Supporting Information

Estimation of the acid dissociation constant of perfluoroalkyl carboxylic acids through an experimental investigation of their water-to-air transport

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1. Names and abbreviations of standards and internal standards

Table S 1: Abbreviations and names of analytes including the suppliers and purity for crystalline standards. 8:2 FTUCA was dissolved in methanol.

Abbreviation	Name	Supplier	Purity
PFBA	Perfluorobutanoic acid	Aldrich	99 %
PFHxA	Perfluorohexanoic acid	ABCR	98 %
PFHpA	Perfluoroheptanoic acid	Aldrich	99 %
PFOA	Perfluorooctanoic acid	ABCR	98 %
PFNA	Perfluorononanoic acid	Aldrich	97 %
PFDA	Perfluorodecanoic acid	Fluka	≥ 97 %
PFUnDA	Perfluoroundecanoic acid	Aldrich	95 %
PFDoDA	Perfluorododecanoic acid	Aldrich	95 %
PFBS	Perfluorobutane sulfonic acid	Dyneon (potassium salt)	unknown
PFHxS	Perfluorohexane sulfonic acid	Interchim (potassium salt)	98 %
PFOS	Perfluorooctane sulfonic acid	Fluka (potassium salt)	≥ 98 %
8:2 FTUCA	2H-Perfluorodecanoic acid	Wellington Laboratories	unknown

Table S 2: Names, abbreviations and suppliers of mass-labeled internal standards (IS).

Abbreviation	Name	Supplier
MPFHxS[1]	Perfluoro-1-hexane-[$^{18}O_2$]sulfonic acid	Wellington Laboratories (MPFAC-MXA)
MPFOS	Perfluoro-1-[1,2,3,4-$^{13}C_4$]octane sulfonic acid	
MPFBA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid	
MPFHxA	Perfluoro-n-[1,2,-$^{13}C_2$]hexanoic acid	
MPFOA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	
MPFNA	Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid	
MPFDA	Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	
MPFUnDA	Perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid	
MPFDoDA	Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	
MPFHpA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid	Wellington Laboratories
M8:2 FTUCA	2H-Perfluorooctyl-[1,2-$^{13}C_2$]-decanoic acid	Wellington Laboratories

[1] MPFHxS has also been used as IS for PFBS.

2. Quality assurance

Table S 3: Absolute recoveries of IS in different samples compared to the calibration standards (averages ± standard deviation, in %, n = 35).

Name	Water	Top	Bottom
PFBA	184 ± 42	122 ± 26	125 ± 26
PFHxA	128 ± 27	124 ± 45	127 ± 36
PFHpA	132 ± 25	128 ± 30	129 ± 30
PFOA	123 ± 27	126 ± 34	124 ± 35
PFNA	137 ± 25	135 ± 30	133 ± 29
PFDA	116 ± 21	116 ± 24	113 ± 25
PFUnDA	133 ± 32	124 ± 35	111 ± 36
PFDoDA	182 ± 53	158 ± 46	143 ± 50
PFHxS	117 ± 13	115 ± 13	101 ± 17
PFOS	117 ± 19	111 ± 20	95 ± 22
8:2 FTUCA	51 ± 90	not analyzed	not analyzed

Table S 4: Nominal and measured pH over an experimental period of four days.

Nominal	Measured (± standard dev.; n = 6)
0	0.32 ± 0.01
0.5	0.73 ± 0.01
1.5	1.59 ± 0.01
2.5	2.57 ± 0.01
3	3.07 ± 0.01
3.5	3.64 ± 0.01
4.5	4.99 ± 0.04
neutral	6.90 ± 0.05

3. 14-days time series for sorption to top part of vessel at pH 0

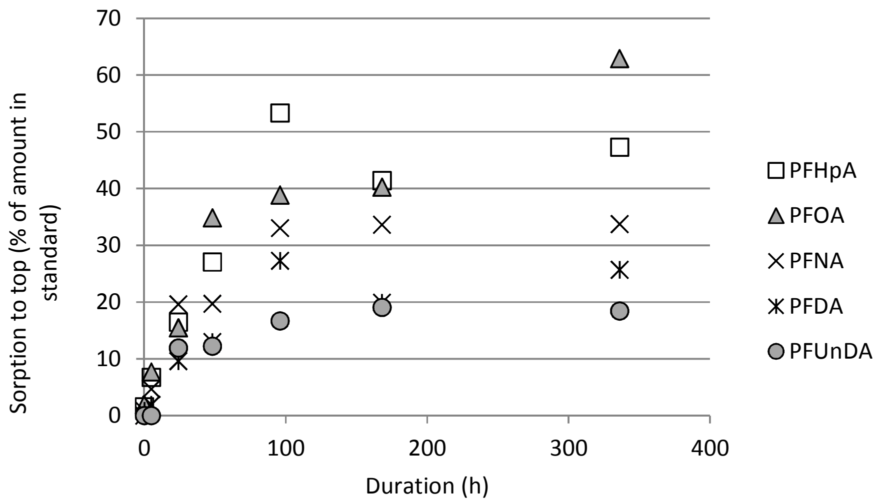

Figure S 1: Fraction (in % of amount in the standard used for spiking) sorbed to the top part of the vessel at certain time points at pH 0 (semi-quantitative, analytical method not fully optimized).

5. Quantified amounts of target compounds

Table S 5: Amounts (in ng) in 1 mL water for duplicates of each setup at t0 (to be multiplied with a factor 20 to calculate the whole amount in the water of the system).

Nominal pH	Blank	neutral		4.5		3.5		3		2.5		1.5		0.5		0	
PFBA	n.d.	1.1	1.1	1.0	0.98	1.7	1.3	0.9	1.1	0.97	0.88	1.1	1.4	1.4	0.97	2.1	1.0
PFHxA	n.d.	1.9	2.4	1.6	1.7	1.6	1.5	1.6	1.7	1.5	1.6	1.6	1.6	1.8	1.8	7.0	1.7
PFHpA	n.d.	0.82	0.87	0.89	0.85	0.96	0.93	0.82	0.89	0.89	0.90	0.93	0.91	0.83	0.9	0.91	0.85
PFOA	n.d.	1.1	0.99	1.3	1.2	1.1	0.99	1.1	1.1	1.2	1.1	1.3	1.1	1.1	1.3	1.3	1.0
PFNA	n.d.	1.0	0.96	0.93	0.96	1.1	0.9	1.0	0.91	1.2	1.0	1.1	1.1	1.1	1.1	0.86	1.0
PFDA	n.d.	1.0	0.94	0.98	1.1	0.92	0.95	0.83	1.1	1.1	1.0	1.0	0.94	1.2	0.96	0.94	0.98
PFUnDA	n.d.	0.24	0.41	0.19	0.3	0.28	0.21	0.27	0.18	0.29	0.20	0.22	0.22	0.24	0.36	0.24	0.3
PFDoDA	n.d.	0.06	0.07	0.09	0.06	0.14	0.11	0.06	0.05	0.07	0.09	0.09	0.08	0.03	0.06	0.06	0.06
PFTeDA	n.d.	0.35	0.31	0.19	0.22	0.68	0.24	0.33	0.34	0.14	0.45	0.33	0.19	n.d.	n.d.	n.d.	n.d.
PFBS	n.d.	0.96	1.2	1.1	1.1	1.2	1.1	1.0	1.2	1.2	1.1	1.1	1.2	1.1	1.2	1.2	1.3
PFHxS	n.d.	0.98	1.1	1.0	1.1	1.1	1.1	1.0	1.2	1.1	1.0	0.94	1.1	0.86	1.0	1.0	1.1
PFOS	n.d.	0.84	0.89	0.86	0.98	0.76	0.94	0.77	1.1	0.75	1.0	0.56	0.74	0.91	0.92	0.9	0.93
8:2 FTUCA	n.d.	1.9	1.9	2.7	2.9	2.1	1.7	1.7	2.1	1.7	1.9	2.2	1.8	2.2	1.8	2.3	2.1

Table S 6: Amounts (in ng) in 1 mL water for duplicates of each setup at t2 (to be multiplied with a factor 20 to calculate the whole amount in the water of the system).

Nominal pH	Blank		neutral		4.5		3.5		3		2.5		1.5		0.5		0	
PFBA	n.d.	n.d.	0.97	1.1	1.3	1.4	1.5	1.1	1.0	0.93	1.1	1.0	1.5	2.0	1.1	1.2	1.1	1.4
PFHxA	n.d.	n.d.	1.8	1.8	1.7	1.7	1.7	1.8	1.8	1.8	1.7	1.5	1.7	1.8	1.7	1.5	1.0	1.1
PFHpA	n.d.	n.d.	0.83	0.88	0.83	0.92	0.89	0.9	0.82	0.83	0.86	0.88	0.77	0.92	0.68	0.61	0.33	0.31
PFOA	n.d.	n.d.	1.1	0.97	1.1	1.4	1.1	1.1	1.0	0.96	0.99	0.96	0.95	0.9	0.49	0.50	0.32	0.34
PFNA	n.d.	n.d.	0.9	0.9	0.96	0.95	0.91	0.91	0.86	0.93	1.0	0.93	0.6	0.71	0.35	0.38	0.31	0.31
PFDA	n.d.	n.d.	0.44	0.91	0.76	0.85	1.1	1.2	1.0	0.75	0.67	0.5	0.36	n.d.	0.35	0.31	0.35	0.24
PFUnDA	n.d.	n.d.	0.26	0.31	0.19	0.3	0.27	0.27	0.28	0.24	0.16	0.25	0.20	0.26	0.12	0.14	<MQL	0.12
PFDoDA	n.d.	n.d.	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL
PFTeDA	n.d.	n.d.	0.22	0.27	1.2	0.24	0.2	0.39	0.26	0.24	0.56	0.30	<MQL	0.58	n.d.	n.d.	n.d.	n.d.
PFBS	n.d.	n.d.	1.2	1.2	1.4	1.3	1.3	1.2	1.1	1.2	1.4	0.93	1.1	1.3	1.0	1.1	1.2	1.2
PFHxS	n.d.	n.d.	1.1	1.1	1.3	1.2	1.1	1.0	0.95	1.1	1.2	0.92	1.1	1.1	0.88	0.97	1.0	1.0
PFOS	n.d.	n.d.	1.1	1.1	1.5	1.1	0.96	1.2	1.5	0.91	1.0	0.93	0.72	1.2	0.99	1.0	1.3	0.98
8:2 FTUCA	n.d.	n.d.	2.0	2.2	2.1	1.9	0.52	0.59	0.26	0.14	0.23	0.19	0.28	0.19	0.38	0.61	0.14	0.07

Table S 7: Amounts (in ng) extracted from the top part of the vessels for duplicates of each setup at t2.

Nominal pH	Blank		neutral		4.5		3.5		3		2.5		1.5		0.5		0	
PFBA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	0.7	1.2
PFHxA	<MQL	<MQL	<MQL	n.d.	n.d.	<MQL	<MQL	n.d.	<MQL	<MQL	0.17	<MQL	0.28	0.42	2.3	2.2	6.8	7.0
PFHpA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	<MQL	<MQL	0.38	0.42	2.5	2.5	5.6	5.9
PFOA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	<MQL	<MQL	0.20	0.19	1.1	1.3	4.9	5.0	6.4	7.7
PFNA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	0.1	<MQL	0.33	0.33	1.5	1.6	4.0	5.3	4.6	6.2
PFDA	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	<MQL	<MQL	0.1	0.1	0.3	0.29	1.2	1.5	2.7	5.1	3.6	3.3
PFUnDA	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	<MQL	<MQL	<MQL	<MQL	<MQL	0.17	0.29	0.52	0.64	0.77	0.73
PFDoDA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL
PFTeDA	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBS	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.
PFHxS	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	<MQL	n.d.	<MQL
PFOS	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table S 8: Amounts (in ng) extracted from the bottom part of the vessels for duplicates of each setup at t2.

Nominal pH	Blank		neutral		4.5		3.5		3		2.5		1.5		0.5		0	
PFBA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	<MQL	<MQL
PFHxA	<MQL	<MQL	n.d.	n.d.	<MQL	<MQL	<MQL	0.4	n.d.	<MQL	<MQL	<MQL	0.31	<MQL	0.89	0.82	0.84	1.0
PFHpA	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	n.d.	0.17	n.d.	<MQL	<MQL	<MQL	0.17	<MQL	0.64	0.84	0.68	0.75
PFOA	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	<MQL	0.23	<MQL	<MQL	0.15	0.12	0.48	0.17	1.5	1.8	1.2	0.91
PFNA	n.d.	n.d.	<MQL	<MQL	<MQL	<MQL	<MQL	0.29	0.13	0.23	0.30	0.3	0.86	0.32	2.0	2.2	1.5	1.1
PFDA	n.d.	n.d.	0.16	0.25	0.26	0.14	0.33	0.38	0.21	0.53	0.54	0.53	1.4	0.61	2.3	2.4	1.6	1.4
PFUnDA	n.d.	n.d.	0.23	0.33	0.16	<MQL	0.17	0.17	0.12	0.16	0.32	0.18	0.59	0.32	0.84	1.2	0.88	1.4
PFDoDA	n.d.	n.d.	<MQL	<MQL	<MQL	n.d.	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	0.12	0.1	0.33	0.27	0.25	0.21
PFTeDA	n.d.	n.d.	0.11	<MQL	0.27	n.d.	<MQL	n.d.	0.1	0.24	0.19	0.12	<MQL	0.18	n.d.	n.d.	0.23	0.19
PFBS	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	n.d.	0.2	n.d.	<MQL	<MQL	n.d.	<MQL	<MQL	0.23	0.13	<MQL	<MQL
PFHxS	n.d.	n.d.	n.d.	n.d.	<MQL	<MQL	<MQL	0.21	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	0.46	0.29	0.2	0.15
PFOS	n.d.	n.d.	0.1	0.1	0.23	<MQL	0.20	0.35	<MQL	0.30	0.26	0.14	0.58	0.33	3.3	2.5	1.9	1.3

5. 8:2 FTUC(A) as a reference chemical

Figure 4 shows the fraction of the total amount found in the vessels at t0 that was found in water at t2 for 8:2 FTUC(A) compared to PFC(A)s. The loss of 8:2 FTUC(A) from water compared to the loss of PFC(A)s from water shows that 8:2 FTUC(A) is already lost from water at higher pHs (3.5 - 5) and that the loss is leveling off at lower pHs (<3). It can be concluded that the system is showing different results for chemicals with different pK_a's indicating that the results are influenced by the pK_a.

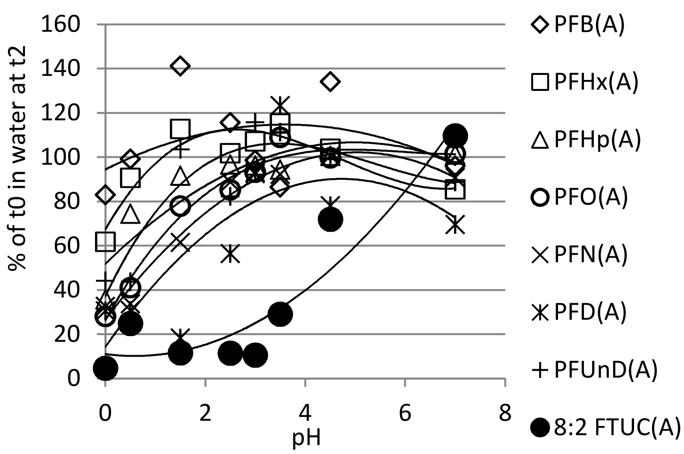

Figure S 2: Percentage of 8:2 FTUC(A) (semi-quantitative) and PFC(A)s remaining at t2 (relative to the total amount in the system at t0) plotted as a function of the water pH. Lines represent a polynomical fit for the data point of each analyte.

6. Mass balances

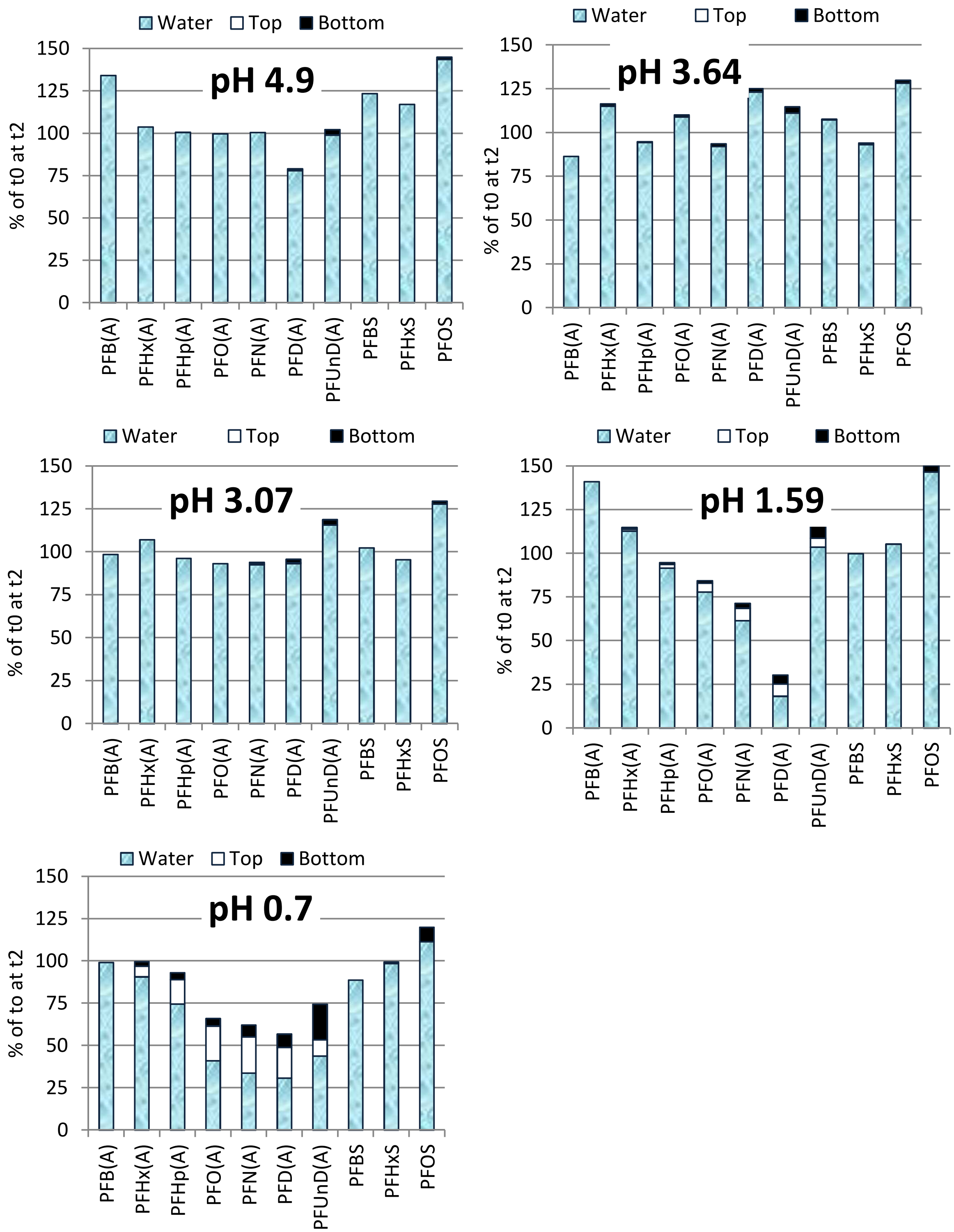

Figure S 3: Percentages of the total amount remaining in the systems at t2 (found in the water and sorbed to the top and bottom parts of the vessel) relative to the amount at t0 for selected water pHs.

7. Model fit for PFOA

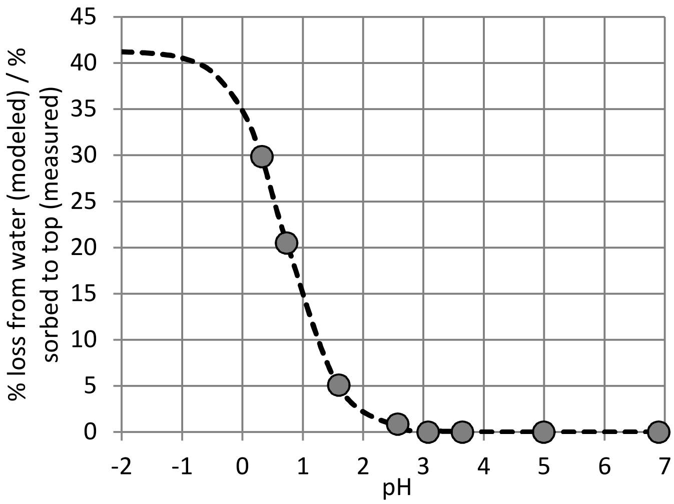

Figure S 4: Least square fit of modeled results to measured data for PFOA. Calculated loss from water after two days (dashed line, in %) and measured fraction sorbed to the top part after two days (dots, in % of amount found at t0) plotted against the pH of the water.