

# APPENDIX C

## $K_{ow}$ , $K_{oc}$ and Mass Distribution Calculations

## APPENDIX C

### MEASURED $K_{ow}$ AND CALCULATED $K_{oc}$ FOR TABLE 3+ COMPOUNDS

Laboratory studies were performed at Chemours Experimental Station in Wilmington, Delaware to determine Table 3+ PFAS octanol-water partition coefficients ( $K_{ow}$ ) using liquid chromatography elution times (OECD, 2014). In this method, Table 3+ PFAS partition between the mobile solvent phase and the hydrocarbon stationary phase as they are transported along the column by the mobile phase. Compounds elute in proportion to their hydrocarbon-water partition coefficient, with hydrophilic chemicals eluted earlier and lipophilic chemicals later.  $K_{ow}$  is then estimated by determining the retention time for each compound in relation to reference compounds with known  $K_{ow}$  values.

$K_{ow}$  tests were conducted on an Agilent 1290 Infinity II HPLC with an Agilent 6470 triple quad with an AJS-ESI source as the detector in multiple reaction monitoring mode (MS/MS filtering). The analytical column was a Phenomenex Gemini reversed phase C18 column 100 x 3 mm, 3 um particle size with 110 A pore size and TMS endcapping. The column was maintained at 50° C +/- 0.1° C by the LC column compartment oven. Mobile phase flow was isocratic at 0.5 mL/min. Table 3+ were separated into 4 groups to facilitate separation under isocratic conditions:

- Group 1 - MMF, DFSA, MTP, Byproduct 4, Byproduct 5, and R-EVE;
- Group 2 - PPF Acid and PMPA;
- Group 3 - PFMOAA, NVHOS, PFO2HxA, PEPA, PES, PFECA B, and PFO3A; and
- Group 4 - By product 6, Hydro Eve, By product 2, PFECA G, PFO4DA, Byproduct 1, Eve Acid, and PFO5DoA.

Mobile phases were prepared daily. Tests were conducted with different isocratic mobile phases methanol/water compositions for each group, and at two pH values (pH 5 [4.89 - 5.10] and pH 8 [8.10 – 8.29]) to span Site pH conditions. Mobile phases were buffered with 20 mM ammonium salt buffer (acetate for pH 5 and bicarbonate for pH 8). Analytes were prepared in a minimum of 90% mobile phase.

The retention time is described by the capacity factor  $k$ :

$$k = \frac{t_R - t_0}{t_0}$$

where  $t_R$  is the retention time of the Table 3+ compound, and  $t_0$  is the average time a solvent molecule needs to pass through the column (the dead-time).  $K_{ow}$  values for Table 3+

compounds were estimated by experimentally determining *k* and then calculating K<sub>ow</sub> using the following equation:

$$\log K_{ow} = a + b \times \log k$$

where a, b = linear regression coefficients were calculated with a linear regression curve of log K<sub>ow</sub> and k of 11 reference PFAS compounds of varying structures (Table C-1 and Figure C-1). For DFSA, MTP, PPF, and PFMOAA, t<sub>R</sub> was found to be less than t<sub>0</sub>, thus log K<sub>ow</sub> was estimated by extrapolation and extrapolated values are provided in parenthesis.

A linear regression curve between log K<sub>ow</sub> and log K<sub>oc</sub> was then developed using 20 reference compounds with known log K<sub>ow</sub> and log K<sub>oc</sub> (Table C-2 and Figure C-2). Results of the log K<sub>ow</sub> and log K<sub>oc</sub> values for Table 3+ PFAS are provided in Table 3 of the main CAP text.

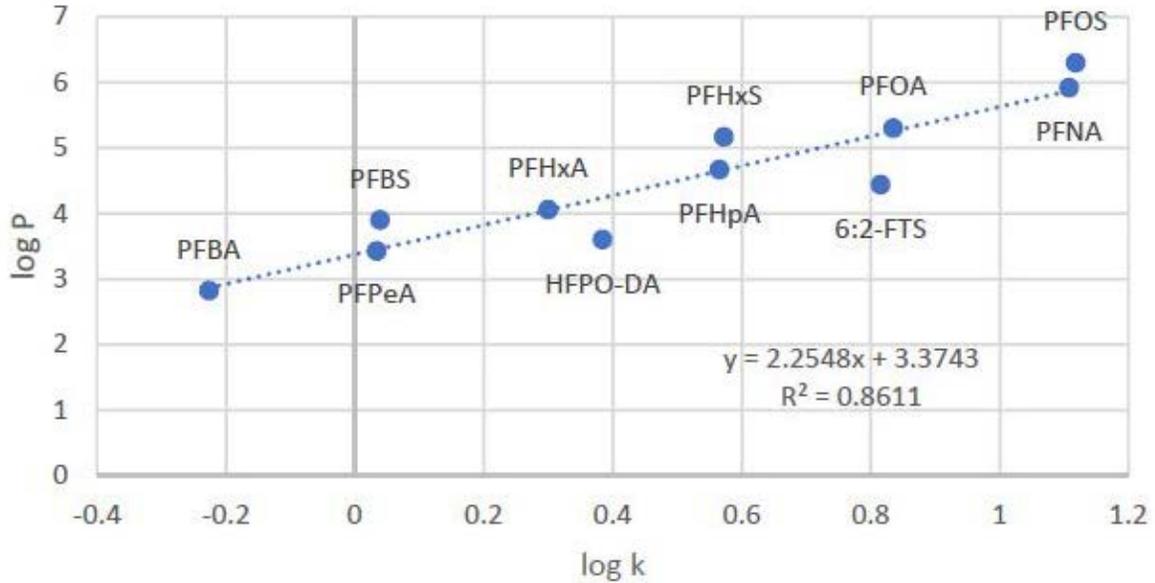
**Table C-1: Reference Compounds for Log Kow versus Retention Time Linear Regression Curve**

Acronym	Name	Formula	CAS #	Log K <sub>ow</sub> <sup>1</sup>
<b>Perfluoroalkyl Ether Carboxylic Acids</b>				
HFPO-DA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propionic acid	C6HF11O3	13252-13-6	3.6
<b>Perfluoroalkyl Carboxylic Acids</b>				
PFBA	Perfluoro-n-butanoic acid	C4HF7O2	375-22-4	2.82
PFPeA	Perfluoro-n-pentanoic acid	C5HF9O2	2706-90-3	3.43
PFHxA	Perfluoro-n-hexanoic acid	C6HF11O2	307-24-4	4.06
PFHpA	Perfluoro-n-heptanoic acid	C7HF13O2	375-85-9	4.67
PFOA	Perfluoro-n-octanoic acid	C8HF15O2	335-67-1	5.3
PFNA	Perfluoro-n-nonanoic acid	C9HF17O2	375-95-1	5.92
<b>Perfluoroalkyl Sulfonic Acids</b>				
PFBS	Perfluorobutanesulfonic acid	C4HF9O3S	375-73-5	3.9
PFHxS	Perfluorohexanesulphonic acid	C6HF13O3S	355-46-4	5.17
PFOS	Perfluorooctanesulfonic acid	C8HF17O3S	1763-23-1	6.3
<b>Fluorotelomer sulfonic acids (Polyfluorinated)</b>				
6:2 FTS	Fluorotelomer sulfonate	C8H5F13O3S	27619-97-2	4.44

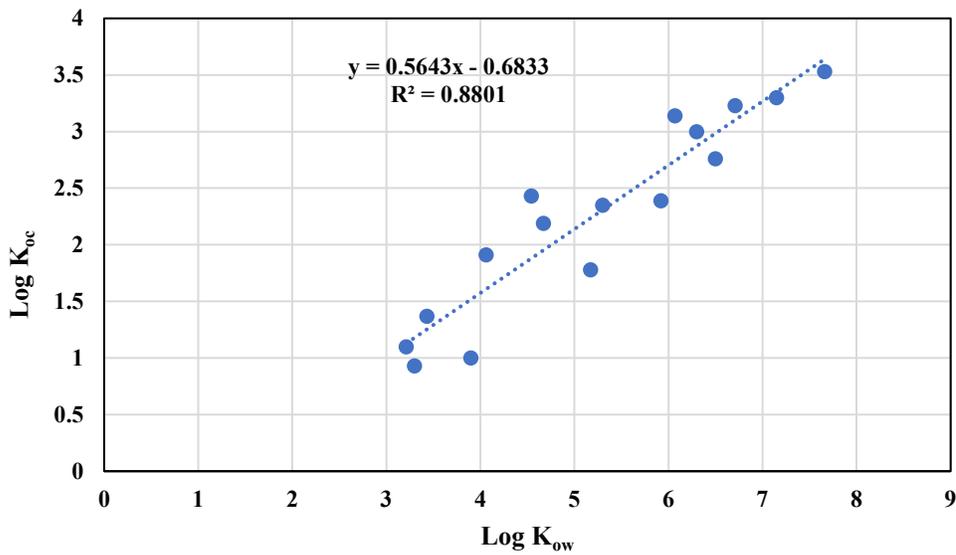
<sup>1</sup> HFPO-DA value from Hopkins et al, 2018.

PFOS value from Zhao et al., 2016.

All other values from Concawe, 2016.



**Figure C-1: Linear Regression Curve for Log P (log  $K_{ow}$ ) vs Log k (represents the retention time) at pH 5.10 for Select Reference Compounds**



**Figure C-2: Linear Regression Curve of Log  $K_{ow}$  vs Log  $K_{oc}$  for Reference PFAS Compounds**

**Table C-2: Reference Compounds for Log K<sub>ow</sub> and Log K<sub>oc</sub> Linear Regression Curve**

Acronym	Name	Formula	CAS #	Log K <sub>ow</sub> <sup>1</sup>	Log K <sub>oc</sub> [L/kg] <sup>1</sup>
<b>Perfluoroalkyl Carboxylates / Perfluoroalkyl Carboxylic Acids</b>					
PFBA	Perfluorobutanoic Acid	C <sub>4</sub> HF <sub>7</sub> O <sub>2</sub>	375-22-4	2.82	1.88
PFPeA	Perfluoropentanoic Acid	C <sub>5</sub> HF <sub>9</sub> O <sub>2</sub>	2706-90-3	3.43	1.37
PFHxA	Perfluorohexanoic Acid	C <sub>6</sub> HF <sub>11</sub> O <sub>2</sub>	307-24-4	4.06	1.91
PFHpA	Perfluoroheptanoic Acid	C <sub>7</sub> HF <sub>13</sub> O <sub>2</sub>	375-85-9	4.67	2.19
PFOA	Perfluorooctanoic Acid	C <sub>8</sub> HF <sub>15</sub> O <sub>2</sub>	335-67-1	5.3	2.35
PFNA	Perfluorononanoic Acid	C <sub>9</sub> HF <sub>17</sub> O <sub>2</sub>	375-95-1	5.92	2.39
PFDA	Perfluorodecanoic Acid	C <sub>10</sub> HF <sub>19</sub> O <sub>2</sub>	335-76-2	6.5	2.76
PFUnA	Perfluoroundecanoic Acid	C <sub>11</sub> HF <sub>21</sub> O <sub>2</sub>	2058-94-8	7.15	3.3
<b>Perfluoroalkyl Sulfonates / Perfluoroalkyl Sulfonic Acids</b>					
PFBS	Perfluorobutane Sulfonate	C <sub>4</sub> HF <sub>9</sub> O <sub>3</sub> S	375-73-5	3.9	1
PFHxS	Perfluorohexane Sulfonate	C <sub>6</sub> HF <sub>13</sub> O <sub>3</sub> S	432-50-8	5.17	1.78
PFOS	Perfluorooctane Sulfonate	C <sub>8</sub> HF <sub>17</sub> O <sub>3</sub> S	1763-23-1	6.3	3
PFDS	Perfluorodecane Sulfonate	C <sub>10</sub> HF <sub>21</sub> O <sub>3</sub> S	333-77-3	7.66	3.53
<b>Perfluorooctane Sulfonamide and Derivatives</b>					
N-MeFOSA	N-Methyl-Perfluorooctane Sulfonamide	C <sub>9</sub> H <sub>4</sub> F <sub>17</sub> NO <sub>2</sub> S	31506-32-8	6.07	3.14
N-EtFOSA	N-Ethyl-Perfluorooctane Sulfonamide	C <sub>10</sub> H <sub>6</sub> F <sub>17</sub> NO <sub>2</sub> S	4151-50-2	6.71	3.23
<b>Perfluoroalkyl Ether Carboxylic Acids</b>					
HFPO-DA	Hexafluoropropylene oxide dimer acid	C <sub>6</sub> HF <sub>11</sub> O <sub>3</sub>	13252-13-6	3.21	1.1
<b>Fluorotelomer Alcohols</b>					
4:2 FTOH	Perfluoroethylethanol 4:2	C <sub>6</sub> H <sub>3</sub> F <sub>9</sub> O	2043-47-2	3.3	0.93
6:2 FTOH	Perfluorohexylethanol 6:2	C <sub>8</sub> H <sub>5</sub> F <sub>13</sub> O	647-42-7	4.54	2.43
(8:2 FTOH)	Perfluorocyclethanol 8:2	C <sub>10</sub> H <sub>5</sub> F <sub>17</sub> O	865-86-1	5.58	3.84
(10:2 FTOH)	Perfluorodecylethanol 10:2	C <sub>12</sub> H <sub>5</sub> F <sub>21</sub> O	678-39-8	6.63	6.2
<b>Fluorotelomer sulfonic acids</b>					
(8:2 FTS)	1H, 1H, 2H, 2H-Perfluorodecanesulfonic Acid	C <sub>10</sub> H <sub>5</sub> O <sub>3</sub> F <sub>17</sub> S	39108-34-4	5.66	0.01

<sup>1</sup> PFOS values from NGWA, 2019.

HFPO-DA value from Hopkins et al., Recently Detected Drinking Water Contaminants: GenX and Other Per- and Polyfluoroalkyl Ether Acids, 2018.

All other values from: Concawe. Environmental fate and effects of poly and perfluoroalkyl substances (PFAS), 2011.

Compounds in parentheses were excluded from linear regression curve due to values not being compatible with PFAS structure correlations

## MASS DISTRIBUTION CALCULATIONS FOR TABLE 3+ COMPOUNDS

The total mass of PFAS in saturated aquifers was calculated by summing PFAS in groundwater and PFAS sorbed on soils. The PFAS sorbed on saturated soil was calculated by taking the groundwater concentrations from a groundwater sample for each PFAS to PFAS sorbed on 0.1 kg soil using median fraction organic carbon  $f_{oc}$  similar lithologic units and  $K_{oc}$  values. For locations where  $f_{oc}$  wasn't measured, a median  $f_{oc}$  value from all lithologic units was used.

An analysis was performed to determine whether PFAS mass on and offsite was primarily associated with the unsaturated zone or the saturated zone. This analysis was conducted to help evaluate the potential relative benefit between corrective action for soils versus groundwater. The analysis was conducted by comparing the unsaturated zone total mass (mass in pore water and soil) to the saturated zone total mass (mass in groundwater and soil) for samples taken from the same location. Total mass was calculated for one cubic meter of material (unsaturated or saturated).

The total Table 3+ PFAS mass in the unsaturated zone was estimated by summing the total Table 3+ PFAS mass measured in soil samples from the unsaturated zone (this is assumed to include both PFAS in the pore water and PFAS sorbed on the soil).

The total Table 3+ PFAS mass in the saturated zone was calculated using groundwater data from samples representative of the saturated zone to estimate the total mass of PFAS in the soil from which the groundwater sample originated. Parameters used for the calculations were:

- Measured fraction organic carbon ( $f_{oc}$ ) - values used for  $f_{oc}$  were the median value for the lithological unit from which the groundwater sample was collected.  $f_{oc}$  data are presented in the On and Offsite Assessment report (Geosyntec, 2019);
- Calculated  $K_{oc}$  values - provided earlier in this Appendix;
- Dry bulk density of the subsurface material -1.602 kg/L was used for all lithological units;
- Porosity – 40% was used for all lithological units.

The total mass of PFAS in groundwater and the total mass of PFAS in the soil were then added together to calculate a total mass of PFAS in the saturated zone. For this exercise, non-detects were not included in any calculations.

Results are provided in Table C-3. Results are shown in Figure 4 in the main CAP text.

**Table C-3: PFAS Mass Distribution Between Saturated and Unsaturated Zone**

Location ID	Sample Date	Onsite/Offsite	Sample Type	Aquifer Saturation	Total Mass per Cubic Meter (kg/m <sup>3</sup> )
Bladen-2S	8/27/2019	Offsite	GW	saturated	5.79E-08
Bladen-2S	8/16/2019	Offsite	S	unsaturated	nd
Bladen-3S	8/28/2019	Offsite	GW	saturated	5.24E-08
Bladen-3S	8/20/2019	Offsite	S	unsaturated	nd
Bladen-4S	8/28/2019	Offsite	GW	saturated	7.19E-09
Bladen-4S	8/21/2019	Offsite	S	unsaturated	nd
Cumberland-1S	9/16/2019	Offsite	groundwater	saturated	1.27E-08
Cumberland-1S	9/13/2019	Offsite	soil	unsaturated	nd
Cumberland-2S	9/16/2019	Offsite	groundwater	saturated	1.94E-08
Cumberland-2S	9/12/2019	Offsite	soil	unsaturated	nd
Cumberland-3S	9/16/2019	Offsite	groundwater	saturated	9.69E-08
Cumberland-3S	9/12/2019	Offsite	soil	unsaturated	nd
Cumberland-4S	9/16/2019	Offsite	groundwater	saturated	2.50E-07
Cumberland-4S	9/11/2019	Offsite	soil	unsaturated	5.13E-07
Cumberland-4S	9/11/2019	Offsite	soil	unsaturated	6.25E-07
Cumberland-5S	9/16/2019	Offsite	groundwater	saturated	1.50E-08
Cumberland-5S	9/11/2019	Offsite	soil	unsaturated	nd
PW-01	9/9/2019	Onsite	groundwater	saturated	2.53E-05
PW-01	9/9/2019	Onsite	groundwater	saturated	2.31E-05
PW-01	7/31/2019	Onsite	soil	unsaturated	1.92E-06
PW-01	7/30/2019	Onsite	soil	unsaturated	7.05E-06
PW-02	9/11/2019	Onsite	groundwater	saturated	6.31E-03
PW-02	9/11/2019	Onsite	groundwater	saturated	6.62E-03
PW-02	7/29/2019	Onsite	soil	unsaturated	2.40E-06
PW-03	9/11/2019	Onsite	groundwater	saturated	1.78E-04
PW-03	9/11/2019	Onsite	groundwater	saturated	1.52E-04
PW-03	7/23/2019	Onsite	soil	unsaturated	1.07E-05
PW-05	9/9/2019	On Site	groundwater	saturated	2.11E-06
PW-05	7/26/2019	On Site	soil	unsaturated	1.36E-06
PW-06	9/10/2019	On Site	groundwater	saturated	1.35E-06
PW-06	7/29/2019	On Site	soil	unsaturated	nd

Location ID	Sample Date	Onsite/Offsite	Sample Type	Aquifer Saturation	Total Mass per Cubic Meter (kg/m <sup>3</sup> )
PW-07	9/13/2019	Onsite	groundwater	saturated	2.08E-06
PW-07	9/13/2019	Onsite	groundwater	saturated	1.95E-06
PW-07	7/24/2019	Onsite	soil	unsaturated	nd
PW-07	7/24/2019	Onsite	soil	unsaturated	nd
PW-09	9/11/2019	Onsite	groundwater	saturated	1.31E-06
PW-09	9/11/2019	Onsite	groundwater	saturated	1.24E-06
PW-09	8/12/2019	Onsite	soil	unsaturated	nd
PW-09	8/12/2019	Onsite	soil	unsaturated	nd
PW-11	9/10/2019	Onsite	groundwater	saturated	2.23E-04
PW-11	9/10/2019	Onsite	groundwater	saturated	2.42E-04
PW-11	7/25/2019	Onsite	soil	unsaturated	9.94E-07
PW-12	9/11/2019	Onsite	groundwater	saturated	7.07E-09
PW-12	9/11/2019	Onsite	groundwater	saturated	nd
PW-12	7/31/2019	Onsite	soil	unsaturated	1.33E-06
PW-12	7/31/2019	Onsite	soil	unsaturated	nd
PW-13	9/10/2019	Onsite	groundwater	saturated	nd
PW-13	9/10/2019	Onsite	groundwater	saturated	nd
PW-13	8/21/2019	Onsite	soil	unsaturated	nd
Robeson-1S	9/12/2019	Offsite	groundwater	saturated	2.36E-08
Robeson-1S	9/9/2019	Offsite	soil	unsaturated	nd
Robeson-1S	9/9/2019	Offsite	soil	unsaturated	nd

Notes:

nd – no Table 3+ compounds were detected

## REFERENCES

Concawe. Environmental fate and effects of poly and perfluoroalkyl substances (PFAS), June 2016.

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