

*Supporting Information for:*

**Storms Mobilize Organophosphate Esters, Bisphenols, PFASs, and Vehicle-derived  
Contaminants to San Francisco Bay Watersheds**

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February 24, 2024

Manuscript in preparation for submission to:  
***Environmental Science: Processes & Impacts***

44 pages, 24 tables, and 7 figures

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67	FieldCalcType indicate the calculation used to evaluate variability across lab and field	
68	replicates, respectively, with the corresponding values in LabCalcValue and FieldCalcValue,	
69	respectively. QA codes are consistent with those used by the California Environmental Data	
70	Exchange Network (CEDEN):	
71	<a href="http://ceden.org/CEDEN_Checker/Checker/DisplayCEDENLookUp.php?List=QALookUp">http://ceden.org/CEDEN_Checker/Checker/DisplayCEDENLookUp.php?List=QALookUp</a> ,	
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94 separate (c) compounds analyzed in all samples vs. (e) in only 2 of the reference sites and 14  
95 of the urban stormwater samples. Non-detects (i.e., concentrations <MDL) are not plotted  
96 (i.e., represented as a concentration of zero) (see **Table S8** for MDL values). Sample names  
97 indicate SiteType\_SiteName\_Year, where OB = open Bay sites, NF = near field sites, Ref =  
98 reference sites, and US = urban stormwater sites. Site types are also separated by a  
99 horizontal black line. Site order from top to bottom is based on 1) the percent of impervious  
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104 (i.e., represented as a concentration of zero) (see **Table S16** for MDL values). Sample  
105 names indicate SiteType\_SiteName\_Year, where Ref = reference sites and US = urban  
106 stormwater sites. Site types are also separated by a horizontal black line. Site order from top  
107 to bottom is based on 1) the percent of impervious landcover in the watershed that  
108 corresponds to each sampling site (see **Table S2**), and 2) chronological order for repeat  
109 sampling at a given site (see **Table S3**). .....38

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111 stormwater samples, by individual analyte. Non-detects (i.e., concentrations <MDL) are not  
112 plotted (i.e., represented as a concentration of zero) (see **Table S16** for MDL values).  
113 Sample names indicate SiteType\_SiteName\_Year, where Ref = reference sites and US =  
114 urban stormwater sites. Site types are also separated by a horizontal black line. Site order  
115 from top to bottom is based on 1) the percent of impervious landcover in the watershed that  
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120 OPEs, (c) Chlorinated OPEs, (d) ITPs, and (e) TBPPs. Non-detects (i.e., concentrations  
121 <MDL) are not plotted (i.e., represented as a concentration of zero) (see **Table S16** for MDL  
122 values). Sample names indicate SiteType\_SiteName\_Year, where Ref = reference sites and  
123 US = urban stormwater sites. Site types are also separated by a horizontal black line. Site  
124 order from top to bottom is based on 1) the percent of impervious landcover in the  
125 watershed that corresponds to each sampling site (see **Table S2**), and 2) chronological order  
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130 names indicate SiteType\_SiteName\_Year, where Ref = reference sites and US = urban  
131 stormwater sites. Site types are separated by a horizontal black line. Site order from top to  
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138 SiteType\_SiteName\_Year, where Ref = reference sites and US = urban stormwater sites.  
139 Site types are separated by a horizontal black line. Site order from top to bottom is based on  
140 1) the percent of impervious landcover in the watershed that corresponds to each sampling  
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145 with detection frequency (DF) > 15%. Concentrations for PFDoDA are semi-quantitative.  
146 Detection frequencies are based on 26 urban stormwater samples, except for PFPrA and  
147 PFBA (n=18). Boxes indicate 25<sup>th</sup> – 75<sup>th</sup> percentile, whiskers indicate 10<sup>th</sup>-90<sup>th</sup> percentile,  
148 and a point is plotted for every sampling event, with all non-detects (i.e., concentrations  
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154 **Text S1. Chemicals and Reagents**

155

156 All analytical standards and suppliers are detailed in **Table S1**. Additional solvents and reagents  
157 are detailed below for each analytical method/laboratory.

158

159 Text S1.1. Stormwater Tracer CECs

160 Methanol (MeOH, LCMS grade), ethanol (absolute, 200 proof), and formic acid (HPLC grade)  
161 were obtained from Fisher Scientific (Fair Lawn, NJ, USA). A Thermo Barnstead Nanopure  
162 Diamond UV water purification system (Dubuque, IA, USA) was used to provide 18 MΩ water.  
163 Near-field and open Bay field blanks consisted of Optima™ LCMS grade water from Fisher  
164 Scientific (Hanover Park, IL).

165

166 Text S1.2. Organophosphate Esters and Bisphenols

167 HPLC-grade solvents (hexane, DCM, Optima water) were purchased from Fisher Scientific  
168 (Hanover Park, IL).

169

170 Text S1.3. PFASs (Colorado School of Mines)

171 Optima® grade methanol, Optima® grade isopropyl alcohol, 0.01% ammonium hydroxide,  
172 Optima® LC/MS grade water, LC/MS grade 2,2,2-trifluoroethanol were purchased from Fisher  
173 Scientific (Hanover Park, IL).

174

175 Text S1.4. PFASs (Eurofins)

176 Acetonitrile and Methanol, HPLC Grade, Fisher. Formic Acid, CH<sub>2</sub>O<sub>2</sub>, Fisher PN A118P-  
177 500Acetic acid, glacial, Fisher PN BP2401-500. Ammonium hydroxide (NH<sub>4</sub>OH), concentrated,  
178 reagent grade.

179

180

181

182

**Table S1.** Analytical, surrogate, and internal standards – abbreviations, CAS numbers, and suppliers.

<b>Compound</b>	<b>Abbreviation</b>	<b>CAS No.</b>	<b>Supplier</b>
<i>Stormwater Tracer CECs (SWCECs)</i>			
6PPD-quinone (98.8% purity)	6PPDQ	2754428-18-5	HPC (Atlanta, GA)
1,3-dicyclohexylurea	DCU	2387-23-7	Sigma Aldrich (St. Louis, MO)
1,3-diphenylguanidine	DPG	102-06-7	Sigma Aldrich (St. Louis, MO)
Hexa(methoxymethyl)melamine	HMMM	3089-11-0	Combi-Blocks Ltd (San Diego, CA)
N-cyclohexyl-1,3-benzothiazol-2-amine	NCBA	28291-75-0	Enamine (Monmouth Junction, NJ)
Caprolactam	--	105-60-2	Sigma Aldrich (St. Louis, MO)
Benzotriazole	BTR	95-14-7	Sigma Aldrich (St. Louis, MO)
5-methyl-1-H-benzotriazole	5-methyl-1H-BTR	136-85-6	Sigma Aldrich (St. Louis, MO)
2-amino-benzothiazole	2-NH <sub>2</sub> -BTH	136-95-8	Sigma Aldrich (St. Louis, MO)
2-hydroxy-benzothiazole	2-OH-BTH	934-34-9	Sigma Aldrich (St. Louis, MO)
2-(4-morpholinyl)benzothiazole	2,4-MoBT	4225-26-7	Sigma Aldrich (St. Louis, MO)
Clothianidin	--	210880-92-5	Sigma Aldrich (St. Louis, MO)
Imidacloprid	--	138261-41-3	Sigma Aldrich (St. Louis, MO)
Thiamethoxam	--	153719-23-4	Sigma Aldrich (St. Louis, MO)
Carbendazim	--	10605-21-7	Sigma Aldrich (St. Louis, MO)
Diuron	--	330-54-1	Sigma Aldrich (St. Louis, MO)
Iprodione	--	36734-19-7	Sigma Aldrich (St. Louis, MO)
Prometon	--	1610-18-0	Sigma Aldrich (St. Louis, MO)
Caffeine	--	58-08-2	Sigma Aldrich (St. Louis, MO)
Cotinine	--	486-56-6	Sigma Aldrich (St. Louis, MO)
Diclofenac	--	15307-86-5	Sigma Aldrich (St. Louis, MO)
N,N-diethyl-meta-toluamide	DEET	134-62-3	Sigma Aldrich (St. Louis, MO)
Mecoprop	--	93-65-2	Sigma Aldrich (St. Louis, MO)
Pentachlorophenol	PCP	87-86-5	Sigma Aldrich (St. Louis, MO)
Cetirizine	--	83881-51-0	Sigma Aldrich (St. Louis, MO)
Ibuprofen	--	15687-27-1	Sigma Aldrich (St. Louis, MO)
Triclosan	--	3380-34-5	Toronto Research Chemicals (North York, ON, Canada)
<i>SWCEC Internal Standards</i>			
5-methyl-1-H-benzotriazole-d <sub>6</sub>	--	1246820-65-4	Toronto Research Chemicals (North York, ON, Canada)
6PPDQ-d <sub>5</sub>	--	--	HPC (Atlanta, GA)

Caffeine- <sup>13</sup> C <sub>3</sub>	--	78072-66-9	Sigma Aldrich (St. Louis, MO)
Carbendazim-d <sub>4</sub>	--	291765-95-2	CDN Isotopes (Pointe-Claire, QC, Canada)
Cetirizine-d <sub>8</sub>	--	2070015-04-0	Toronto Research Chemicals (North York, ON, Canada)
Cotinine-d <sub>3</sub>	--	110952-70-0	Sigma Aldrich (St. Louis, MO)
DEET-d <sub>7</sub>	--	1219799-37-7	CDN Isotopes (Pointe-Claire, QC, Canada)
Diclofenac-d <sub>4</sub>	--	153466-65-0	Toronto Research Chemicals (North York, ON, Canada)
Diphenyl-d <sub>10</sub> -urea	--	108009-46-7	Toronto Research Chemicals (North York, ON, Canada)
Diuron-d <sub>6</sub>	--	1007536-67-5	Toronto Research Chemicals (North York, ON, Canada)
Ibuprofen-d <sub>3</sub>	--	121662-14-4	Sigma Aldrich (St. Louis, MO)
Imidacloprid-d <sub>4</sub>	--	1015855-75-0	Toronto Research Chemicals (North York, ON, Canada)
Prometon-d <sub>3</sub>	--	1219803-43-6	CDN Isotopes (Pointe-Claire, QC, Canada)
Triclosan-d <sub>3</sub>	--	1020719-98-5	CDN Isotopes (Pointe-Claire, QC, Canada)
<i>Aryl Organophosphate Esters (OPEs)</i>			
Bisphenol A bis (diphenyl phosphate)	BPA-BDPP	5945-33-5	AccuStandard (New Haven, CT, USA)
2-ethylhexyl-diphenyl phosphate	EHDPP	1241-94-7	AccuStandard (New Haven, CT, USA)
Isodecyl diphenyl phosphate	IDDP	29761-21-5	AccuStandard (New Haven, CT, USA)
Resorcinol bis (diphenyl phosphate)	RBDPP	57583-54-7	AccuStandard (New Haven, CT, USA)
Tris (3,5-dimethylphenyl) phosphate	T35DMPP	25653-16-1	Wellington Laboratories (Guelph, ON, Canada)
Triphenyl phosphate	TPhP	115-86-6	AccuStandard (New Haven, CT, USA)
Tris (2-methylphenyl) phosphate	TMPP	1330-78-5	AccuStandard (New Haven, CT, USA)
Cresyl diphenyl phosphate	CrDPP	26444-49-5	AccuStandard (New Haven, CT, USA)
<i>Alkyl OPEs</i>			
Tris (2-butoxyethyl) phosphate	TBOEP	78-51-3	AccuStandard (New Haven, CT, USA)
Tris (2-ethylhexyl) phosphate	TEHP	78-42-2	AccuStandard (New Haven, CT, USA)
Triethyl phosphate	TEP	78-40-0	AccuStandard (New Haven, CT, USA)
Tripropyl phosphate	TPrP	513-08-6	AccuStandard (New Haven, CT, USA)
Triisobutyl phosphate	TiBP	126-71-6	Wellington Laboratories (Guelph, ON, Canada)
Tri-n-butyl phosphate	TnBP	126-73-8	AccuStandard (New Haven, CT, USA)
Tris (2,3-dibromopropyl) phosphate	TDBPP	126-72-7	AccuStandard (New Haven, CT, USA)
<i>Br OPEs</i>			
Tris(tribromoneopentyl) phosphate	TTBNPP	19186-97-1	AccuStandard (New Haven, CT, USA)
<i>Cl OPEs</i>			
Tris (2-chloroethyl) phosphate	TCEP	115-96-8	AccuStandard (New Haven, CT, USA)
Tris (1-chloro-2-propyl) phosphate	TCIPP	13674-84-5	AccuStandard (New Haven, CT, USA)
Tris (1,3-dichloro-2-propyl) phosphate	TDCIPP	13674-87-8	AccuStandard (New Haven, CT, USA)



Tetrakis (2-chloroethyl) dichloroisopentyl diphosphate	V6	38051-10-4	AccuStandard (New Haven, CT, USA)
<i>Isopropylated triarylphosphate esters (ITPs)</i>			
2-isopropylphenyl diphenyl phosphate	2iPPDPP	64532-94-1	Wellington Laboratories (Guelph, ON, Canada)
4-isopropylphenyl diphenyl phosphate	4iPPDPP	55864-04-5	Wellington Laboratories (Guelph, ON, Canada)
2,4-diisopropylphenyl diphenyl phosphate	24DiPPDPP	96107-55-0	Wellington Laboratories (Guelph, ON, Canada)
bis(2-isopropylphenyl) phenyl phosphate	B2iPPP	69500-29-4	Wellington Laboratories (Guelph, ON, Canada)
bis(3-isopropylphenyl) phenyl phosphate	B3iPPP	69500-30-7	Wellington Laboratories (Guelph, ON, Canada)
bis(4-isopropylphenyl) phenyl phosphate	B4iPPP	55864-07-8	Wellington Laboratories (Guelph, ON, Canada)
bis(2,4-diisopropylphenyl) phenyl phosphate	B24DiPPP	2190501-29-0	Wellington Laboratories (Guelph, ON, Canada)
tris(2-isopropylphenyl) phosphate	T2iPPP	64532-95-2	AccuStandard (New Haven, CT, USA)
tris(3-isopropylphenyl) phosphate	T3iPPP	72668-27-0	Wellington Laboratories (Guelph, ON, Canada)
tris(4-isopropylphenyl) phosphate	T4iPPP	2502-15-0	Wellington Laboratories (Guelph, ON, Canada)
<i>Tert-butylated Triarylphosphate Esters (TBPPs)</i>			
2-tert-butylphenyl diphenyl phosphate	2tBPDPP	83242-23-3	Wellington Laboratories (Guelph, ON, Canada)
4-tert-butylphenyl diphenyl phosphate	4tBPDPP	981-40-8	Wellington Laboratories (Guelph, ON, Canada)
bis(2-tert-butylphenyl) phenyl phosphate	B2tBPPP	65652-41-7	Wellington Laboratories (Guelph, ON, Canada)
bis(4-tert-butylphenyl) phenyl phosphate	B4tBPPP	115-87-7	Wellington Laboratories (Guelph, ON, Canada)
tris(4-tert-butylphenyl) phosphate	T4tBPP	78-33-1	Wellington Laboratories (Guelph, ON, Canada)
<i>Bisphenols</i>			
Bisphenol A	BPA	80-05-7	AccuStandard (New Haven, CT, USA)
Bisphenol AF	BPAF	1478-61-1	AccuStandard (New Haven, CT, USA)
Bisphenol AP	BPAP	1571-75-1	AccuStandard (New Haven, CT, USA)
Bisphenol B	BPB	77-40-7	AccuStandard (New Haven, CT, USA)
Bisphenol BP	BPBP	1844-01-5	AccuStandard (New Haven, CT, USA)
Bisphenol C	BPC	79-97-0	AccuStandard (New Haven, CT, USA)
Bisphenol C-dichloride	BPC-dichloride	14868-03-2	AccuStandard (New Haven, CT, USA)
Bisphenol E	BPE	2081-08-5	AccuStandard (New Haven, CT, USA)
Bisphenol F	BPF	620-92-8	AccuStandard (New Haven, CT, USA)
Bisphenol G	BPG	127-54-8	AccuStandard (New Haven, CT, USA)
Bisphenol M	BPM	13595-25-0	AccuStandard (New Haven, CT, USA)
Bisphenol P	BPP	2167-51-3	AccuStandard (New Haven, CT, USA)
Bisphenol PH	BPPH	24038-68-4	AccuStandard (New Haven, CT, USA)
Bisphenol S	BPS	80-09-1	AccuStandard (New Haven, CT, USA)
Bisphenol TMC	BP-TMC	129188-99-4	AccuStandard (New Haven, CT, USA)

Bisphenol Z	BPZ	843-55-0	AccuStandard (New Haven, CT, USA)
Bisphenol A diglycidyl ether	BADGE	1675-54-3	AccuStandard (New Haven, CT, USA)
<i>OPE &amp; Bisphenol Injection Internal Standards** &amp; Internal Standards</i>			
<sup>13</sup> C <sub>18</sub> -Triphenyl phosphate**	<sup>13</sup> C <sub>18</sub> -TPhP	--	Wellington Laboratories (Guelph, ON, Canada)
Tris(1,3-dichloro-2-propyl) phosphate-d <sub>15</sub>	d <sub>15</sub> -TDCIPP	1447569-77-8	Wellington Laboratories (Guelph, ON, Canada)
Tris(2-chloroethyl) phosphate-d <sub>12</sub>	d <sub>12</sub> -TCEP	1276500-47-0	Wellington Laboratories (Guelph, ON, Canada)
Triphenyl phosphate-d <sub>15</sub>	d <sub>15</sub> -TPhP	1173020-30-8	Wellington Laboratories (Guelph, ON, Canada)
Tris (2-butoxy-[ <sup>13</sup> C <sub>2</sub> ]-ethyl) phosphate	M <sub>6</sub> -TBOEP	--	Wellington Laboratories (Guelph, ON, Canada)
Tri-n-butyl phosphate-d <sub>27</sub>	d <sub>27</sub> -TnBP	61196-26-7	Wellington Laboratories (Guelph, ON, Canada)
Triethyl phosphate-d <sub>15</sub>	d <sub>15</sub> -TEP	135942-11-9	Wellington Laboratories (Guelph, ON, Canada)
Bisphenol A-d <sub>16</sub> **	d <sub>16</sub> -BPA	96210-87-6	Sigma Aldrich (St. Louis, MO)
Bisphenol A-d <sub>6</sub>	d <sub>6</sub> -BPA	86588-58-1	Sigma Aldrich (St. Louis, MO)
Bisphenol S-d <sub>8</sub>	d <sub>8</sub> -BPS	2483831-28-1	Toronto Research Chemicals (North York, ON, Canada)
<i>PFASs – PFCAs</i>			
Perfluoro-n-butanoic acid	PFBA	375-22-4	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3	Wellington Laboratories (Guelph, ON, Canada)
Pentafluoropropionic acid	PFPrA	422-64-0	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-n-hexanoic acid	PFHxA	307-24-4	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-n-heptanoic acid	PFHpA	375-85-9	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-n-octanoic acid	PFOA	335-67-1	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-n-nonanoic acid	PFNA	375-95-1	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-n-decanoic acid	PFDA	335-76-2	Wellington Laboratories (Guelph, ON, Canada)
Perfluoroundecanoic acid	PFUnDA	2058-94-8	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-n-dodecanoic acid	PFDoDA	307-55-1	Wellington Laboratories (Guelph, ON, Canada)
Perfluorotridecanoic acid	PFTrDA	72629-94-8	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5	Wellington Laboratories (Guelph, ON, Canada)
<i>PFASs – PFSAs</i>			
Perfluoropropane sulfonate	PFPrS	423-41-6	Wellington Laboratories (Guelph, ON, Canada)
Perfluorobutane sulfonate	PFBS	375-73-5	Wellington Laboratories (Guelph, ON, Canada)
Perfluoropentane sulfonate	PFPeS	2706-91-4	Wellington Laboratories (Guelph, ON, Canada)
Perfluorohexane sulfonate	PFHxS	355-46-4	Wellington Laboratories (Guelph, ON, Canada)
Perfluoroheptane sulfonate	PFHpS	375-92-8	Wellington Laboratories (Guelph, ON, Canada)
Perfluorooctane sulfonate	PFOS	1763-23-1	Wellington Laboratories (Guelph, ON, Canada)
Perfluorononane sulfonate	PFNS	68259-12-1	Wellington Laboratories (Guelph, ON, Canada)

Perfluorodecane sulfonate	PFDS	335-77-3	Wellington Laboratories (Guelph, ON, Canada)
Perfluorododecane sulfonate	PFDoDS	79780-39-5	Wellington Laboratories (Guelph, ON, Canada)
<i>PFASs – FOSA/FOSAA/FOSE</i>			
N-methylperfluoro-1-octane sulfonamide	NMeFOSA	4151-50-2	Wellington Laboratories (Guelph, ON, Canada)
N-ethylperfluoro-1-octane sulfonamide	NEtFOSA	31506-32-8	Wellington Laboratories (Guelph, ON, Canada)
Perfluorooctane sulfonamido acetic acid	FOSAA	2806-24-8	Wellington Laboratories (Guelph, ON, Canada)
N-methylperfluorooctane sulfonamido acetic acid	NMeFOSAA	2355-31-9	Wellington Laboratories (Guelph, ON, Canada)
N-ethylperfluorooctane sulfonamido acetic acid	NEtFOSAA	2991-50-6	Wellington Laboratories (Guelph, ON, Canada)
N-Methylperfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7	Wellington Laboratories (Guelph, ON, Canada)
N-Ethyl-N-(2-hydroxyethyl)perfluorooctylsulphonamide	NEtFOSE	1691-99-2	Wellington Laboratories (Guelph, ON, Canada)
Perfluorooctane sulfonamide	PFOSA	754-91-6	Wellington Laboratories (Guelph, ON, Canada)
<i>Cl-PFASs</i>			
8-chloro-perfluorooctane sulfonate	8Cl-PFOS	1651215-26-7	Wellington Laboratories (Guelph, ON, Canada)
9-chloro-3-oxa-perfluorononane sulfonate	F-53B Major	756426-58-1	Wellington Laboratories (Guelph, ON, Canada)
11-chloro-3-oxa-perfluoroundecane sulfonate	F-53B Minor	763051-92-9	Wellington Laboratories (Guelph, ON, Canada)
<i>PFASs – FTS</i>			
4:2 fluorotelomer sulfonate	4:2 FTS	757124-72-4	Wellington Laboratories (Guelph, ON, Canada)
6:2 fluorotelomer sulfonate	6:2 FTS	27619-97-2	Wellington Laboratories (Guelph, ON, Canada)
8:2 fluorotelomer sulfonate	8:2 FTS	39108-34-4	Wellington Laboratories (Guelph, ON, Canada)
10:2 fluorotelomer sulfonate	10:2 FTS	120226-60-0	Wellington Laboratories (Guelph, ON, Canada)
<i>PFASs – FTCA/FTUCA</i>			
3:3 fluorotelomer carboxylic acid	3:3 FTCA	356-02-5	Wellington Laboratories (Guelph, ON, Canada)
5:3 fluorotelomer carboxylic acid	5:3 FTCA	914637-49-3	Wellington Laboratories (Guelph, ON, Canada)
7:3 fluorotelomer carboxylic acid	7:3 FTCA	812-70-4	Wellington Laboratories (Guelph, ON, Canada)
6:2 fluorotelomer carboxylic acid	6:2 FTCA	53826-12-3	Wellington Laboratories (Guelph, ON, Canada)
8:2 fluorotelomer carboxylic acid	8:2 FTCA	27854-31-5	Wellington Laboratories (Guelph, ON, Canada)
10:2 fluorotelomer carboxylic acid	10:2 FTCA	53826-13-4	Wellington Laboratories (Guelph, ON, Canada)
2H-Perfluoro-2-octenoic acid (6:2)	6:2 FTUCA	70887-88-6	Wellington Laboratories (Guelph, ON, Canada)
2H-Perfluoro-2-decenoic acid (8:2)	8:2 FTUCA	70887-84-2	Wellington Laboratories (Guelph, ON, Canada)
2H-Perfluoro-2-dodecenoic acid (10:2)	10:2 FTUCA	70887-94-4	Wellington Laboratories (Guelph, ON, Canada)
<i>PFASs – PFECA</i>			
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6	Wellington Laboratories (Guelph, ON, Canada)

Dodecafluoro-3H-4,8-dioxanonanoate	ADONA	919005-14-4	Wellington Laboratories (Guelph, ON, Canada)
Tetrafluoro-2-(heptafluoropropoxy)propanoic acid	HFPO-DA	13252-13-6	Wellington Laboratories (Guelph, ON, Canada)
2,2,3,3-Tetrafluoro-3-{{1,1,1,2,3,3-hexafluoro-3-(1,2,2,2-tetrafluoroethoxy)propan-2-yl}oxy}propanoic acid	Hydro-EVE Acid	773804-62-9	Wellington Laboratories (Guelph, ON, Canada)
Tetrafluoro-3-(trifluoro-1-(trifluoromethyl)-2-((trifluorovinyl)oxy)ethoxy) propionic acid	EVE Acid	69087-46-3	Wellington Laboratories (Guelph, ON, Canada)
2,3,3,3-Tetrafluoro-2-(pentafluoroethoxy)propanoic acid	PEPA	267239-61-2	Wellington Laboratories (Guelph, ON, Canada)
3-(Methoxy)tetrafluoropropionic acid	MTP	93449-21-9	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-3,6-dioxaheptanoic acid	PFECA B	151772-58-6	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro(4-methoxybutanoic) acid	PFECA A	863090-89-5	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-3-methoxypropanoic acid	PFECA F	377-73-1	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-2-methoxyacetic acid	PFMOAA	674-13-5	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-3,5-dioxahexanoic acid	PFO2HxA	39492-88-1	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-3,5,7-trioxaoctanoic acid	PFO3OA	39492-89-2	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-3,5,7,9-butaoxidecanoic acid	PFO4DA	39492-90-5	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-3,5,7,9,11-pentaoxidodecanoic acid	PFO5DA	39492-91-6	Wellington Laboratories (Guelph, ON, Canada)
2,3,3,3-Tetrafluoro-2-(trifluoromethoxy)propanoic acid	PMPA	13140-29-9	Wellington Laboratories (Guelph, ON, Canada)
4-(2-Carboxy-1,1,2,2-tetrafluoroethoxy)-perfluoropentanoic acid	R-EVE	2416366-22-6	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro-4-isopropoxybutanoic acid	PFPE-1 (or PFECA G)	801212-59-9	Wellington Laboratories (Guelph, ON, Canada)
<i>PFASs – PFESA</i>			
7H-Perfluoro-4-methyl-3,6-dioxaoctanesulfonic acid	Hydro-PS Acid	749836-20-2	Wellington Laboratories (Guelph, ON, Canada)
Nafion Byproduct 5	Hydrolyzed PSDA	2416366-19-1	Wellington Laboratories (Guelph, ON, Canada)
Sodium 1,1,2,2-Tetrafluoro-2-(1,2,2,2-tetrafluoroethoxy)ethane-1-sulfonate	NVHOS	1132933-86-8	Wellington Laboratories (Guelph, ON, Canada)
Perfluoro(2-ethoxyethane)sulphonic acid	PES	113507-82-7	Wellington Laboratories (Guelph, ON, Canada)
Cyclohexanesulfonic acid, 1,2,2,3,3,4,5,5,6,6-decafluoro-4-(1,1,2,2,2-pentafluoroethyl)	PFECHS	133201-07-7	Wellington Laboratories (Guelph, ON, Canada)
1-(Trifluorovinyl)oxy-2-(2-	PS Acid	29311-67-9	Wellington Laboratories (Guelph, ON, Canada)

sulfotetrafluoroethoxy)hexafluoropropane			
Perfluoro-4-(2-sulfoethoxy)pentanoic acid	R-PSDA	2416366-18-0	Wellington Laboratories (Guelph, ON, Canada)
Nafion Byproduct 6	R-PSDCA	2416366-21-5	Wellington Laboratories (Guelph, ON, Canada)
<i>PFASs – diPAPs</i>			
6:2 Fluorotelomer phosphate diester	6:2-diPAP	57677-95-9	Wellington Laboratories (Guelph, ON, Canada)
8:2 Fluorotelomer phosphate diester	8:2-diPAP	678-41-1	Wellington Laboratories (Guelph, ON, Canada)
10:2 Fluorotelomer phosphate diester	10:2-diPAP	1895-26-7	Wellington Laboratories (Guelph, ON, Canada)
6:2/8:2 Fluorotelomer phosphate diester	6:2/8:2-diPAP	943913-15-3	Wellington Laboratories (Guelph, ON, Canada)
<i>PFAS Internal Standards</i>			
<sup>13</sup> C <sub>4</sub> -PFBA	<sup>13</sup> C <sub>4</sub> -PFBA		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>5</sub> -PFPeA	<sup>13</sup> C <sub>5</sub> -PFPeA		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>2</sub> -PFHxA	<sup>13</sup> C <sub>2</sub> -PFHxA		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>4</sub> -PFHpA	<sup>13</sup> C <sub>4</sub> -PFHpA		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>4</sub> -PFOA	<sup>13</sup> C <sub>4</sub> -PFOA		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>5</sub> -PFNA	<sup>13</sup> C <sub>5</sub> -PFNA		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>2</sub> -PFDA	<sup>13</sup> C <sub>2</sub> -PFDA		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>2</sub> -PFUdA	<sup>13</sup> C <sub>2</sub> -PFUdA		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>2</sub> -PFDoA	<sup>13</sup> C <sub>2</sub> -PFDoA		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>2</sub> -PFTeDA	<sup>13</sup> C <sub>2</sub> -PFTeDA		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>2</sub> -PFHxDA	<sup>13</sup> C <sub>2</sub> -PFHxDA		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>3</sub> -PFBS	<sup>13</sup> C <sub>3</sub> -PFBS		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>2</sub> -PFOS	<sup>13</sup> C <sub>2</sub> -PFOS		Wellington Laboratories (Guelph, ON, Canada)
<sup>18</sup> O <sub>2</sub> -PFHxS	<sup>18</sup> O <sub>2</sub> -PFHxS		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>4</sub> -PFOS	<sup>13</sup> C <sub>4</sub> -PFOS		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>8</sub> -FOSA	<sup>13</sup> C <sub>8</sub> -FOSA		Wellington Laboratories (Guelph, ON, Canada)
MeFOSA- d <sub>3</sub>	MeFOSA- d <sub>3</sub>		Wellington Laboratories (Guelph, ON, Canada)
EtFOSA- d <sub>5</sub>	EtFOSA- d <sub>5</sub>		Wellington Laboratories (Guelph, ON, Canada)
MeFOSAA- d <sub>3</sub>	MeFOSAA- d <sub>3</sub>		Wellington Laboratories (Guelph, ON, Canada)
EtFOSAA- d <sub>5</sub>	EtFOSAA- d <sub>5</sub>		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>2</sub> -4:2 FTS	<sup>13</sup> C <sub>2</sub> -4:2 FTS		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>2</sub> -6:2 FTS	<sup>13</sup> C <sub>2</sub> -6:2 FTS		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>2</sub> -8:2 FTS	<sup>13</sup> C <sub>2</sub> -8:2 FTS		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>2</sub> -6:2 FTCA	<sup>13</sup> C <sub>2</sub> -6:2 FTCA		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>2</sub> -8:2 FTCA	<sup>13</sup> C <sub>2</sub> -8:2 FTCA		Wellington Laboratories (Guelph, ON, Canada)
<sup>13</sup> C <sub>2</sub> -10:2 FTCA	<sup>13</sup> C <sub>2</sub> -10:2 FTCA		Wellington Laboratories (Guelph, ON, Canada)

$^{13}\text{C}_2\text{-6:2 UFTCA}$	$^{13}\text{C}_2\text{-6:2 UFTCA}$		Wellington Laboratories (Guelph, ON, Canada)
$^{13}\text{C}_2\text{-8:2 UFTCA}$	$^{13}\text{C}_2\text{-8:2 UFTCA}$		Wellington Laboratories (Guelph, ON, Canada)
$^{13}\text{C}_2\text{-10:2 UFTCA}$	$^{13}\text{C}_2\text{-10:2 UFTCA}$		Wellington Laboratories (Guelph, ON, Canada)
$^{13}\text{C}_3\text{-HFPO-DA}$	$^{13}\text{C}_3\text{-HFPO-DA}$		Wellington Laboratories (Guelph, ON, Canada)

## Text S2. Site and Storm Characteristics

Site characteristics and sampling events are summarized in **Table S2** and **Table S3**, respectively.

**Table S2.** Summary of sampling sites and land-use characteristics by San Francisco Bay watershed. References for land-use data and characteristics are provided in SI Text S2 (Excel).

**Table S3.** Summary of sampling events and storm event characteristics for sampling in San Francisco Bay Area watersheds 2018-2022. Event 9 was a post-storm sampling event and does not include storm characteristics (Excel).

To better display the level of development within watersheds, the most recent, currently unpublished, land use dataset for the region [Metropolitan Transportation Commission (MTC). 2023. Interim 2020 San Francisco Bay Area Land Use data (draft)] was disaggregated into two sub-classes for each major land use category (residential, commercial, industrial, transportation, agriculture, open space, unclassified). One subclass is for the area of the parcels within a given land use category that have greater than 10% imperviousness, and the other is for the area of the parcels that have less than 10% imperviousness.

Percent imperviousness was calculated using a zonal statistics analysis based on data from Dewitz, J. (2021). *National Land Cover Database (NLCD) 2019 Impervious Products*. U.S. Geological Survey. <https://doi.org/10.5066/P9KZCM54>

Road lengths and types were extracted from the U.S. Census Bureau (2021) TIGER/Line 2020 Census Roads Shapefile. Released February 2, 2021. Accessed October 10, 2022. <https://www.census.gov/geographies/mapping-files/time-series/geo/tiger-line-file.2020.html#list-tab-790442341>

NLCD area was from Dewitz, J. (2021). *National Land Cover Database (NLCD) 2019 Impervious Products*. U.S. Geological Survey. <https://doi.org/10.5066/P9KZCM54>

### Text S3. Sample Collection Information

Sampling teams wore nitrile gloves for all sample collection activities. Storm durations were estimated based on the weather forecast, prevailing on-site conditions, and radar imagery. Additional sample collection methods are detailed in **Table S4**.

**Table S4.** Sample collection details by contaminant class

Contaminant Class	Collection Apparatus & Method	Bottle Type & Size	Minimum Volume	Head Space?	Bottle rinse in field?
SWCECs (including 6PPDQ)	ISCO pump; aliquots added directly to container, measured by pump times (field composite)	1 x 2.5 L amber glass	Full	None	Site water 3x
PFASs	Stainless steel bailer; each aliquot filled tubes (composited in laboratory)	3 x 50 mL HDPE tubes per aliquot	Full	Minimal	No
OPEs and bisphenols	Stainless steel bailer; standard volumes measured via graduated cylinder, then added to container (field composite)	2 x 1 L amber glass	800 mL (shoulder)	OK	Rinse outside of container with site water (cap on)

#### Text S3.1 Class-specific sample collection techniques

Sample collection for SWCEC analysis used a pump (ISCO 6712 Portable Pump Sampler) fitted with a Teflon suction line attached to a sampling pole that was held in the deepest part of the channel. The suction line end was lowered/raised in the water column to create a depth-integrated sample. Sample collection for OPE, bisphenol, and PFAS analysis used a stainless-steel bailer (to avoid potential contamination from Teflon or other plastics) lowered into the center of the channel near the surface (i.e., not depth-integrated). The bailer was rinsed once with site water prior to sample collection. After sample collection, the bailer was agitated multiple times while decanting sample water into a glass graduated cylinder to measure sub-sample volumes that were collected into sample containers. All near-field and open Bay samples were collected with the stainless-steel bailer.

#### Text S3.2 Field blank sample collection

During storm event sampling, SWCEC blanks were collected at the beginning of the sampling event, before any other sample collection. MilliQ blank water (~2.5 L) was run through the ISCO pump to thoroughly rinse the equipment; this water was discarded. The pump was then similarly rinsed with Reagent Grade DI water (~0.5 L), just prior to pumping the same grade water into the field blank sample container. For PFASs, Optima LC/MS grade water or lab-supplied blank



water was poured into the stainless-steel bailer and then into the collection tubes. For OPEs and bisphenols, blank samples were collected by opening an empty sampling container at the same time as field sample collection, then closing it upon completion.

During near-field and mid-Bay sampling, SWCEC field blanks were collected at the beginning of the sampling event, before any other sample collection, by rinsing the clean bailer three times with MilliQ water, then filling the bailer with MilliQ water that was subsequently transferred to the field blank sample container.

## Text S4. Analytical Methods

### Text S4.1. Stormwater Tracer CECs (UWT)

**Sample Extraction.** Water samples (1 L) were spiked with an isotope labeled internal standard (ISTD) mixture (50  $\mu$ L; n=14; ISTD concentrations 2 – 20  $\mu$ g/L in final extracts, see **Table S7**) and 25 ng (50  $\mu$ L) 6PPDQ-*d*<sub>5</sub> (the latter only spiked in final extracts for samples collected 10/24/2021 and earlier). To prevent clogging, 0.5 g pre-cleaned micro glass beads (Filter Aid 400, 3M, MN) were added to SPE cartridges (200 mg, 6 mL Oasis HLB, Waters, MA). Cartridges were preconditioned (10 mL methanol, 25 mL DI water), then water samples (1 L) were loaded (5-10 mL/min). Cartridges were rinsed (10 mL DI water), dried for 15 min under vacuum, and eluted with methanol (4 x 2.5 mL). Eluates were concentrated to 1 mL under N<sub>2</sub>, transferred into autosampler vials, and were stored at -20 °C until instrumental analysis.

**LC-MS/MS Methods.** Analysis (for both the combined SWCEC/6PPDQ method and the 6PPDQ-specific method) was based on previously published methods.<sup>1,2</sup> The chromatography column and other LC parameters are provided in **Table S5**. Detection used electrospray ionization (ESI+) and dynamic multiple reaction monitoring mode; additional parameters are provided in **Table S6**. Quantitative and qualitative ion transitions are provided in Tian et al. and Hou et al.<sup>1,2</sup> Minimum levels of detection (MDL) and quantitation (MQL) for SWCECs are summarized in **Table S8**. The MDL and MQL for 6PPDQ were 2.5 and 5.1 ng/L in the original water sample, respectively.

**Table S5.** LC method settings for combined SWCEC/6PPDQ analysis and for 6PPDQ-specific analysis.

Parameter	SWCEC/Combined Method	6PPDQ-specific Method
LC column	Eclipse Plus-C18, 2.1 mm×100 mm, 1.8 $\mu$ m particle size (Agilent, USA)	Poroshell HPH-C18, 2.1 × 100 mm, 2.7 $\mu$ m particle size (Agilent, USA)
Guard column	Zorbax Eclipse XDB-C18 Guard Column, 2.1×12.5 mm, 5 $\mu$ m particle size (Agilent, USA)	Zorbax Eclipse XDB-C18 Guard Column, 2.1 × 12.5 mm, 5 $\mu$ m particle size (Agilent, USA)
Column temp	25°C	45 °C
Injection volume	10 $\mu$ L	5 $\mu$ L
Mobile phase	DI water (A) and methanol (B), both with 5 mM ammonium acetate plus 0.1% ammonium hydroxide	DI water (A) and methanol (B) both with 0.1% formic acid
Gradient & flow rate	10% B 0-1 min, 60% B at 1 min, 100% B 10-12 min (0.2 mL/min flow rate), 100% B at 13-16 min (0.5 mL/min flow rate, to prevent peak-splitting for SDPAs), 10% B at 17-24 min (0.2 mL/min flow rate)	0.2 mL/min; 50% B 0 – 0.5 min, 50-100% B 0.5-10.5 min, 100% B 10.5-12 min, 100-50% B 12-13 min, 50% B 13-15 min

**Table S6.** MS/MS method settings for SWCEC analysis

Parameter	SWCEC/Combined Method	6PPDQ-specific Method
ESI mode	+/-	+
Gas temp	350 °C	300 °C
Gas flow	10 L/min	5 L/min
Sheath gas temp	400 °C	400 °C
Sheath gas flow	11 L/min	11 L/min
Capillary voltage	3.5 kV	3.0 kV
Nozzle voltage	0.5 kV	0.5 kV
Nebulizer	45 psi	45 psi
Fragmentor voltage	110 V	110 V

**Table S7.** Summary of calibration ranges and internal standard (ISTD) information for targeted stormwater-derived analytes.

Target Analyte	Calibration range (µg/L)	ISTD	ISTD Concentration in final extract (µg/L)
6PPD-quinone (6PPDQ)	0.025 – 100	6PPDQ- <i>d</i> <sub>5</sub>	25
1,3-diphenylguanidine (DPG)	0.1 – 100	Diphenyl- <i>d</i> <sub>10</sub> -urea	5
Hexa(methoxymethyl)melamine (HMMM)	0.05 – 100	Prometon- <i>d</i> <sub>3</sub>	2
<i>N</i> -cyclohexyl-1,3-benzothiazole-2-amine (NCBA)	0.05 – 100	5-methyl-1- <i>H</i> -Benzotriazole- <i>d</i> <sub>6</sub>	20
1,3-dicyclohexylurea (DCU)	0.05 – 100	Diphenyl- <i>d</i> <sub>10</sub> -urea	5
Caprolactam	2 – 200	Caffeine- <i>13</i> C <sub>3</sub>	10
Benzotriazole (BTR)	2 – 200	5-methyl-1- <i>H</i> -Benzotriazole- <i>d</i> <sub>6</sub>	20
5-methyl-1- <i>H</i> -benzotriazole (5-methyl-1 <i>H</i> -BTR)	2 – 200	5-methyl-1- <i>H</i> -Benzotriazole- <i>d</i> <sub>6</sub>	20
2-amino-benzothiazole (2-NH <sub>2</sub> -BTH)	0.2 – 100	5-methyl-1- <i>H</i> -Benzotriazole- <i>d</i> <sub>6</sub>	20
2-hydroxy-benzothiazole (2-OH-BTH)	1 – 100	5-methyl-1- <i>H</i> -Benzotriazole- <i>d</i> <sub>6</sub>	20
2-(4-morpholinyl)benzothiazole (2,4-MoBT)	0.2 – 100	5-methyl-1- <i>H</i> -Benzotriazole- <i>d</i> <sub>6</sub>	20
Carbendazim	0.05 – 100	Carbendazim- <i>d</i> <sub>4</sub>	5
Clothianidin	0.5 – 100	Imidacloprid- <i>d</i> <sub>4</sub>	20
Diuron	0.1 – 100	Diuron- <i>d</i> <sub>6</sub>	10
Imidacloprid	0.5 – 100	Imidacloprid- <i>d</i> <sub>4</sub>	20

Iprodione	5 – 500	DEET-d7	20
Mecoprop	1 – 100	Diclofenac-d4	20
Pentachlorophenol (PCP)	5 – 500	Triclosan-d3	25
Prometon	0.02 – 100	Prometon-d3	2
Thiamethoxam	5 – 500	Imidacloprid-d4	20
Caffeine	0.5 – 100	Caffeine-13C3	10
Cetirizine	0.02 – 100	Cetirizine-d8	1
Cotinine	0.1 – 100	Cotinine-d3	10
DEET	0.05 – 100	DEET-d7	20
Diclofenac	5 – 500	Diclofenac-d4	20
Ibuprofen	20 – 2000	Ibuprofen-d3	200
Triclosan	2 – 200	Triclosan-d3	25

**Table S8.** Minimum, median, mean, and maximum MDLs and MQLs for SWCEC analytes across all analysis dates. Units are ng/L in the original water sample (Excel).

#### Text S4.2. 6PPDQ (Eurofins)

**Extraction/Cleanup:** Aqueous samples in 250 mL amber glass bottles with minimal headspace were briefly shaken and a small aliquot was taken for percent solids determination. Samples and QC were then fortified with 0.5 mL (20 µg/L) <sup>13</sup>C<sub>6</sub>-6PPDQ (internal standard used for isotope dilution quantitation) prior to SPE. SPE used 200 mg, 6 mL Strata-XL 100 µm polymeric reversed phase cartridges (Phenomenex, 8B-S043-FCH). The 100 µm cartridge was less prone to clogging than standard 30 µm and 60 µm cartridges and glass wool above the media was typically not needed. Cartridges were conditioned with acetonitrile and water prior to sample loading. Samples were loaded at a rate of 10-15 mL/minute, assuring cartridge did not go dry. After loading, the original sample bottle was washed with 5 mL 1:1 methanol:water and transferred to the SPE, then discarded to waste. The SPE was dried under vacuum for 5 minutes. The original sample bottle was washed with 5 mL acetonitrile and transferred to SPE, collecting eluent in a 15 mL PP tube after applying a small vacuum. This step was repeated once with 4 mL acetonitrile. Then, 0.5 mL (20 µg/L) of Injection Internal Standard 6PPDQ-*d*<sub>3</sub> was added and the extract volume was adjusted with acetonitrile to achieve 10 mL final volume. Samples were sealed and briefly vortexed before aliquoting a small volume for analysis.

**LC-MS/MS Analysis:** Extracts were analyzed on a SCIEX 5500+ paired with a Shimadzu Exion LC. 20 µL of extract was introduced into the Shimadzu HPLC system for separation on a 100 mm solid-core C18 column (Phenomenex, 00D-4744-E0). Detailed LC conditions are presented in **Table S9**. The MS was operated in positive polarity with a run time of approximately 10 minutes; detailed MS conditions are in **Table S10**. An initial calibration consisting of six points using an average response factor was injected prior to sample analysis (**Table S11**). Isotope dilution quantitation was employed and percent recovery of the <sup>13</sup>C<sub>6</sub>-6PPD-Q standard was generated for every sample and QC sample. Data were processed on an

internal Laboratory Information Management System (LIMS) and reviewed by two separate analysts. Any samples with concentrations above the calibration were diluted appropriately and reanalyzed. The MDL and MQL are summarized in **Table S12**.

**Table 9.** LC method settings for 6PPDQ analysis at Eurofins.

Column (Column temp = 45°C)	Phenomenex Kinetex C18 3.5 µm, 3.6 mm x 100mm				
Mobile Phase Composition	A = 0.2% Formic acid in Water B = Acetonitrile				
Gradient Program (Maximum Pressure limit = 7,500 psi)	Time	%A	%B	Curve	Flow Rate mL/min.
	0	90	10	0	0.60
	1.0	90	10	0	0.60
	3.0	45	55	0	0.60
	6.0	1	99	0	0.60
	8.0	1	99	0	0.60
	8.50	90	10	0	0.60
	9.0	90	10	0	0.60
Injection Size	20 µL (fixed amount throughout the sequence)				
Run Time	~10.0 minutes				

**Table 10.** Mass spectrometer settings for 6PPDQ analysis at Eurofins.

Parameter	Setting
MS Interface Mode	ESI Positive Ion
Ion Spray Voltage (kV)	5.5
Desolvation Temp	600°C
Curtain Gas (nitrogen) Flow	305 psi
Collision Gas (nitrogen) Flow	58 psi

**Table 11.** Calibration standards for 6PPDQ analysis at Eurofins. \*Internal Standard used for isotope dilution quantitation. \*\*Injection Internal Standard. \*\*\*L1 is used for a sensitivity check and L2 is the low point for quantitation.

Analyte	Standard Level - Concentration (ng/mL)						
	L1***	L2	L3	L4*	L5	L6	L7
6PPD-Q	0.025	0.05	0.1	0.5	1	5	10
13C6-6PPDQ*	1	1	1	1	1	1	1
6PPDQ-d5**	1	1	1	1	1	1	1

**Table 12.** Summary of MDL and MQL for 6PPDQ analysis at Eurofins, ng/L in the water samples.

	Min	Median	Mean	Max
MDL	0.54	3.0	2.0	3.1
MQL	1.7	10	6.7	10

### Text S4.3. OPEs and Bisphenols

**Sample Extraction.** Filtered water samples (~1 L) were adjusted to pH ~3, spiked with isotope dilution internal standards (10 ng for OPEs and 20 ng for bisphenols; ISTD concentrations 50 – 100 µg/L in final extracts, see **Table S15**), then liquid-liquid extracted with dichloromethane (DCM) three times. Extracts were combined, concentrated (to 200 µL), and divided into two equal volume aliquots. One aliquot was solvent-exchanged to hexane (HEX; 200 µL) and cleaned further by passing through an SPE cartridge (1 g ammonium silica; Biotage, Charlotte, NC). The SPE cartridge was then cleaned (2 mL of HEX:DCM, 20:80 v/v), and eluted (4 mL HEX:DCM, 20:80 v/v; 8 mL DCM). The final extract (~200 µL) was spiked with an injection internal standard (<sup>13</sup>C<sub>18</sub>-TPhP, 10 ng) for OPE analysis. The second aliquot was concentrated to near dryness under gentle nitrogen flow, re-constituted with 200 µL methanol, and spiked with internal standard (d<sub>16</sub>-BPA, 10 ng) for bisphenol analysis.

Dried particulates retained after initial filtration were spiked with isotope dilution internal standards (10 ng for OPEs and 20 ng for bisphenols; ISTD concentrations 50 – 100 µg/L in final extracts, see **Table S15**), and extracted twice with ultrasonication (5 mL of HEX:DCM, 1:1 v/v; 5 min). Extracts were combined, concentrated (to 200 µL), and divided into two equal volume aliquots. Subsequent processing of the two aliquots for OPE and bisphenol analysis followed the same procedures detailed above.

**LC-MS/MS Methods.** Analysis of OPEs and bisphenols was based on previously published methods.<sup>3</sup> LC-MS/MS analyses used a Shimadzu HPLC coupled to an AB Sciex Q Trap 5500 MS equipped with a TurboIonSpray® ESI probe. The chromatography column and other LC parameters are provided in **Table S13**. Detection used ESI+ for OPE analysis and ESI- for bisphenol analysis and MRM; additional parameters are provided in **Table S14** and **Table S15**.

**Table S13.** LC method settings for OPE and bisphenol analysis.

Parameter	OPE Method	Bisphenol Method
LC column	Kinetex EVO C18, 100Å, 2.1 mm×100 mm, 5 µm particle size (Phenomenex, USA)	ZORBAX Extended-C18, 80Å, 2.1 × 100 mm, 3.5 µm particle size (Agilent, USA)
Guard column	SecurityGuard ULTRA cartridges for EV0-C18, sub-2µm and core-shell columns with 2.1mm internal diameters (Phenomenex, USA)	ZORBAX Extend-C18, 80Å Guard Column, 2.1 × 12.5 mm, 5 µm particle size (Agilent, USA)
Column temp	40°C	40°C
Injection volume	5 µL	5 µL
Mobile phase	Water with 0.1% formic acid (A) and methanol (B)	Water with 0.2mM ammonium acetatae (A) and methanol (B)
Gradient & flow rate	0.3 mL/min; 5% B 0-2 min, 5-40% B 2-4 min, 40-100% B 4-14 min,	0.5 mL/min; 10% B 0-0.5 min, 10-50% B 0.5-1 min, 50-100% B 1-7

	100% B 14-17 min, 100-5% B 17-17.1 min, 5% B 17.1-20 min	min, 100% B 7-8.5 min, 100-10% B 8.5-8.6 min, 10% B 8.6-10.5 min
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**Table S14.** MS/MS method settings for OPE and bisphenol analysis.

Parameter	OPE Method	Bisphenol Method
ESI mode	+	-
Ion source temperature	350°C	450°C
Curtain gas	20 psi	35 psi
Collision gas	9	9
IonSpray Voltage	4000 V	-4500 V
Ion source gas 1	50 psi	45 psi
Ion source gas 2	20 psi	45 psi

**Table S15.** Summary of MRM transitions (quantitative and qualitative, respectively) and internal standard (ISTD) information (used for isotope dilution quantitation) for OPEs and bisphenols.

Analyte	MRM Pairs ( <i>m/z</i> )	ISTD	ISTD Conc. in final extract ( $\mu\text{g/L}$ )
V6	582.9 $\rightarrow$ 99.1 582.9 $\rightarrow$ 65.1	$d_{15}$ -TDCIPP	50
TCEP	284.9 $\rightarrow$ 99 284.9 $\rightarrow$ 62.9	$d_{12}$ -TCEP	50
TCIPP	329 $\rightarrow$ 99 329 $\rightarrow$ 81	$d_{15}$ -TDCIPP	50
TDCIPP	430.9 $\rightarrow$ 99 430.9 $\rightarrow$ 81	$d_{15}$ -TDCIPP	50
TDBPP	698.4 $\rightarrow$ 98.9 698.4 $\rightarrow$ 118.9	$d_{15}$ -TPhP	50
TTBNPP	1018.5 $\rightarrow$ 145 1018.5 $\rightarrow$ 147	$d_{15}$ -TPhP	50
BPA-BDPP	693 $\rightarrow$ 367.2 693 $\rightarrow$ 178.2	$d_{15}$ -TPhP	50
RBDPP	575 $\rightarrow$ 152.2 575 $\rightarrow$ 77.1	$d_{15}$ -TPhP	50
T35DMPP	411.1 $\rightarrow$ 179.1 411.1 $\rightarrow$ 194	$d_{15}$ -TPhP	50
CrDPP	340.9 $\rightarrow$ 151.9 340.9 $\rightarrow$ 91.1	$d_{15}$ -TPhP	50
IDDPP	391 $\rightarrow$ 251.1 391 $\rightarrow$ 77.1	$d_{15}$ -TPhP	50
EHDPP	363.2 $\rightarrow$ 250.9 363.2 $\rightarrow$ 76.9	$M_6$ -TBOEP <sup>a</sup>	50
TPhP	327.1 $\rightarrow$ 77.1 327.1 $\rightarrow$ 152.1	$d_{15}$ -TPhP	50
TMPP	369.1 $\rightarrow$ 165 369.1 $\rightarrow$ 91	$M_6$ -TBOEP <sup>a</sup>	50
TBOEP	399.1 $\rightarrow$ 199.1	$M_6$ -TBOEP <sup>a</sup>	50

	399.1 → 101		
TEHP	435.3 → 99 435.3 → 81	M <sub>6</sub> -TBOEP <sup>a</sup>	50
TiBP	267.1 → 80.9 267.1 → 98.9	d <sub>27</sub> -TnBP	50
TPrP	225.1 → 80.9 225.1 → 98.9	d <sub>15</sub> -TDCIPP	50
TnBP	267.1 → 80.9 267.1 → 98.9	d <sub>27</sub> -TnBP	50
TEP	183.1 → 81 183.1 → 99	d <sub>15</sub> -TEP	50
2iPPDPP	369.2 → 327 369.2 → 233	d <sub>15</sub> -TPhP	50
4iPPDPP	369.2 → 327 369.2 → 233	d <sub>15</sub> -TPhP	50
24DiPPDPP	411.2 → 369 411.2 → 327	d <sub>15</sub> -TPhP	50
B2iPPP	411.3 → 369 411.3 → 327	d <sub>15</sub> -TPhP	50
B4iPPP	411.3 → 369 411.3 → 327	d <sub>15</sub> -TPhP	50
B24DiPPP	495.3 → 411 495.3 → 369	d <sub>15</sub> -TPhP	50
T2iPPP	452.9 → 326.9 452.9 → 91	d <sub>15</sub> -TPhP	50
T3iPPP	453.2 → 411.3 453.2 → 369.3	d <sub>15</sub> -TPhP	50
T4iPPP	453.2 → 411.3 453.2 → 369.3	d <sub>15</sub> -TPhP	50
2tBPDPP	383.1 → 327 383.1 → 251	d <sub>15</sub> -TPhP	50
4tBPDPP	383.1 → 327 383.1 → 233	d <sub>15</sub> -TPhP	50
B2tBPPP	439.3 → 383.2 439.3 → 327	d <sub>15</sub> -TPhP	50
B4tBPPP	439.3 → 383 439.3 → 327	d <sub>15</sub> -TPhP	50
T4tBPP	495.3 → 439 495.3 → 383	d <sub>15</sub> -TPhP	50
BPA	226.8 → 132.9 226.8 → 92.9	d <sub>6</sub> -BPA	100
BPAF	335.1 → 264.9 335.1 → 69.1	d <sub>6</sub> -BPA	100
BPAP	289.1 → 211 289.1 → 195	d <sub>6</sub> -BPA	100
BPB	240.9 → 211 240.9 → 93	d <sub>6</sub> -BPA	100
BPBP	351.1 → 272.8 351.1 → 258.1	d <sub>6</sub> -BPA	100
BPC	255.1 → 146.7	d <sub>6</sub> -BPA	100



	255.1 → 107.2		
BPC-dichloride	280.2 → 97 280.2 → 134	d <sub>6</sub> -BPA	100
BPE	213.1 → 118.8 213.1 → 92.7	d <sub>6</sub> -BPA	100
BPF	198.9 → 92.9 198.9 → 77	d <sub>10</sub> -BPF	100
BPG	311.0 → 175.3 311.0 → 182.9	d <sub>6</sub> -BPA	100
BPM	345.1 → 251.1 345.1 → 132.7	d <sub>6</sub> -BPA	100
BPP	345.2 → 132.9 345.2 → 315.4	d <sub>6</sub> -BPA	100
BPPH	379.1 → 208.8 379.1 → 192.9	d <sub>6</sub> -BPA	100
BPS	248.9 → 108 248.9 → 92.1	d <sub>8</sub> -BPS	100
BP-TMC	309.2 → 215.2 309.2 → 183	d <sub>6</sub> -BPA	100
BPZ	267.1 → 173.2 267.1 → 145	d <sub>6</sub> -BPA	100
BADGE	339.3 → 119 339.3 → 197	d <sub>6</sub> -BPA	100

**Table S16.** Minimum, median, mean, and maximum MDLs and MQLs for bisphenol and OPE analytes across all analyses. Units are ng/L in the original water sample. \*Denotes semi-quantitative analytes (Excel).

#### Text S4.4. PFASs, Colorado School of Mines

Sample preparation at Colorado School of Mines (Mines) started with creation of triplicate composite total water samples by combining replicate time-paced sub-samples (first shaken for 60 seconds) into an HDPE bottle. Based on a previously published method,<sup>4</sup> composite samples were sub-sampled (2 mL) and prepared for analysis by adding 0.528 mL methanol, 0.292 mL isopropyl alcohol, 0.101 mL basic water (0.01% ammonium hydroxide in water), 0.303 mL 2,2,2-trifluoroethanol, and 0.112 mL isotope-labeled PFAS ISTD mixture (2,000 ng/L; **Table S17**). Samples were vortexed (60 sec) then sonicated (1 h, 50-55°C).

Sample analysis at Mines used HPLC coupled to a SCIEX X500R QTOF-MS system and followed a previously published method.<sup>4</sup> Quantitative data acquisition and processing was completed using SCIEX OS Version 1.5.0. Confirmation of targeted analytes with signal to noise ratio > 10:1 is based on retention time and accurate mass (XIC window 0.02 Da) compared to analytical standards. Generally, a mass error of <5 ppm was considered acceptable. Initial

integration parameters included defining 90% of lowest-intensity peaks as noise, using a baseline-subtract window of two minutes, a minimum peak height of 10, a peak width of 3 points, and a gaussian smooth value of 1. Peaks that fell outside of these thresholds were manually integrated where retention time, accurate mass, and isotope confidence were determined to be satisfactory. Only concentrations above the MQL were reported. Additional parameters are provided in **Table S17**, and MDLs/MQLs are summarized in **Table S18**.

**Table S17.** Mines laboratory list of targeted PFASs, calibration ranges, and corresponding internal standards.

PFAS	Calibration Range	ISTD	ISTD Conc. in final extract (µg/L)
PFPeA	20 – 5000	13C5-PFPeA	200
PFHxA	2.0 – 5000	13C2-PFHxA	200
PFHpA	2.0 – 1000	13C4-PFHpA	200
PFOA	0.5 – 2000	13C4-PFOA	200
PFNA	10 – 1000	13C5-PFNA	200
PFDA	1.0 – 1000	13C2-PFDA	200
PFUnDA	2.0 – 1000	13C2-PFUdA	200
PFDoDA	1.0 – 2000	13C2-PFDoA	200
PFTTrDA	1.0 – 2000	13C2-PFTeDA	200
PFTeDA	1.0 – 2000	13C2-PFTeDA	200
PFHxDA	0.1 – 500	13C2-PFHxDA	200
PFODA	0.1 – 500	13C2-PFHxDA	200
PFPrS	0.1 – 5000	13C3-PFBS	200
PFBS	0.1 – 5000	13C3-PFBS	200
PFPeS	0.1 – 5000	13C2-PFOS	200
PFHxS <sup>1</sup>	0.5 – 5000	18O2-PFHxS	200
PFHpS	0.1 – 5000	18O2-PFHxS	200
PFOS <sup>1</sup>	5.0 – 5000	13C4-PFOS	200
PFNS	1.0 – 5000	13C4-PFOS	200
PFDS	1.0 – 5000	13C4-PFOS	200
PFDoDS	2.0 – 1000	13C4-PFOS	200
8Cl-PFOS	1.0 – 5000	13C4-PFOS	200
F-53B-major	1.0 – 5000	13C4-PFOS	200
F-53B-minor	2.0 – 5000	13C4-PFOS	200
PFOSA	2.0 – 5000	13C8-FOSA	200
NMeFOSA	5.0 – 2000	d3-MeFOSA	200
NEtFOSA	5.0 – 1000	d5-EtFOSA	200
FOSAA	5.0 – 500	d3-MeFOSAA	200
NMeFOSAA	50 – 2000	d3-MeFOSAA	200
NEtFOSAA	1.0 – 500	d5-EtFOSAA	200

4:2 FTS	5.0 – 1000	13C2-4:2 FTS	200
6:2 FTS	2.0 – 500	13C2-6:2 FTS	200
8:2 FTS	1.0 – 2000	13C2-8:2 FTS	200
10:2 FTS	2.0 – 500	13C2-8:2 FTS	200
3:3 FTCA	10 – 2000	13C2-6:2 FTCA	200
5:3 FTCA	5.0 - 5000	13C2-8:2 FTCA	200
7:3 FTCA	5.0 - 10000	13C2-10:2 FTCA	200
6:2 FTCA	2.0 – 500	13C2-6:2 FTCA	200
8:2 FTCA	5.0 – 5000	13C2-8:2 FTCA	200
10:2 FTCA	2.0 – 5000	13C2-10:2 FTCA	200
6:2 FTUCA	1.0 – 10000	13C2-6:2 UFTCA	200
8:2 FTUCA	1.0 – 10000	13C2-8:2 UFTCA	200
10:2 FTUCA	1.0 – 2000	13C2-10:2 UFTCA	200
ADONA	0.5 - 5000	13C4-PFOA	200
HFPO-DA	5.0 - 1000	13C3-HFPO-DA	200

- i. Exist in the standard as the linear and branched isomers.
- ii. PFHxDA, PFODA, FOSAA, MeFOSAA, and EtFOSAA excluded from high-level (>3.85 ng/mL) calibration standards to prevent instrument carryover.

**Table S18.** Minimum, median, mean, and maximum MDLs and MQLs for PFASs, by laboratory, across all analyses. Units are ng/L in the original water sample. \*Denotes semi-quantitative analytes (Excel).

#### Text S4.5. PFASs, Eurofins West Sacramento

Sample preparation at Eurofins started with creation of single, composited total water samples by combining up to five storm event sub-samples. Each sub-sample was fortified with PFAS ISTDs (total concentration 1.25-2.5 ng/mL in final sample extract; **Table S19**), briefly vortexed, allowed to equilibrate ( $\geq 10$  min), and centrifuged (3300 RCF, 5 min). Supernatants were composited into a 250-mL HDPE bottle, gently inverted, and extracted using multi-phase SPE (500 mg weak-anion exchange [WAX]/50 mg graphite carbon black [GCB]). Original sub-sample tubes were serially rinsed with 8 mL of 0.4% ammonium acetate in methanol. The final tube was centrifuged (3300 RCF, 5 min); the basic methanolic supernatant was used to rinse the 250-mL bottle and then to elute the WAX/GCB SPE. Eluents were adjusted to 80:20 methanol:water, briefly vortexed, and stored at 2-6 °C prior to analysis.

Sample analysis at Eurofins used an Exion LC system with two pumps and a C18 analytical column. Detection used a SCIEX 5500 mass spectrometer with ESI- and MRM. The mobile phases were 25 mM ammonium acetate in methanol (A) and methanol (B). A delay column was plumbed after the mixer and prior to the analytical column to distinguish any system background from positive detections. Separation of analytes (20  $\mu$ L injection) occurred on a C18 analytical

column (Phenomenex Gemini C18 3 $\mu$ m; 50x3 mm) before introduction into the instrument source. Detection used negative polarity electrospray ionization with data acquired in MRM mode (minimum 10 scans per peak). Additional parameters are provided in **Table S19**, and MDLs/MQLs are summarized in **Table S18**.

**Table S19.** Eurofins laboratory list of targeted PFASs, calibration ranges, and corresponding internal standards.

Targeted PFAS	Isotopic Analog	Typical RT (minutes)	Calibration Range (ng/L)	ISTD Conc. in final extract ( $\mu$ g/L)
PFPPrA	13C4 PFBA	2.54	2.0-800	0.025
PFMOAA	13C4 PFBA	2.54	2.0-800	0.025
R-EVE	13C4 PFBA	2.54	5.0-800	0.025
PFBA	13C4 PFBA	2.54	2.0-800	0.025
PMPA	13C4 PFBA	2.54	2.0-800	0.025
PFPPrS	13C3-PFBS	2.98	2.0-800	0.025
NVHOS	13C4 PFBA	2.54	3.0-800	0.025
PFECA-F	13C5 PFPeA	2.97	2.0-800	0.025
PFO2HxA	13C5 PFPeA	2.97	2.0-800	0.025
PEPA	13C5 PFPeA	2.97	2.0-800	0.025
3:3 FTCA	13C3-PFBS	2.98	2.0-800	0.025
PFPeA	13C5 PFPeA	2.97	2.0-800	0.025
PFBS	M3-PFBS	2.98	2.0-800	0.025
PFECA-A	13C5 PFPeA	2.97	2.0-800	0.025
PES	13C3-PFBS	2.98	2.0-800	0.025
PFPeS	13C3-PFBS	2.98	2.0-800	0.025
4:2 FTS	M2-4:2FTS	3.28	2.0-800	0.025
PFECA-B	13C2 PFHxA	3.35	2.0-800	0.025
PFO3OA	13C2 PFHxA	3.35	2.0-800	0.025
PFHxA	13C2 PFHxA	3.35	2.0-800	0.025
HFPO-DA	13C3 HFPO-DA	3.46	4.0-800	0.025
R-PSDCA	13C4 PFHpA	3.74	3.0-800	0.025
Hydro-EVE Acid	13C4 PFHpA	3.74	2.0-800	0.025
5:3 FTCA	13C-6:2 FTCA	3.77	2.0-800	0.025
PFO4DA	13C4 PFHpA	3.74	2.0-800	0.025
PFHpA	13C4 PFHpA	3.74	2.0-800	0.025
PFHxS	18O2 PFHxS	3.74	2.0-800	0.025
Hydro-PS-Acid	13C4 PFHpA	3.74	2.0-800	0.025
6:2 FTUCA	13C-6:2 FTUCA	3.75	2.0-800	0.025
6:2 FTCA	13C-6:2 FTCA	3.77	2.0-800	0.025
PFPE-1	13C-6:2 FTCA	3.77	2.0-800	0.025
PS-Acid	13C4 PFOA	4.14	2.0-800	0.025
EVE-Acid	13C4 PFOA	4.14	2.0-800	0.025
PFECHS	13C4 PFOA	4.14	2.0-800	0.025
6:2 FTS	M2-6:2FTS	4.12	5.0-800	0.025
PFOA	13C4 PFOA	4.14	2.0-800	0.025

PFO5DA	13C4 PFOA	4.14	2.0-800	0.025
ADONA	13C4 PFOS	4.5	2.0-800	0.025
PFHpS	13C4 PFOS	4.5	2.0-800	0.025
8:2 FTUCA	13C-8:2 FTUCA	4.5	2.0-800	0.025
PFOS	13C4 PFOS	4.5	2.0-800	0.025
F-53B-major	13C4 PFOS	4.5	2.0-800	0.025
PFDS	13C4 PFOS	4.5	2.0-800	0.025
11Cl-PF3OUdS	13C4 PFOS	4.5	2.0-800	0.025
PFNA	13C5 PFNA	4.52	2.0-800	0.025
8:2 FTCA	13C-8:2 FTCA	4.55	2.0-800	0.025
7:3 FTCA	13C-8:2 FTCA	4.55	2.0-800	0.025
PFOSA	13C8 PFOSA	4.82	2.0-800	0.025
PFNS	13C4 PFOS	4.5	2.0-800	0.025
PFDoS	13C4 PFOS	4.5	2.0-800	0.025
PFDA	13C2 PFDA	4.86	2.0-800	0.025
8:2 FTS	M2-8:2FTS	4.86	2.0-800	0.025
NMeFOSAA	d3-MeFOSAA	5.03	5.0-800	0.025
10:2 FTUCA	13C-10:2 FTUCA	5.18	2.0-800	0.025
10:2 FTCA	13C-10:2 FTCA	5.18	2.0-800	0.025
PFUnDA	13C2 PFUnDA	5.19	2.0-800	0.025
NEtFOSAA	d5-EtFOSAA	5.19	5.0-800	0.025
NMeFOSE	d7N-MeFOSE	5.25	4.0-800	0.025
NMeFOSA	d3MeFOSA	5.26	2.0-800	0.025
NEtFOSE	d9N-EtFOSE	5.4	2.0-800	0.025
EtFOSA	d5EtFOSA	5.44	2.0-800	0.025
PFDoA	13C2 PFDoA	5.47	2.0-800	0.025
10:2 FTS	M2-10:2FTS	5.48	2.0-800	0.025
PFTTrDA	13C2 PFDoA	5.47	2.0-800	0.025
PFTeDA	13C2 PFTeDA	5.99	2.0-800	0.025
PFHxDA	13C2 PFHxDA	6.39	2.0-800	0.025
PFODA	13C2 PFHxDA	6.39	2.0-800	0.025
6:2 diPAP	13C4-6:2 diPAP	6.87	2.0-800	0.025
6:2/8:2 diPAP	13C4-6:2 diPAP	7.36	2.0-800	0.025
8:2 diPAP	13C4-8:2 diPAP	7.79	2.0-800	0.025
10:2 diPAP	13C4-6:2 diPAP	8.83	2.0-800	0.025

## **Text S5. QA/QC**

### Text S5.1. SWCECs (including 6PPDQ)

Analytes with quality assurance measures outside the semi-quantitative range, including recoveries below 25% or above 400%, and/or relative percent difference or relative standard deviation (RPD/RSD) above 120%, included caprolactam, diclofenac, and iprodione.

Blanks and Spikes. Duplicate method banks (1 L ultrapure water spiked with ISTDs) were extracted and analyzed in every batch. Matrix spikes were performed (duplicate or triplicate) when sufficient field water was available, either using a specific field sample or a pooled (mixed) sample (50 µL methanolic spike, n=24 stormwater-derived analytes other than 6PPDQ, 50 – 500 ng/L in water). A matrix blank was processed alongside matrix spike samples to account for background occurrence of target analytes. The mean recoveries of target analytes in the matrix spike sample (excluding semi- or non-quantitative analytes, benzotriazole, and 5-methyl-1H-benzotriazole) ranged from 69% to 230%. Relative percent differences (RPDs) for matrix-spike replicates were 39% or better.

### Text S5.2. OPEs and Bisphenols

Based on QA review of the spiked recovery samples and lab duplicates (discussed in detail below), semi-quantitative results included the particulate fraction for resorcinol bis (diphenyl phosphate) (RBDPP) and triphenyl phosphate (TPhP).

Blanks and Spikes. Matrix spiking tests were conducted to evaluate method recovery efficiency. Known amounts of target analytes (10 ng each for OPEs and 20 ng each for bisphenols; same for aqueous and particulate spikes) as well as isotope dilution internal standards were spiked into a pooled water sample (i.e., filtered water from multiple field samples was pooled) that was subsequently split into three replicates and extracted/analyzed as described in the main text and Text S4.3. A matrix blank (i.e., pooled water spiked with isotope dilution internal standards only) was also processed. For particulates, spiking tests were conducted with pre-cleaned sodium sulfate and processed in three replicates along with a matrix blank. The mean recoveries of target analytes from the matrix spiking tests ranged from 72.4 (±3.6)% to 91.8 (±8.6)% for aqueous analysis and 74.7 (±4.9)% to 94.6 (±4.2)% for particulate analysis. Relative standard deviations (RSDs) for matrix-spike replicates averaged within 5% or better.

Field Sample Concentration Correction. Quantitation used isotope dilution methods, with analyte concentrations inherently corrected based on the recoveries of corresponding internal standards. Results for field samples were also blank corrected. Dissolved bisphenols A, F, and S, EHDPHP, TBOEP, TCEP, TCIPP, TDCIPP, TEHP, TMPP, TNBP, TPhP contamination was observed in

laboratory blanks (average 0.2, 0.1, 0.6, 0.02, 1.26, 0.2, 0.7, 0.6, 0.02, 0.02, 0.3, 0.2 ng/L, respectively), constituting less than 7% of the median concentrations measured in field samples. Particulate bisphenols A and F, 24DIPDPP, 2IPDPP, 2tBPDPP, 4IPDPP, 4tBPDPP, EHDPHP, TBOEP, TCEP, TCIPP, TDCIPP, TEHP, TEP, TIBP, TMPP, TPhP contamination was observed in laboratory blanks (averages 1.6, 0.3, 0.6, 0.6, 0.6, 1.2, 0.4, 1.2, 0.3, 0.3, 0.4, 0.3, 0.3, 0.3, 1.2, 0.4 ng/L, respectively), constituting less than 3% of the median concentrations measured in field samples. The field blanks indicated modest levels of potential background contamination with TBOEP(0.5 ng/L), TCEP (0.7 ng/L), TCIPP (1.1 ng/L), TDCIPP (0.7 ng/L), TNBP (0.2 ng/L), and TPhP (0.1 ng/L). Final concentration data were reported after subtracting the average contamination levels in laboratory blanks or field blanks. For compounds detectable in both laboratory and field blanks, higher contamination levels were used for blank subtraction.

### Text S5.3. PFASs – Mines

Based on QA review of the spiked recovery samples and lab duplicates (discussed in detail below), semi-quantitative analytes include perfluorooctadecanoate (PFODA) and 6:2 FTCA.

Blanks and Spikes. Field staff obtained field blank samples from one storm during the first wet season using Optima LC/MS grade water. In addition to this, method blanks consisting of Optima LC/MS grade water were prepared alongside samples processed on January 9, 2019 and January 18, 2019. Laboratory blanks (all reagents plus internal standards), double blanks (all reagents without internal standards), and quality control spiked samples (all reagents + internal standards + 300 pg of target PFASs) were prepared directly in autosampler vials at the same percent composition water, methanol, basic water, isopropanol, and 2,2,2-trifluoroethanol as the samples. A trio of one laboratory blank, one double blank, and one quality control spiked sample was prepared and analyzed after every 10 samples. All blanks were used to monitor contamination.

Additionally, three additional field samples were spiked with PFASs and prepared to assess PFAS recovery and matrix effects. Recoveries for the majority of PFASs observed were between 79.1% and 108% for these matrix spike samples. Perfluorooctadecanoate (PFODA) and 6:2 FTCA had average matrix spike recoveries of 10 and 42% respectively; thus, measurements of these analytes are considered semiquantitative.

Instrumental Drift. Quality control (QC) samples were used to monitor instrumental drift. If the concentration of a reported PFAS in the QC sample was not within  $\pm 30\%$  of the known concentration, samples analyzed after the failed QC up until the next passing QC were reanalyzed.

Sample Variability. To assess variability within samples, triplicates of three composite samples were analyzed and reported. Relative standard deviations ranged from 13-47% (average 31%).

SRM Spike Recovery. In preliminary experiments, extraction efficiencies for particulate PFASs within total water samples were determined by adding a standard reference material (SRM 2585 Organic Contaminants in House Dust and SRM 2781 Domestic Sludge) to a known amount of Optima LC/MS grade water. The standard reference materials had been previously analyzed and contained known amounts of PFOS. These suspended sediments underwent identical processing. Extraction efficiencies (mean  $\pm$  standard deviation) from triplicate samples were  $13.8\% \pm 0.9\%$  and  $64.8\% \pm 0.95\%$ , respectively, for household dust and domestic sludge. PFOS extraction efficiency from stormwater sediment likely falls between these two numbers. While these extraction efficiencies are lower than typically desired, they reflect the limitations of attempting to extract primarily aqueous samples with low levels of suspended solids.

#### Text S5.4. PFASs – Eurofins

Based on QA review of the spiked recovery samples and lab duplicates (discussed in detail below), semi-quantitative analytes include 6:2 diPAP, 8:2 diPAP, and perfluorododecanoate (PFDoDA). Analytes with insufficiently quantitative measurements include 6:2/8:2 diPAP, 11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (F53B minor), N-ethyl-perfluorooctanesulfonamidoethanol (NEtFOSE), N-methyl-perfluorooctanesulfonamide (NMeFOSA), and perfluorodecanesulfonate (PFDS).

Analytical QC. Each analytical batch of up to 20 samples included a negative control (Method Blank, MB) and a minimum of a positive control (Laboratory Control Sample, LCS). A duplicate LCS may be included. Data were integrated with the LIMS (Laboratory Informatics Management System) and then reviewed by both a primary and secondary analyst.

Blanks and Spikes. Overall, only minor laboratory and field blank contamination was reported for a handful of analytes, and recoveries were mostly within target ranges for the most common analytes. For laboratory replicates, precision was within the laboratory's target RPD of 30% for about half of the 20 quantifiable analytes. Variation in field replicates was over 50% RPD for 13 quantifiable analytes. Of those, most were analytes that were measured in one field replicate at over six-fold the MDL but not detected in the other replicate. Analytes with RPDs of 65-120% are considered semi-quantitative, and include bis(1H,1H,2H,2H-perfluorodecyl)phosphate (6:2 diPAP), bis(1H,1H,2H,2H-perfluorooctyl)phosphate (8:2 diPAP), and perfluorododecanoate (PFODA). Analytes with quality assurance measures outside the semi-quantitative range had RPDs above 120%: 6:2/8:2 fluorotelomer phosphate diester (6:2/8:2 diPAP), 11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (F53B-minor), N-ethyl-



perfluorooctanesulfonamidoethanol (NEtFOSE), N-methyl-perfluorooctanesulfonamide (NMeFOSA), and perfluorodecanesulfonate (PFDS).

Average laboratory blanks were generally below MDL, aside from 10:2 fluorotelomer phosphate diester (10:2 diPAP), bis(1H,1H,2H,2H-perfluorodecyl) phosphate (6:2 diPAP), and bis(1H,1H,2H,2H-perfluorooctyl) phosphate (8:2 diPAP). Field samples in those batches were flagged (VIP), with results less than 3x the blank also flagged as concentrations not distinguishable from blanks (VIPND), representing 94% and 75% of the results for 10:2 diPAP and 6:2 diPAP, respectively. In the field blank, perfluorooctanesulfonate (PFOS) and perfluorodecanesulfonate (PFDS) were detected. The field blanks that differed by less than a day from the field samples on the same site were used to flag site field samples.

## Text S6. Quantitative Concentration Data

All quantitative results of LC-MS/MS analyses are summarized in a series of Excel tables, listed below.

**Table S20.** Full summary of averaged concentration data, including replicate numbers, variability, and QA/QC information. Sample ID is provided as SiteType\_SiteID\_Year, where NF = near field, OB = open bay, US = urban stormwater, and Ref = reference. UnitName defines the concentration unit for Result, MDL, and MQL. LabCalcType and FieldCalcType indicate the calculation used to evaluate variability across lab and field replicates, respectively, with the corresponding values in LabCalcValue and FieldCalcValue, respectively. QA codes are consistent with those used by the California Environmental Data Exchange Network (CEDEN): [http://ceden.org/CEDEN\\_Checker/Checker/DisplayCEDENLookUp.php?List=QALookUp](http://ceden.org/CEDEN_Checker/Checker/DisplayCEDENLookUp.php?List=QALookUp), with the addition of two codes: DIL (Sample diluted 10x and re-analyzed, quantitation possible within calibration range) and CJ.DIL (Sample diluted 10x and re-analyzed, analyte still above calibration range, result considered semi-quantitative) (Excel).

**Table S21.** Summary of averaged data for SWCECs. Units are ng/L in the original water sample. Note that additional details (e.g., % RPD or % RSD, number of replicates, etc.) are provided in Table S20 (Excel).

**Table S22.** Summaries of averaged data for bisphenols and OPEs that had detections >MDL (top) and of total concentration for bisphenols, total OPEs, and individual OPE classes (bottom). Units are ng/L in the original water sample. \*Semi-quantitative analytes. Note that additional details (e.g., % RPD or % RSD, number of replicates, etc.) are provided in Table S20 (Excel).

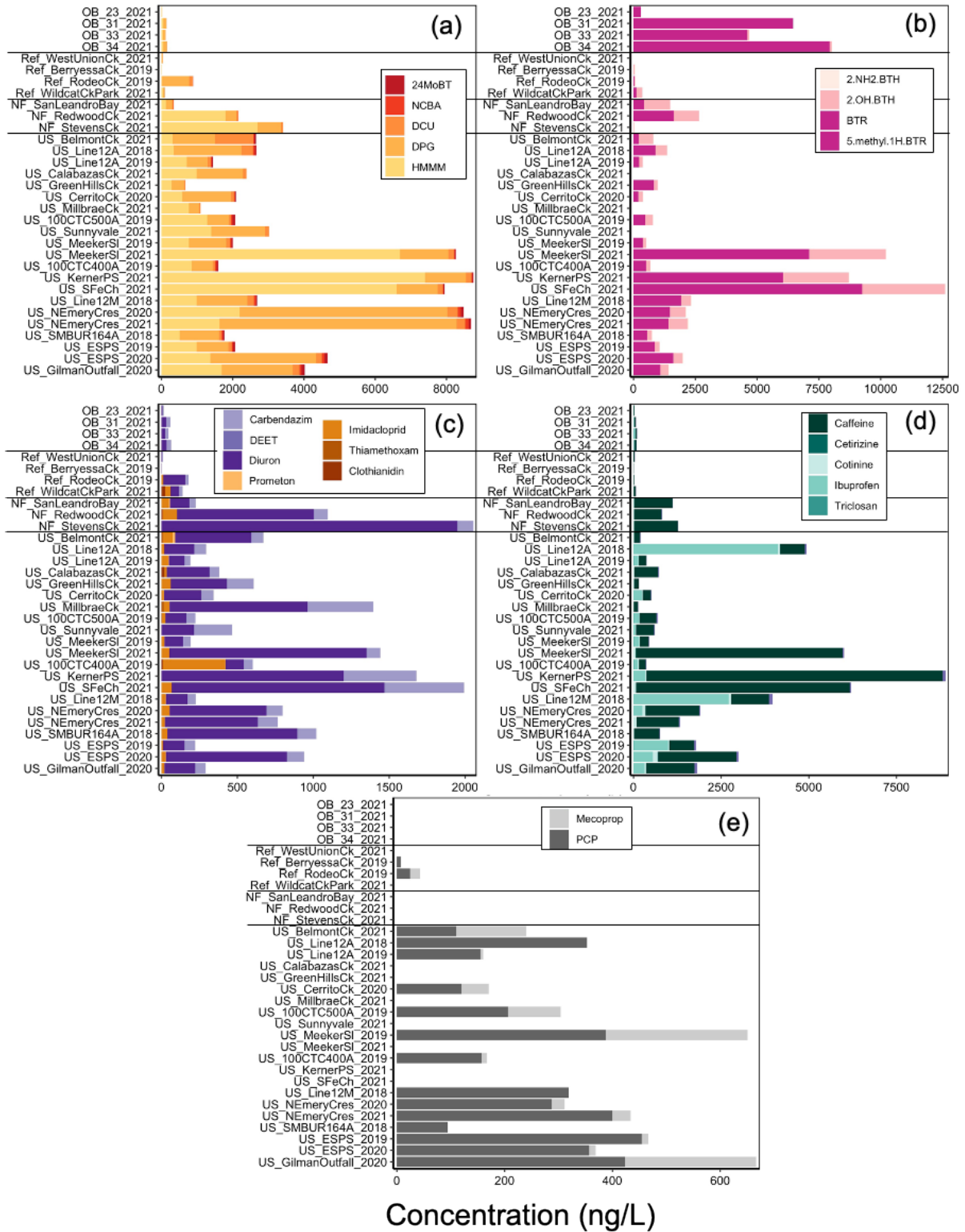
**Table S23.** Summary of averaged data for PFASs (including only PFCAs, PFSAAs, and diPAP analytes). Units are ng/L in the original water sample. Note that additional details (e.g., % RPD or % RSD, number of replicates, etc.) are provided in Table S20 (Excel).

## **Text S7. Statistical Analyses**

Results of non-parametric Spearman rank correlations (statistical significance level was set to  $\alpha = 0.05$ ) are summarized in the below Excel table.

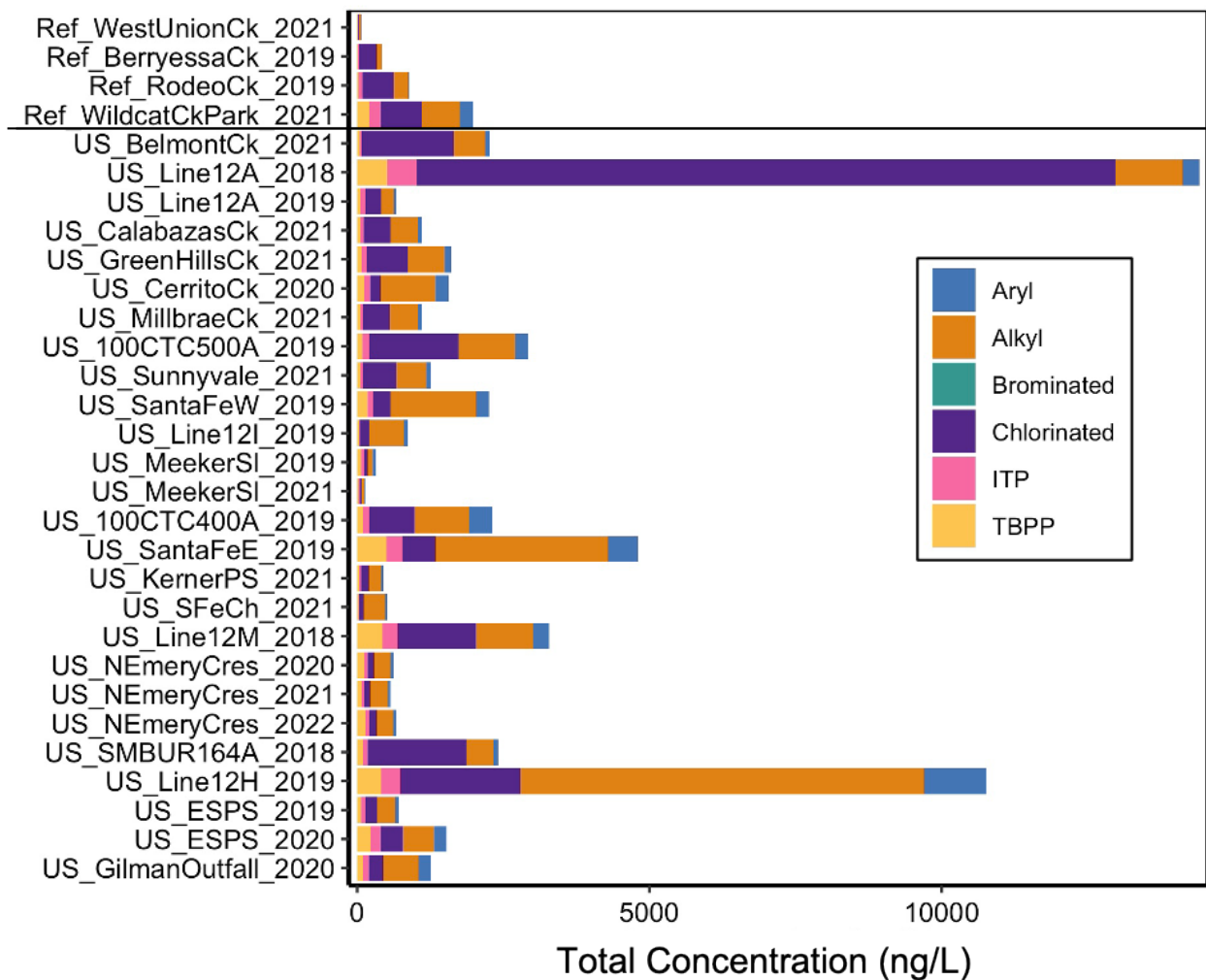
**Table S24.** Pairwise, non-parametric Spearman rank correlations among individual contaminants. Statistical significance level set to  $\alpha = 0.05$ . Correlations were only evaluated for analytes detected in  $\geq 50\%$  of all available samples. Coloration is yellow  $>0.50 - 0.70$ , green  $>0.70-1.0$  (Excel).

# SI Figures

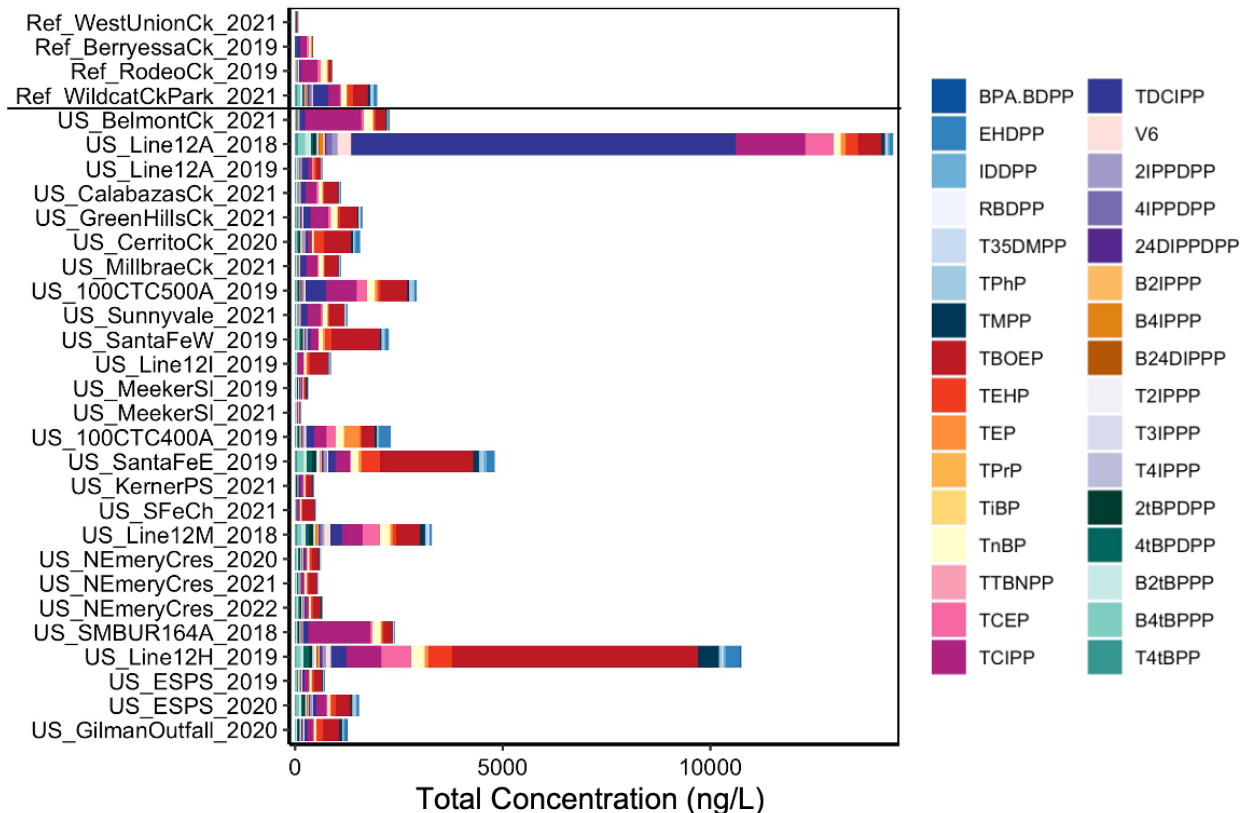


**Figure S1.** Bar chart summarizing all SWCEC concentrations in urban stormwater samples, grouped by compound class: (a) vehicle-derived chemicals (not including 6PPDQ), (b) BTH/BTRs, (c, e) pesticides, and (d) PPCPs. Pesticides are represented in two panels to separate

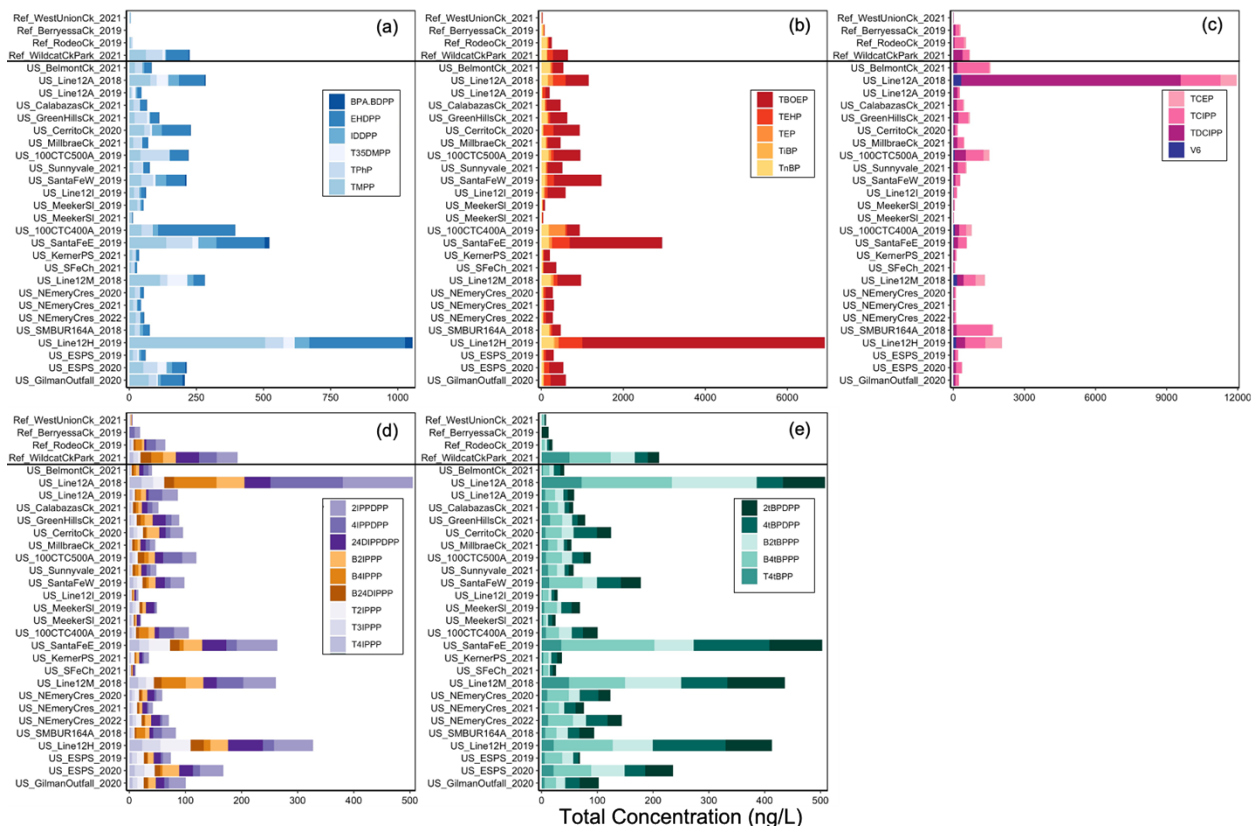
(c) compounds analyzed in all samples vs. (e) in only 2 of the reference sites and 14 of the urban stormwater samples. Non-detects (i.e., concentrations <MDL) are not plotted (i.e., represented as a concentration of zero) (see **Table S8** for MDL values). Sample names indicate SiteType\_SiteName\_Year, where OB = open Bay sites, NF = near field sites, Ref = reference sites, and US = urban stormwater sites. Site types are also separated by a horizontal black line. Site order from top to bottom is based on 1) the percent of impervious landcover in the watershed that corresponds to each sampling site (see **Table S2**), and 2) chronological order for repeat sampling at a given site (see **Table S3**).



**Figure S2.** Bar chart summarizing all organophosphate ester (OPE) concentrations in urban stormwater samples, by OPE class. Non-detects (i.e., concentrations <MDL) are not plotted (i.e., represented as a concentration of zero) (see **Table S16** for MDL values). Sample names indicate SiteType\_SiteName\_Year, where Ref = reference sites and US = urban stormwater sites. Site types are also separated by a horizontal black line. Site order from top to bottom is based on 1) the percent of impervious landcover in the watershed that corresponds to each sampling site (see **Table S2**), and 2) chronological order for repeat sampling at a given site (see **Table S3**).

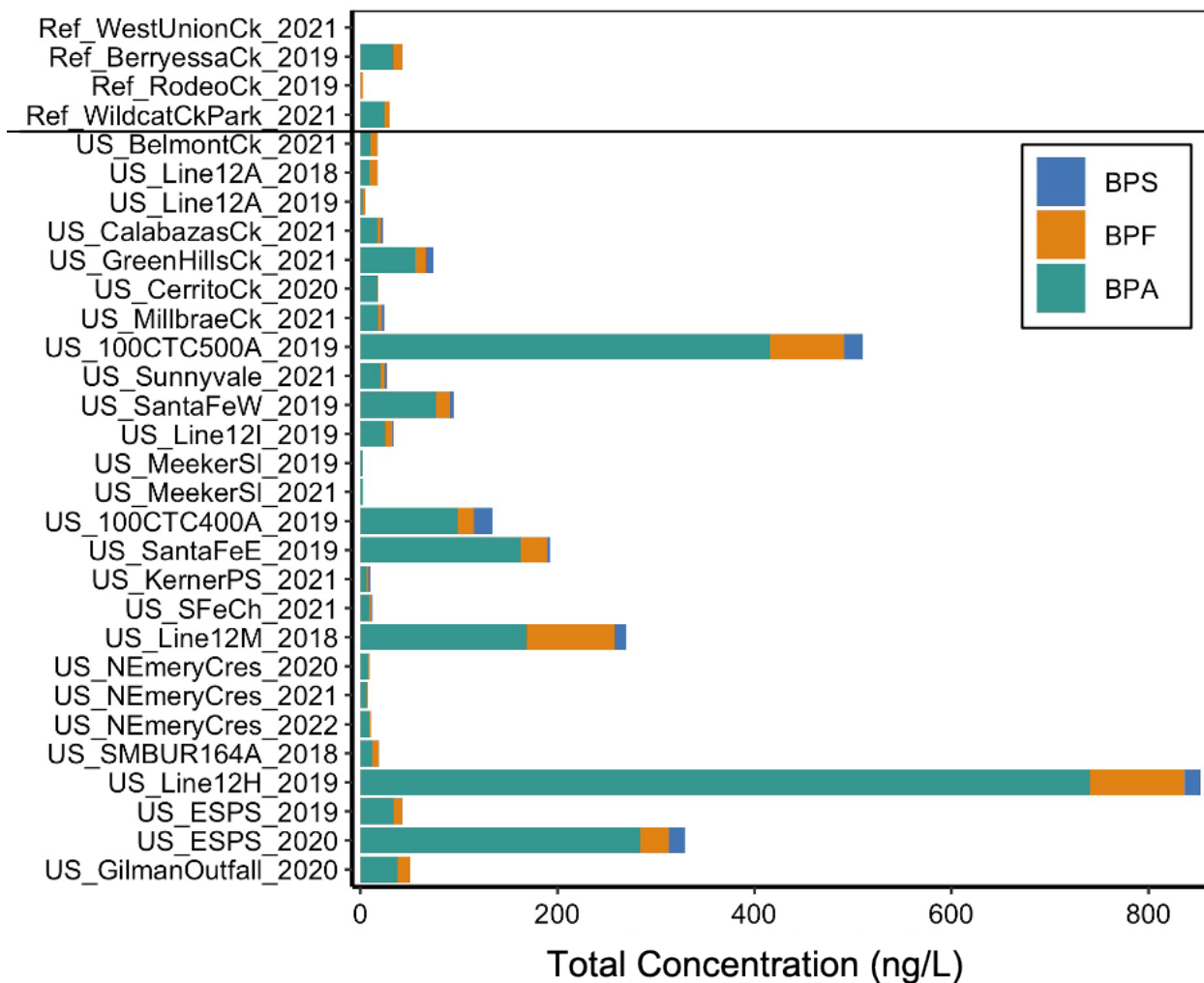


**Figure S3.** Bar chart summarizing all organophosphate ester (OPE) concentrations in urban stormwater samples, by individual analyte. Non-detects (i.e., concentrations <MDL) are not plotted (i.e., represented as a concentration of zero) (see **Table S16** for MDL values). Sample names indicate SiteType\_SiteName\_Year, where Ref = reference sites and US = urban stormwater sites. Site types are also separated by a horizontal black line. Site order from top to bottom is based on 1) the percent of impervious landcover in the watershed that corresponds to each sampling site (see **Table S2**), and 2) chronological order for repeat sampling at a given site (see **Table S3**).

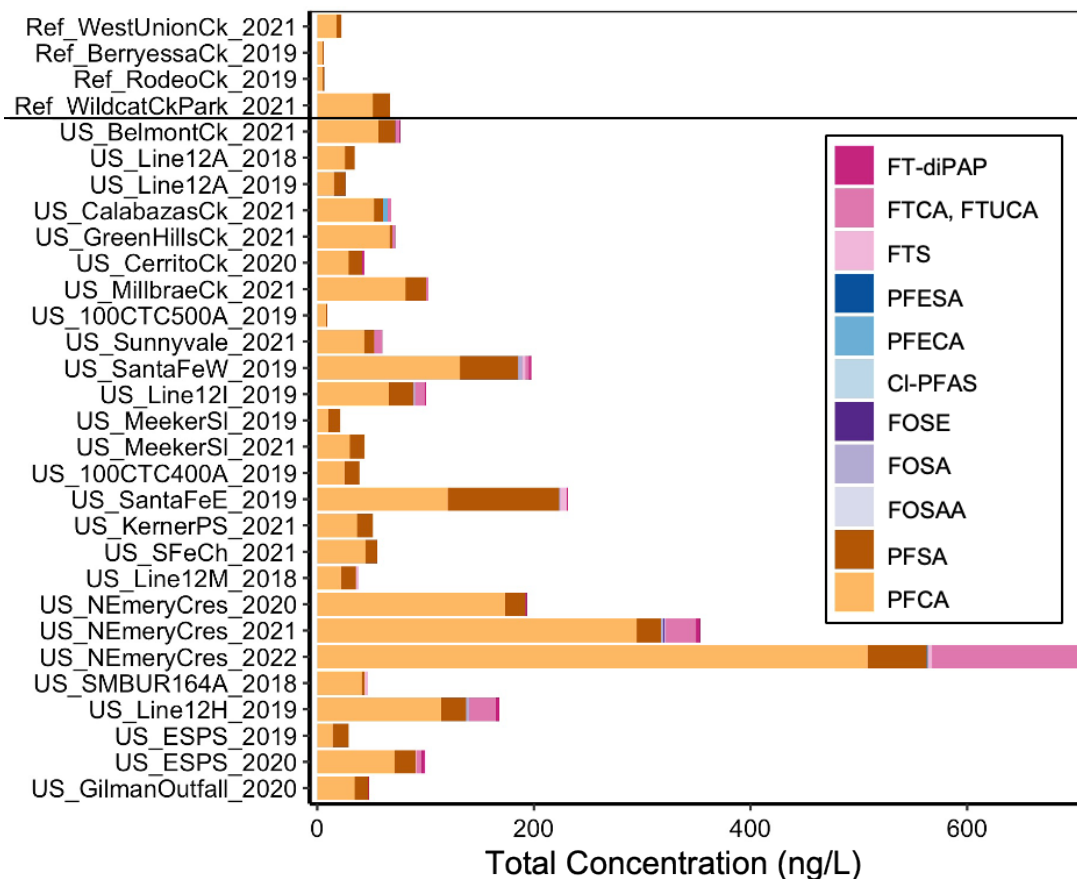


**Figure S4.** Bar chart summarizing organophosphate ester (OPE) concentrations in urban stormwater samples, with each panel representing an OPE class: (a) Aryl OPEs, (b) Alkyl OPEs, (c) Chlorinated OPEs, (d) ITPs, and (e) TBPPs. Non-detects (i.e., concentrations <MDL) are not plotted (i.e., represented as a concentration of zero) (see **Table S16** for MDL values). Sample names indicate SiteType\_SiteName\_Year, where Ref = reference sites and US = urban stormwater sites. Site types are also separated by a horizontal black line. Site order from top to bottom is based on 1) the percent of impervious landcover in the watershed that corresponds to each sampling site (see **Table S2**), and 2) chronological order for repeat sampling at a given site (see **Table S3**).

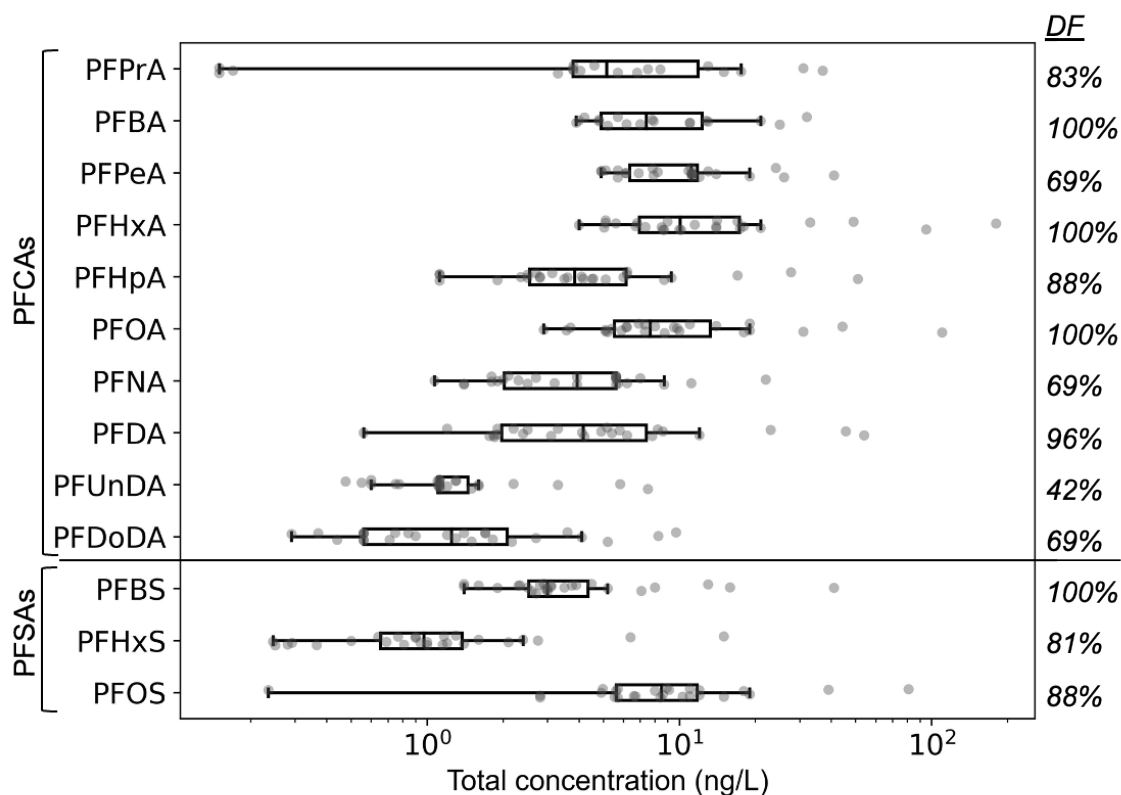




**Figure S5.** Bar chart summarizing bisphenol concentrations with detection frequency (DF) >15% in urban stormwater samples. Non-detects (i.e., concentrations <MDL) are not plotted (i.e., represented as a concentration of zero) (see **Table S16** for MDL values). Sample names indicate SiteType\_SiteName\_Year, where Ref = reference sites and US = urban stormwater sites. Site types are separated by a horizontal black line. Site order from top to bottom is based on 1) the percent of impervious landcover in the watershed that corresponds to each sampling site (see **Table S2**), and 2) chronological order for repeat sampling at a given site (see **Table S3**).



**Figure S6.** Bar chart summarizing all PFAS concentrations in urban stormwater samples, by PFAS class. Non-detects (i.e., concentrations <MDL) are not plotted (i.e., represented as a concentration of zero) (see **Table S18** for MDL values). Sample names indicate SiteType\_SiteName\_Year, where Ref = reference sites and US = urban stormwater sites. Site types are separated by a horizontal black line. Site order from top to bottom is based on 1) the percent of impervious landcover in the watershed that corresponds to each sampling site (see **Table S2**), and 2) chronological order for repeat sampling at a given site (see **Table S3**).



**Figure S7.** Box-and-whisker plot summarizing perfluorocarboxylic acid (PFCA) and perfluorosulfonic acid (PFSA) concentrations in urban stormwater samples, for analytes with detection frequency (DF) > 15%. Concentrations for PFDoDA are semi-quantitative. Detection frequencies are based on 26 urban stormwater samples, except for PFPrA and PFBA (n=18). Boxes indicate 25<sup>th</sup> – 75<sup>th</sup> percentile, whiskers indicate 10<sup>th</sup>-90<sup>th</sup> percentile, and a point is plotted for every sampling event, with all non-detects (i.e., concentrations <MDL) shown on the plot as ½\*MDL (see **Table S18** for MDL values).

## References

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- (4) Murray, C. C.; Vatankhah, H.; McDonough, C. A.; Nickerson, A.; Hedtke, T. T.; Cath, T. Y.; Higgins, C. P.; Bellona, C. L. Removal of Per- and Polyfluoroalkyl Substances Using Super-Fine Powder Activated Carbon and Ceramic Membrane Filtration. *Journal of Hazardous Materials* **2019**, *366*, 160–168. <https://doi.org/10.1016/j.jhazmat.2018.11.050>.