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Supplementary Information

Efficient Removal of Per- and Polyfluoroalkyl Substances (PFASs) in Drinking Water Treatment: Nanofiltration combined with Active Carbon or Anion Exchange

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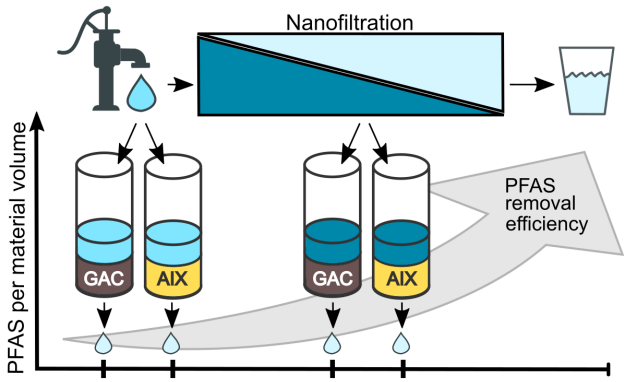

Figure S1: Graphical abstract.

Raw data for nanofiltration experiment

Table S1: Concentrations [$\mu g\,L^{-1}$] of PFASs in raw water, water permeating the NF 270 membrane and membrane reject water throughout the 35 week experimental period in which the nanofiltration experiment was run. Samples were analyzed by ALS Scandinavia, according to accredited methods.[1] Concentrations below the reporting limits given by ALS Scandinavia for each sample and compound are denoted with "<".

Start	Time	Type	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA
2015-03-17	11:00	Feedwater	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
2015-03-23	14:45	Feedwater	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
2015-04-29	15:00	Feedwater	<0.010	<0.010	0.015	<0.010	<0.010	<0.010
2015-05-05	13:50	Feedwater	<0.010	<0.010	0.016	<0.010	<0.010	<0.010
2015-06-15	10:00	Feedwater	<0.0025	<0.0025	0.0136	0.0032	0.0082	<0.0025
2015-06-29	11:00	Feedwater	<0.0025	0.0041	0.0143	0.0032	0.008	<0.0025
2015-06-29	10:45	Feedwater	<0.0025	0.0039	0.0142	0.0032	0.008	<0.0025
2015-07-13	14:15	Feedwater	<0.0025	<0.0025	0.0162	0.0026	0.0106	<0.0025
2015-07-28	11:05	Feedwater	<0.010	<0.010	0.021	<0.010	<0.0100	<0.010
2015-07-28	10:59	Feedwater	<0.010	<0.010	0.018	<0.0100	<0.010	<0.010
2015-08-04	15:00	Feedwater	<0.0025	0.003	0.0161	0.0036	0.0084	<0.0025
2015-08-19	14:30	Feedwater	<0.0025	0.0027	0.0167	0.0041	0.0087	<0.0025
2015-09-08	10:00	Feedwater	<0.0025	<0.0025	0.0122	0.0029	0.0081	<0.0025
2015-10-13	15:00	Feedwater	<0.010	<0.010	0.011	<0.010	<0.0100	<0.010
2015-10-27	14:00	Feedwater	<0.0025	<0.0025	0.0076	<0.0025	0.0041	<0.0025
2015-12-17	13:45	Feedwater	0.0031	0.0029	0.0096	<0.0025	0.005	<0.0025
2015-03-17	11:15	Permeate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
2015-03-23	14:35	Permeate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
2015-04-29	15:00	Permeate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
2015-05-05	13:30	Permeate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
2015-06-29	11:00	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	<0.0010	<0.0025
2015-07-13	14:00	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	<0.0010	<0.0025
2015-07-28	10:59	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	0.0015	<0.0025
2015-08-04	15:00	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	<0.0010	<0.0025
2015-08-19	14:30	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	<0.0010	<0.0025
2015-09-08	10:00	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	<0.0010	<0.0025
2015-10-13	15:00	Permeate	<0.010	<0.010	<0.010	<0.010	<0.0100	<0.010
2015-10-27	14:00	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	<0.0010	<0.0025
2015-12-17	13:45	Permeate	0.0044	<0.0025	<0.0025	<0.0025	<0.0010	<0.0025
2015-03-17	11:10	Retentate	0.012	<0.010	<0.010	<0.010	<0.010	<0.010
2015-03-23	14:40	Retentate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
2015-04-29	15:00	Retentate	0.012	0.011	0.055	0.011	0.0273	<0.010
2015-05-05	13:40	Retentate	<0.010	<0.010	0.076	0.026	0.0477	<0.010
2015-06-15	10:00	Retentate	<0.010	<0.010	0.071	0.016	0.037	<0.010
2015-06-29	11:00	Retentate	<0.010	<0.010	0.077	0.019	0.0423	<0.010
2015-06-29	10:45	Retentate	<0.010	<0.010	0.08	0.015	0.0439	<0.010
2015-07-13	15:00	Retentate	<0.010	0.025	0.083	0.019+	0.0517	<0.010
2015-07-13	14:15	Retentate	<0.010	0.028	0.089	0.02	0.0542	<0.010
2015-07-28	11:00	Retentate	0.016	<0.010	0.096	0.017	0.0322	<0.010
2015-07-28	10:58	Retentate	0.027	<0.010	0.086	0.018	0.031	<0.010
2015-08-04	15:00	Retentate	<0.010	0.025	0.079	0.016	0.0492	<0.010
2015-08-19	14:30	Retentate	<0.010	0.014	0.086	0.018	0.0526	<0.010
2015-09-08	10:00	Retentate	<0.010	0.021	0.07	0.012	0.0426	<0.010
2015-10-13	15:00	Retentate	<0.010	0.016	0.056	0.012	0.0358	<0.010
2015-10-27	14:00	Retentate	<0.010	<0.010	0.037	<0.010	0.0217	<0.010
2015-12-17	13:45	Retentate	<0.010	0.012	0.044	<0.010	0.0258	<0.010

Start	Time	Type	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS
2015-03-17	11:00	Feedwater	<0.010	<0.010	<0.010	<0.010	0.018	<0.010
2015-03-23	14:45	Feedwater	<0.010	<0.010	<0.010	<0.010	0.023	<0.010
2015-04-29	15:00	Feedwater	<0.010	<0.010	<0.010	0.012	0.101	0.0469
2015-05-05	13:50	Feedwater	<0.010	<0.010	<0.010	0.011	0.098	0.0419
2015-06-15	10:00	Feedwater	<0.0025	<0.0025	<0.0025	0.0093	0.121	0.0524
2015-06-29	11:00	Feedwater	<0.0025	<0.0025	<0.0025	0.0094	0.125	0.0465
2015-06-29	10:45	Feedwater	<0.0025	<0.0025	<0.0025	0.0094	0.124	0.0516
2015-07-13	14:15	Feedwater	<0.0025	<0.0025	<0.0025	0.0125	0.128	0.0492
2015-07-28	11:05	Feedwater	<0.010	<0.010	<0.010	0.015	0.191	0.0428
2015-07-28	10:59	Feedwater	<0.010	<0.010	<0.010	0.01	0.208	0.061
2015-08-04	15:00	Feedwater	<0.0025	<0.0025	<0.0025	0.0112	0.124	0.036
2015-08-19	14:30	Feedwater	<0.0025	<0.0025	<0.0025	0.0102	0.112	0.0575
2015-09-08	10:00	Feedwater	<0.0025	<0.0025	<0.0025	0.0105	0.104	0.0409
2015-10-13	15:00	Feedwater	<0.010	<0.010	<0.010	<0.010	0.081	0.0289
2015-10-27	14:00	Feedwater	<0.0025	<0.0025	<0.0025	0.0082	0.0667	0.0207
2015-12-17	13:45	Feedwater	<0.0025	<0.0025	<0.0025	0.0097	0.0803	0.0278
2015-03-17	11:15	Permeate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
2015-03-23	14:35	Permeate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
2015-04-29	15:00	Permeate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
2015-05-05	13:30	Permeate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
2015-06-29	11:00	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	0.0064	0.0017
2015-07-13	14:00	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	0.0062	0.0019
2015-07-28	10:59	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	0.0075	<0.0010
2015-08-04	15:00	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	0.0066	0.0012
2015-08-19	14:30	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	0.0078	0.0018
2015-09-08	10:00	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	0.0058	0.0014
2015-10-13	15:00	Permeate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.0100
2015-10-27	14:00	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	0.0037	<0.0010
2015-12-17	13:45	Permeate	<0.0025	<0.0025	<0.0025	<0.0025	0.0042	<0.0010
2015-03-17	11:10	Retentate	<0.010	<0.010	<0.010	0.016	0.11	0.025
2015-03-23	14:40	Retentate	<0.010	<0.010	<0.010	0.015	0.11	0.024
2015-04-29	15:00	Retentate	<0.010	<0.010	<0.010	0.04	0.369	0.126
2015-05-05	13:40	Retentate	<0.010	<0.010	<0.010	0.055	0.507	0.254
2015-06-15	10:00	Retentate	<0.010	<0.010	<0.010	0.046	0.503	0.245
2015-06-29	11:00	Retentate	<0.010	<0.010	<0.010	0.051	0.576	0.255
2015-06-29	10:45	Retentate	<0.010	<0.010	<0.010	0.052	0.595	0.27
2015-07-13	15:00	Retentate	<0.010	<0.010	<0.010	0.058	0.606	0.244
2015-07-13	14:15	Retentate	<0.010	<0.010	<0.010	0.059	0.629	0.251
2015-07-28	11:00	Retentate	<0.010	<0.010	<0.010	0.08	0.592	0.24
2015-07-28	10:58	Retentate	<0.010	<0.010	<0.010	0.045	0.577	0.231
2015-08-04	15:00	Retentate	<0.010	<0.010	<0.010	0.056	0.612	0.238
2015-08-19	14:30	Retentate	<0.010	<0.010	<0.010	0.064	0.657	0.294
2015-09-08	10:00	Retentate	<0.010	<0.010	<0.010	0.048	0.513	0.216
2015-10-13	15:00	Retentate	<0.010	<0.010	<0.010	0.041	0.396	0.159
2015-10-27	14:00	Retentate	<0.010	<0.010	<0.010	0.032	0.313	0.115
2015-12-17	13:45	Retentate	<0.010	<0.010	<0.010	0.036	0.338	0.125

Start	Time	Type	PFDS	FOSA	6:2 FTSA
2015-03-17	11:00	Feedwater	<0.010	<0.010	<0.010
2015-03-23	14:45	Feedwater	<0.010	<0.010	<0.010
2015-04-29	15:00	Feedwater	<0.010	<0.010	<0.010
2015-05-05	13:50	Feedwater	<0.010	<0.010	<0.010
2015-06-15	10:00	Feedwater	<0.0025	<0.0025	<0.0025
2015-06-29	11:00	Feedwater	<0.0025	<0.0025	<0.0025
2015-06-29	10:45	Feedwater	<0.0025	<0.0025	<0.0025
2015-07-13	14:15	Feedwater	<0.0025	<0.0025	<0.0025

2015-07-28	11:05	Feedwater	<0.010	<0.010	<0.010
2015-07-28	10:59	Feedwater	<0.010	<0.010	<0.010
2015-08-04	15:00	Feedwater	<0.0025	<0.0025	<0.0025
2015-08-19	14:30	Feedwater	<0.0025	<0.0025	<0.0025
2015-09-08	10:00	Feedwater	<0.0025	<0.0025	<0.0025
2015-10-13	15:00	Feedwater	<0.010	<0.010	<0.010
2015-10-27	14:00	Feedwater	<0.0025	<0.0025	<0.0025
2015-12-17	13:45	Feedwater	<0.0025	<0.0025	<0.0025
2015-03-17	11:15	Permeate	<0.010	<0.010	<0.010
2015-03-23	14:35	Permeate	<0.010	<0.010	<0.010
2015-04-29	15:00	Permeate	<0.010	<0.010	<0.010
2015-05-05	13:30	Permeate	<0.010	<0.010	<0.010
2015-06-29	11:00	Permeate	<0.0025	<0.0025	<0.0025
2015-07-13	14:00	Permeate	<0.0025	<0.0025	<0.0025
2015-07-28	10:59	Permeate	<0.0025	<0.0025	<0.0025
2015-08-04	15:00	Permeate	<0.0025	<0.0025	<0.0025
2015-08-19	14:30	Permeate	<0.0025	<0.0025	<0.0025
2015-09-08	10:00	Permeate	<0.0025	<0.0025	<0.0025
2015-10-13	15:00	Permeate	<0.010	<0.010	<0.010
2015-10-27	14:00	Permeate	<0.0025	<0.0025	<0.0025
2015-12-17	13:45	Permeate	<0.0025	<0.0025	<0.0025
2015-03-17	11:10	Retentate	<0.010	<0.010	<0.010
2015-03-23	14:40	Retentate	<0.010	<0.010	<0.010
2015-04-29	15:00	Retentate	<0.010	<0.010	<0.010
2015-05-05	13:40	Retentate	<0.010	<0.010	<0.010
2015-06-15	10:00	Retentate	<0.010	<0.010	<0.010
2015-06-29	11:00	Retentate	<0.010	<0.010	<0.010
2015-06-29	10:45	Retentate	<0.010	<0.010	<0.010
2015-07-13	15:00	Retentate	<0.010	<0.010	<0.010
2015-07-13	14:15	Retentate	<0.010	<0.010	<0.010
2015-07-28	11:00	Retentate	<0.010	<0.010	<0.010
2015-07-28	10:58	Retentate	<0.010	<0.010	<0.010
2015-08-04	15:00	Retentate	<0.010	<0.010	<0.010
2015-08-19	14:30	Retentate	<0.010	<0.010	<0.010
2015-09-08	10:00	Retentate	<0.010	<0.010	<0.010
2015-10-13	15:00	Retentate	<0.010	<0.010	<0.010
2015-10-27	14:00	Retentate	<0.010	<0.010	<0.010
2015-12-17	13:45	Retentate	<0.010	<0.010	<0.010

Average PFAS concentrations in membrane treatment process during the time of column experiments

Table S2: Average concentrations [ng L^{-1}] of frequently detected PFASs in raw water, water permeating the NF 270 membrane and membrane reject water throughout the three month period in which the column experiments were run. Molecular weights (MW [g/mol]) are given for comparison with the molecular weight cut-off of the membrane (270 Da). C_{REJ}/C_{RAW} illustrates average concentration factors reached for each compound in reject water compared to raw water during the experiments. Values for C_{REJ}/C_{RAW} relate to average (LOQ) given by ALS Scandinavia, where values $<$LOQ were replaced with 0.5LOQ. Average values below the average reporting limits are denoted with "<". Note that reporting limits can vary for each sample and are highly dependent on the water type.

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFHxS	PFOS	ΣPFASs
MW [g/mol]	213.03	263.04	313.04	363.05	413.06	299.09	399.10	499.12	
Raw water	< 4.0	< 6.0	16	< 10	< 10	11	140	49	$\geq$216
Permeate	< 2.0	< 2.0	< 2.0	< 2.0	< 1.0	< 2.0	9.0	2.0	$\geq$22
Reject water	12	12	82	17	44	56	590	250	1060
C_{REJ}/C_{RAW}	> 3.0	> 2.0	5.1	> 1.7	> 4.4	5.1	4.3	5.1	$\leq$4.9

Specifications of adsorbent materials

F400 is a bituminous coal based agglomerated carbon with an effective size of 0.55-0.75 mm, a minimum iodine number of 1000 $mg\,g^{-1}$ and a surface area of 1050 m^2g^{-1} (Brunauer–Emmett–Teller (BET) N_2 method). A600 is a Type 1 strongly basic quaternary ammonium resin with gel polystyrene cross-linked with divinylbenzene.

Calculation of the treatments removal efficiency R [%]

The treatment's removal efficiency R [%] was calculated according to:

$$R = (1 - \frac{C}{C_0}) \cdot 100$$

where C and C_0 describe concentrations after and before each evaluated treatment, respectively.

Lin Huang parameters

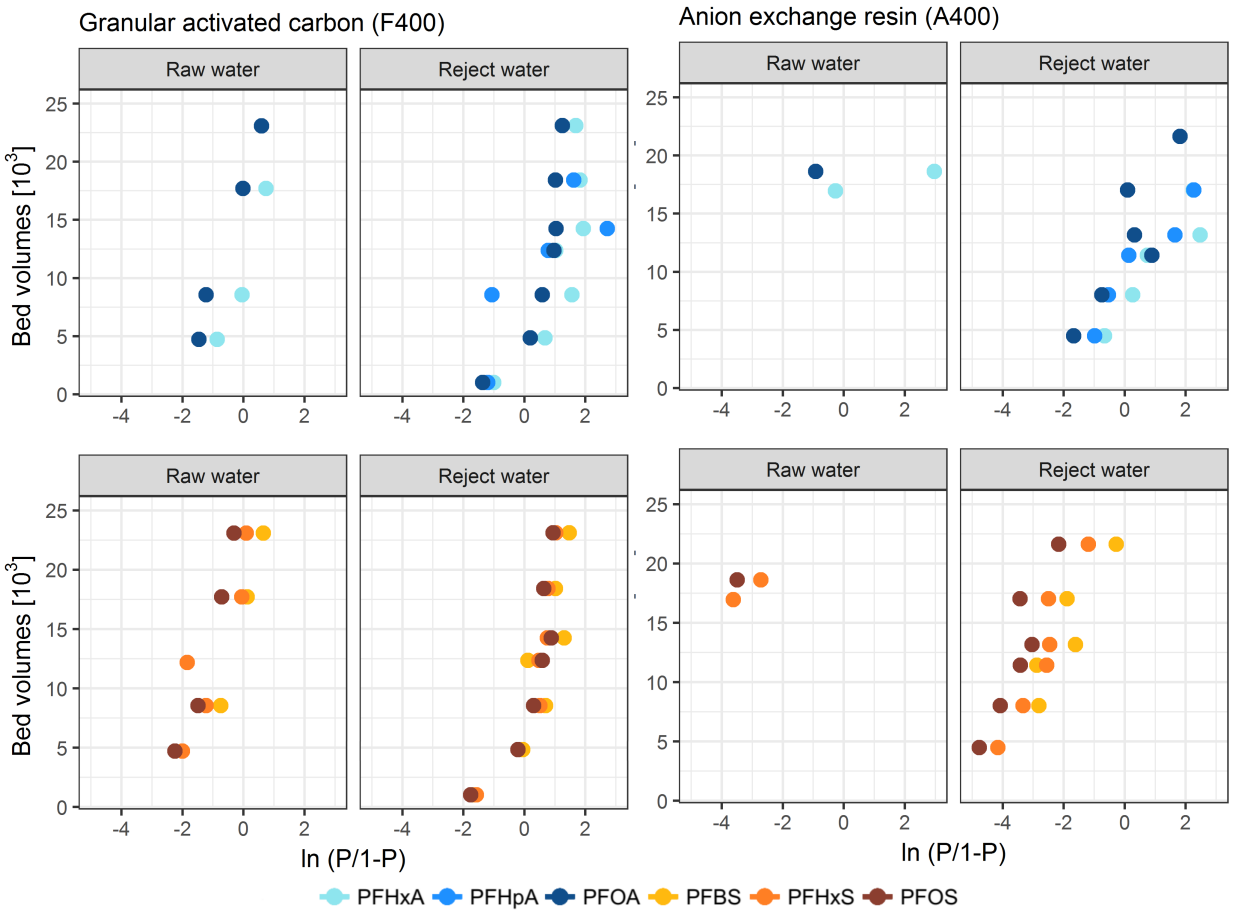

Figure S2: $ln(P/1-P)$ vs. bed volumes treated of frequently detected PFCAs (top) and PFSAs (bottom) for the evaluated granular activated carbon material (F400, left) and anion exchange resin (A600, right). A linear regression gives conclusions about breakthrough time and the adsorption capacity of an adsorption column; see also Table S3.[2,3]

Table S3: Half-times of saturation τ and column constants k_c for frequently detected PFASs. Data is presented depending on water type (RAW = prefiltered raw water; REJ = membrane retentate). Values denoted with R^2 refer to the correlation coefficient of the linear regression attempted in the plots of Figure S2 while n refers to the sample size that could be used for the estimation. p-values>0.05 are marked with *. In case no break through was observed for a certain column-compound combination, calculation of Lin-Huang parameters was not possible.

		GAC F400								AIX A600						
		p-value	τ [BV]	τ [d]	k_c [10^{-3}BV^{-1}]	k_c [d^{-1}]	R^2	n		p-value	τ [BV]	τ [d]	k_c [10^{-3}BV^{-1}]	k_c [d^{-1}]	R^2	n
RAW	PFHxA	0.155*	10819	41.2	0.12	0.033	0.94	3	PFHxA	-	-	-	-	-	-	-
RAW	PFHpA	-	-	-	-	-	-	-	PFHpA	-	-	-	-	-	-	-
RAW	PFOA	0.004	18094	68.9	0.12	0.031	0.99	4	PFOA	-	-	-	-	-	-	-
RAW	PFBS	0.006	16411	62.5	0.10	0.025	1.00	3	PFBS	-	-	-	-	-	-	-
RAW	PFHxS	0.044	19937	75.9	0.15	0.040	0.79	5	PFHxS	-	-	-	-	-	-	-
RAW	PFOS	0.018	25050	95.4	0.10	0.027	0.96	4	PFOS	-	-	-	-	-	-	-
REJ	PFHxA	0.034	5356	20.3	0.17	0.045	0.62	7	PFHxA	0.025	7487	30.2	0.30	0.074	0.85	5
REJ	PFHpA	0.089*	9133	34.7	0.31	0.083	0.67	5	PFHpA	0.011	9198	37.1	0.30	0.075	0.91	5
REJ	PFOA	0.016	8046	30.6	0.14	0.037	0.72	7	PFOA	0.023	12145	49.0	0.23	0.056	0.76	6
REJ	PFBS	0.013	9308	35.4	0.16	0.043	0.74	7	PFBS	0.035	22761	91.8	0.22	0.055	0.82	5
REJ	PFHxS	0.012	9985	38.0	0.13	0.035	0.75	7	PFHxS	0.003	28717	116	0.17	0.041	0.91	6
REJ	PFOS	0.017	10497	40.0	0.15	0.038	0.71	7	PFOS	0.007	35156	142	0.15	0.038	0.87	6

* Not significant at 95 % confidence level (p>0.05)

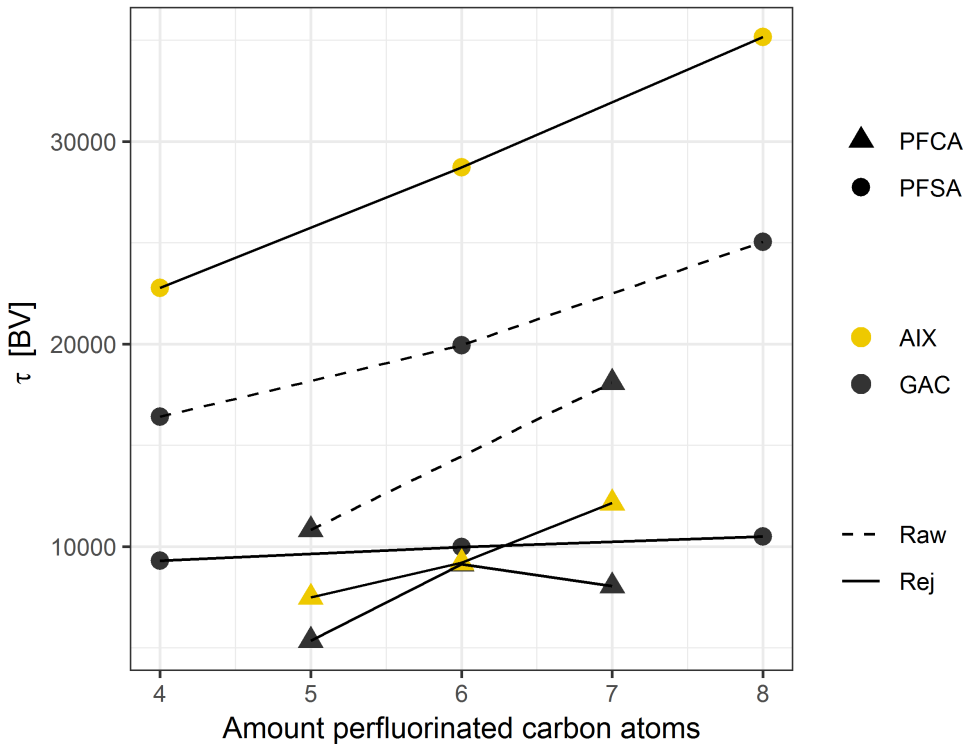

Figure S3: Column half-times of saturation τ [BV] of PFAS compounds frequently detected in this study vs. amount of perfluorinated carbons of these compounds. Since perfluoroalkyl sulfonates (◯) are retained better for both evaluated materials GAC (Filtrasorb 400, black) and AIX (Purolite 600; yellow) than perfluoroalkyl carboxylates (△), values for τ are larger for these compounds. Half-times of saturation for columns treating feedwater (Raw) were found to be higher than for columns treating membrane retentate (Rej).

References

(1) ALS Scandinavia, OV-34a Perfluorinated compounds in water.

(2) Lin, S. H.; Huang, C. Y. Adsorption of BTEX from aqueous solution by macroreticular resins. *Journal of hazardous materials* **1999**, *70*, 21–37.

(3) McCleaf, P.; Englund, S.; Östlund, A.; Lindegrena, K.; Wiberg, K.; Ahrens, L. Removal efficiency of multiple poly- and perfluoroalkyl substances (PFASs) in drinking water using granular activated carbon (GAC) and anion exchange (AE) column tests. *Water Res.* **2017**,