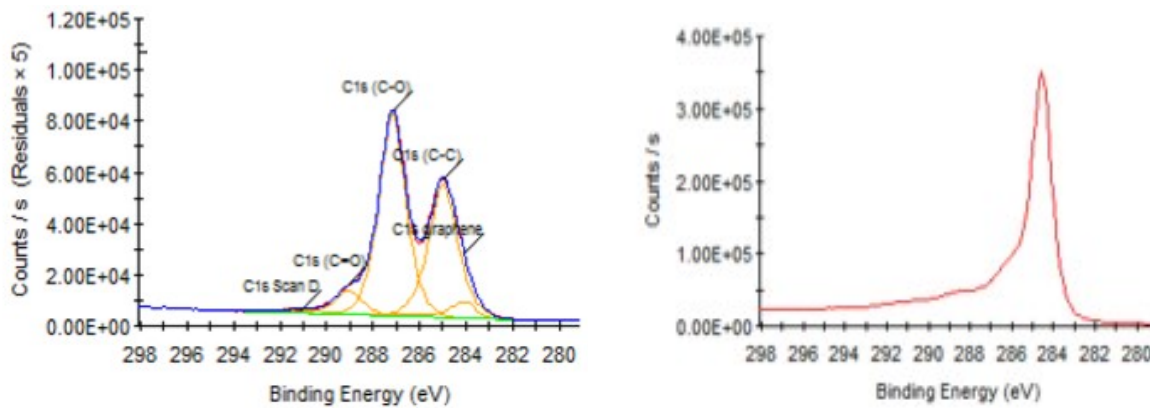


Figure SI 6: High resolution XPS characterization of graphene oxide precursor and fabricated graphene monolith. Left: XPS on C1s orbital on drop cast graphene oxide; Left: High resolution XPS on C1s orbital on freeze dried graphene monolith. Comparison shows the large decrease in C-O and C=O bonds during hydrothermal synthesis of the monolith, leaving a high fraction of C-C bonds.

Table SI 8 Partition coefficient: pristine graphene hydrogel sampler water partition coefficient (K_{sw}) of individual PFASs concentration of individual PFASs in graphene hydrogel (ng/g) and water (ng/mL)

	GRAPHENE HYDROGEL SAMPLER					WATER					PARTITION COEFFICIENT	
	Concentration (ng/g)					Concentration (ng/mL)					K_{sw}	Log $K_{sw} \pm$ SD
	EXP #11	EXP #12	EXP #13	Mean	relative SD	EXP #11	EXP #12	EXP #13	Mean	relative SD		
PFBA	459	390	423	424	7%	33.4	23.6	26.4	27.8	15%	15.2	1.18 ± 0.07
PFPeA	204	238	209	217	7%	13.2	13.5	12.2	13.0	4%	16.7	1.22 ± 0.03
PFHxA	284	183	223	230	18%	12.9	13.0	12.5	12.8	2%	18.0	1.25 ± 0.07
PFHpA	461	318	334	371	17%	14.3	11.2	12.5	12.7	10%	29.3	1.47 ± 0.08
PFOA	867	773	790	810	5%	10.7	12.1	12.4	11.7	6%	69.0	1.84 ± 0.03
PFNA	3375	2200	1825	2467	27%	16.1	11.6	9.5	12.4	22%	199.0	2.3 ± 0.13
PFDA	6150	4192	4667	5003	17%	9.7	16.7	10.3	12.2	26%	409.3	2.61 ± 0.12
PFUnDA	10333	6983	7758	8358	17%	10.0	10.7	10.2	10.3	3%	811.5	2.91 ± 0.07
PFDoDA	12250	8667	11667	10861	14%	8.0	10.7	8.2	9.0	14%	1208.6	3.08 ± 0.08
PFTTrDA	8192	7108	9192	8164	10%	2.9	4.3	3.1	3.4	18%	2382.5	3.38 ± 0.08
PFTeDA	2308	3033	2975	2772	12%	2.6	3.9	4.7	3.7	23%	745.2	2.87 ± 0.1
PFBS	248	208	179	212	13%	12.0	8.8	8.3	9.7	17%	21.8	1.34 ± 0.08
PFHxS	850	487	717	684	22%	9.8	10.0	8.6	9.5	7%	72.3	1.86 ± 0.09
PFHpS	39.2	40.0	51.7	43.6	13%	0.4	0.3	0.3	0.3	16%	142.2	2.15 ± 0.08
PFOS	3142	2017	1292	2150	35%	8.0	6.3	8.5	7.6	12%	283.3	2.45 ± 0.14
FOSA	7383	8583	8750	8239	7%	6.4	10.6	6.7	7.9	25%	1046.9	3.02 ± 0.1
MeFOSA	1075	3358	4642	3025	49%	6.4	3.6	4.6	4.9	24%	822.0	2.91 ± 0.21
EtFOSA	958	4375	4267	3200	50%	2.1	3.4	1.3	2.3	37%	1407.6	3.15 ± 0.21
HFPO-DA	194	198	219	204	5%	12.5	16.9	13.9	14.4	13%	14.1	1.15 ± 0.06
6:2 FTS	2417	1908	1942	2089	11%	17.3	14.1	17.7	16.4	10%	127.6	2.11 ± 0.06

Table SI 10 PFAS concentration in water in Delaware River at sites A, B & C (ng/L)

Compound	Concentration ng/L		
	Site A	Site B	Site C
PFBA	6.78	<MDL	<MDL
PFPeA	7.88	6.24	3.58
PFHxA	9.16	8.47	4.11
PFHpA	2.07	2.48	1.01
PFOA	7.75	38.55	5.19
PFNA	3.05	44.83	12.14
PFDA	0.82	1.22	0.37
PFUnDA	0.69	3.19	1.51
PFDoDA	<MDL	<MDL	<MDL
PFTTrDA	<MDL	0.46	<MDL
PFBS	3.24	2.52	1.83
PFPeS	0.24	0.51	0.12
PFHxS	1.70	4.52	1.57
PFHpS	<MDL	0.27	<MDL
PFOS	4.98	14.34	4.98
PFNS	<MDL	<MDL	<MDL
PFDS	<MDL	<MDL	<MDL
4:2 FTS	<MDL	2.16	0.16
6:2 FTS	4.86	15.34	8.73
8:2 FTS	<MDL	<MDL	<MDL
N-MeFOSAA	<MDL	<MDL	<MDL
N-EtFOSAA	<MDL	<MDL	<MDL
HFPO-DA	<MDL	0.26	<MDL

Table SI 11 Method detection limit (MDL) for PFAS concentration in water (ng/L) derived by graphene sampler detection limits (DL, ng/sampler) and partitioning coefficients (K_{SW})

Compound	DL (ng/sampler)	MDL (ng/L)
PFBA	0.13	73.7
PFPeA	0.12	27.8
PFHxA	1.11	116
PFHpA	0.11	4.72
PFOA	0.45	4.38
PFNA	1.14	5.83
PFDA	0.54	1.77
PFUnDA	0.06	0.15
PFDoDA	0.01	0.02
PFTTrDA	0.04	0.15
N-MeFOSAA	0.13	NA*
N-EtFOSAA	0.13	NA
HFPO-DA	0.18	22.7
4:2 FTS	0.13	12.5
6:2 FTS	0.12	3.49
8:2 FTS	0.03	0.26
PFBS	0.13	13.7
PFPeS	0.13	NA
PFHxS	0.13	3.22
PFHpS	0.13	2.18
PFOS	0.06	0.37
PFNS	0.13	NA
PFDS	0.13	NA

* K_{SW} not determine

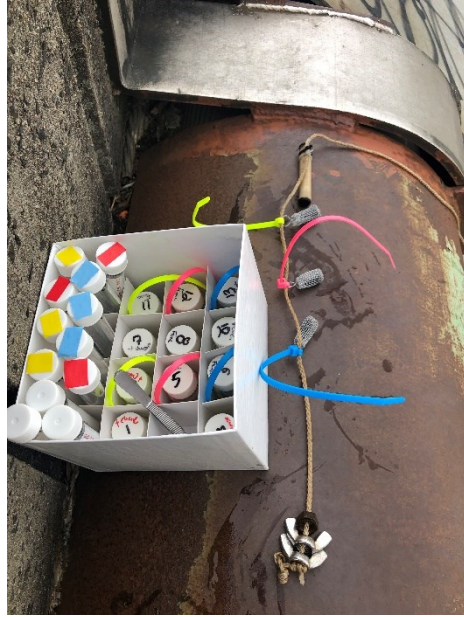


Figure SI 7 Field deployment: graphene sampler (triplicates) deployed in Delaware River