

Supporting information

Impact of treatment processes on the occurrence of perfluoroalkyl acids in the drinking water production chain

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Chemicals used

The non-labeled calibration standards and the isotopically labeled internal standards of Perfluorocarboxylates and Perfluorosulfonates were obtained from Wellington Laboratories (Ontario, Canada). A list with abbreviations of the non-labeled and labeled standards is shown in Table S1. Methanol of ULC/MS grade was obtained from Biosolve (Valkenswaard, Netherlands). NH_4OH of 33 weight % was obtained from Sigma Aldrich (St. Louis, USA). Materials used for sample treatment and analysis included SPE Oasis WAX 3cc (60 mg) cartridges (particle size: 30 μm , pore size: 80 \AA) from Waters (Wexford, Ireland); Acrodisc LC13 GHPPall 0.2 μm filters from Pall Corporation (NY, USA); 1 L and 250 mL polypropylene (PP) tubes with screw caps from Nalgene (Rochester, USA) and 2 mL PP vials from Supelco (Bellefonte, USA).

Analytical method

Approximately 250 mL sample was carefully weighed in a methanol pre-washed (three times MeOH and three times with the sample) PP tube. The internal standards (60 ng) (See Table S5 and S6 for which internal standards) were subsequently added to the water sample. Cartridges were conditioned by eluting with 4 mL of 0.1% NH_4OH in methanol and 4 mL of nanopure water, consecutively. Water samples were subsequently filtered over the SPE cartridge via a vacuum extraction manifold, the eluent was discarded and the cartridge was dried under a gentle vacuum air flow. The cartridge was then washed with 2 mL 40/60 vol.% MeOH/ H_2O mixture which was discarded after controlling for two samples that no PFASs were present in the washing solution. The compounds retained on the SPE cartridge were desorbed with 1 mL of 2% NH_4OH in methanol which was then filtered through an Acrodisc LC 13 GHPPall in a 2 mL PP vial and stored at 4 $^{\circ}\text{C}$ prior analysis.

The analytical protocol was described in detail before [4]. Briefly, PFAS were analyzed by injecting 20 μL from the extract into a High Performance Liquid Chromatograph (HPLC, Shimadzu, Kyoto, Japan) connected to a tandem mass spectrometer (4000 Q Trap, Applied Biosystems, Toronto, Canada) operating in the negative ionization mode with scheduled MRM. An ACE 3 C18-300 column (ID 2.1 mm; length 150 mm, particle size 3 μm , Advanced Chromatography Technologies, Aberdeen, Scotland) was used and the pre-column used for lowering the background of PFAS from the HPLC system was a Pathfinder 300 PS C18 column (ID 4.6 mm; length 50 mm; Shimadzu, Duisburg, Germany), placed before the injection valve.

Drinking water production scheme

1 water is taken in at the Lek canal near Nieuwegein. 2 the water is coagulated by addition of ferric chloride and subsequently sedimentated; the deep extraction wells are used as emergency water supply might surface water be contaminated and therefore not in function 3 rapid sand filtration and pH neutralization with caustic soda (see Figure S for a schematic representation); 4 After the pre-treatment steps water is transported to the post-treatment location in the Western part of the Netherlands.

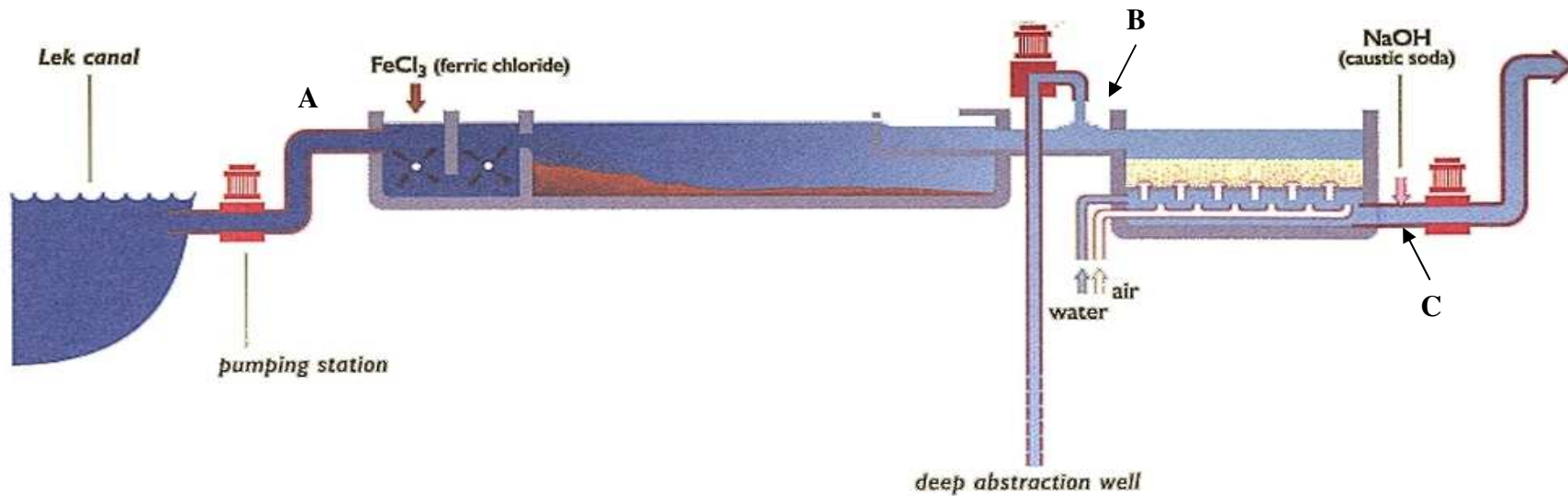


Figure S1 Pre-treatment of the source water (in Nieuwegein)

5 infiltration of the water in the dune area via a system of distribution lakes and recharge channels; 6 drainage of the water after a residence time of approximately 60 to 400 days and an aquifer passage of 40 to 100 meters and collection of the water in the Oranjekom;

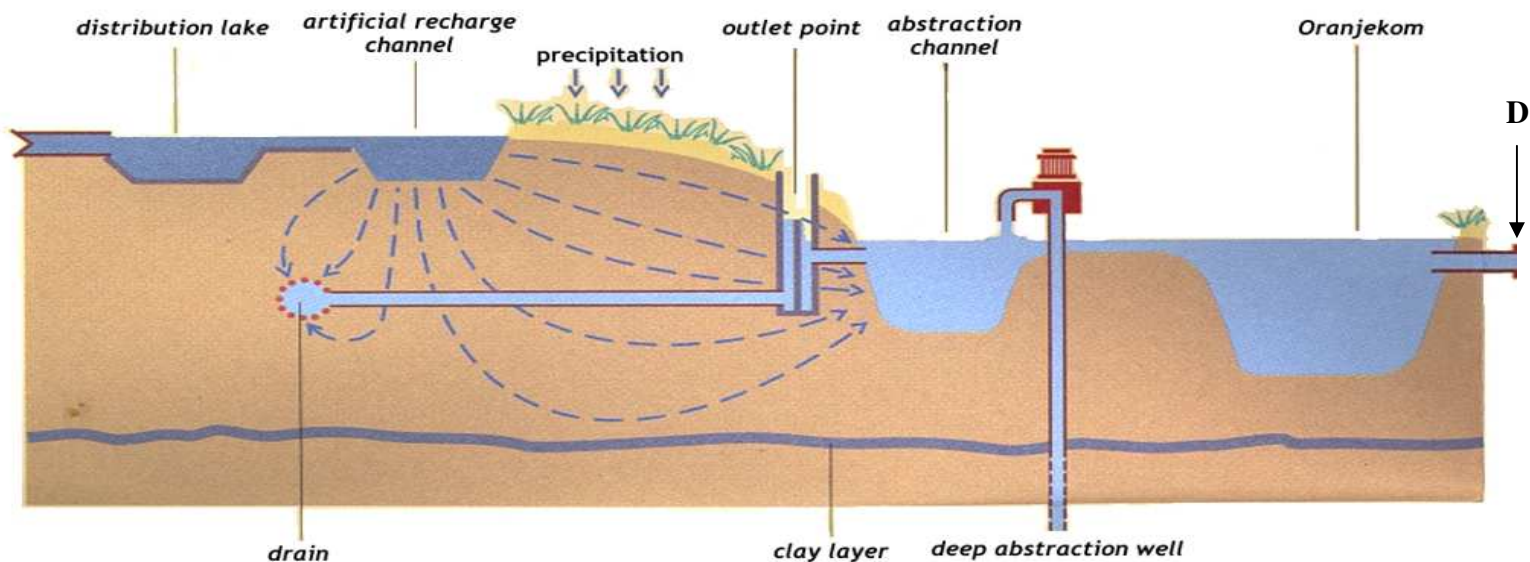


Figure S2 Dune filtration following pre-treatment and transport from Nieuwegein.

7 rapid sand filtration; 8 ozonization

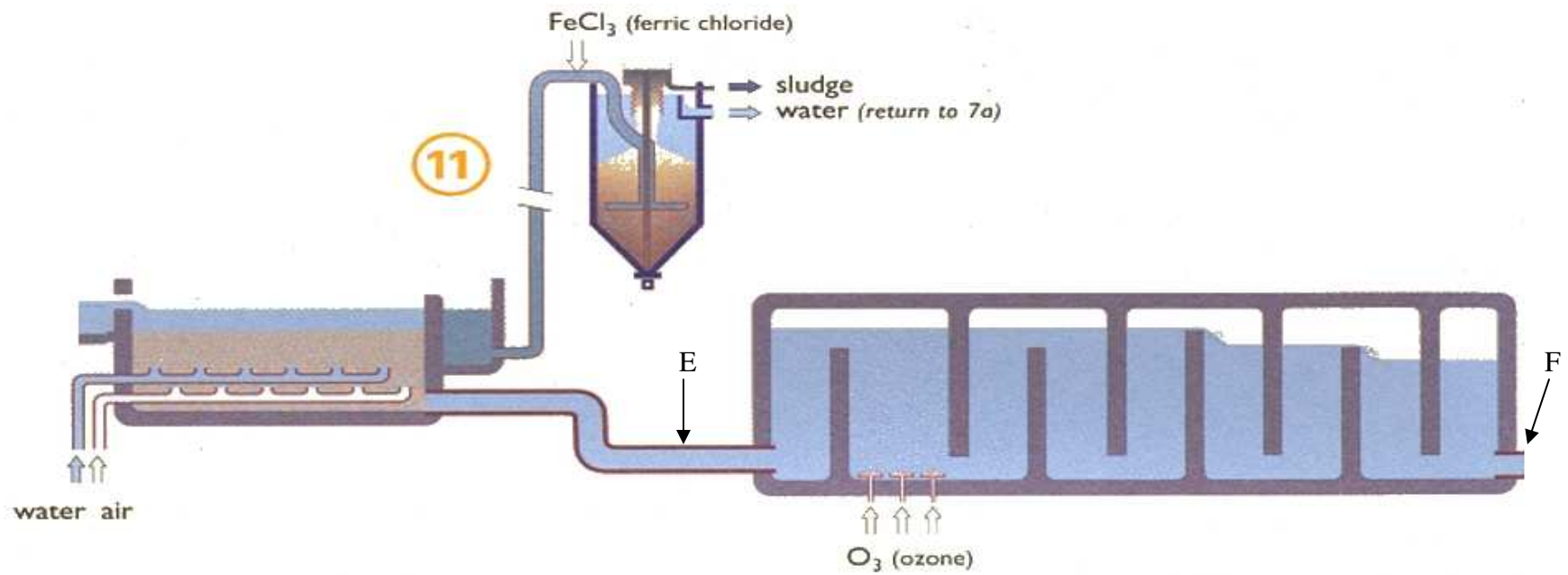


Figure S3 Post-treatment (1) following dune infiltration

9 Softening of the water in a pellet reactor with addition of NaOH and hydrochloric addition to neutralize pH; 10 two step activated carbon filtration operated in series (first and second stage); water is distributed evenly over 19-20 first stage beds, collected and redistributed over 19-20 second stage beds. The contact time of the water is twice 23 min and regeneration frequency of GAC beds is approximately 2.5 years. When a first stage GAC bed is exhausted, a second stage bed is switched to the first stage position; the coal in the exhausted bed is regenerated and after return of the regenerated coal the bed starts in second stage again 11 backwash water purification; 12 slow sand filtration; 13 storage to buffer the variation in water demand and finally distribution to the consumers.

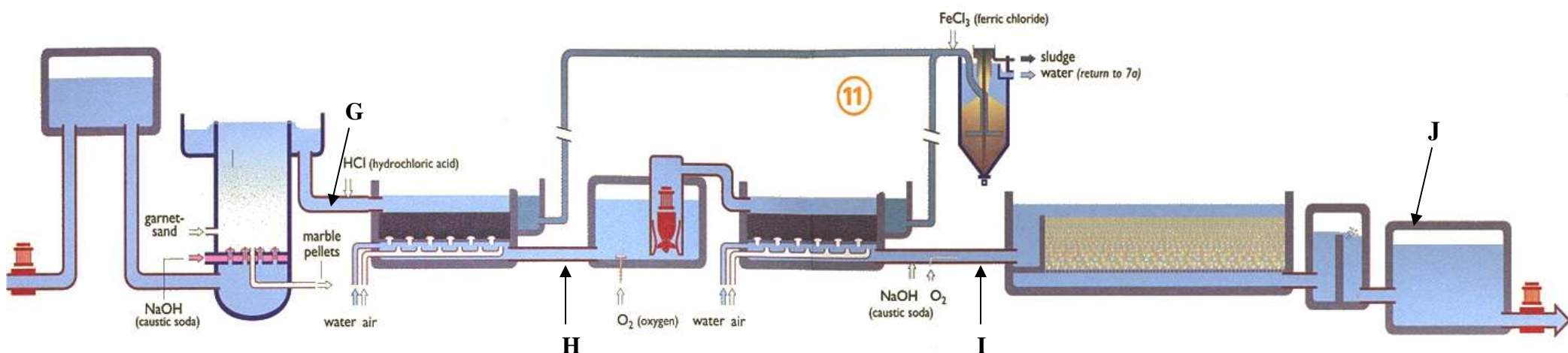


Figure S4 Post treatment (2) following Dune infiltration

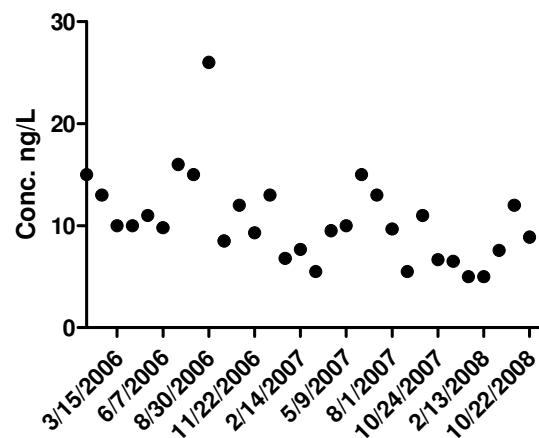


Figure S5. PFOS concentration in the Lek canal around Nieuwegein [1-3]. Data can be found at:

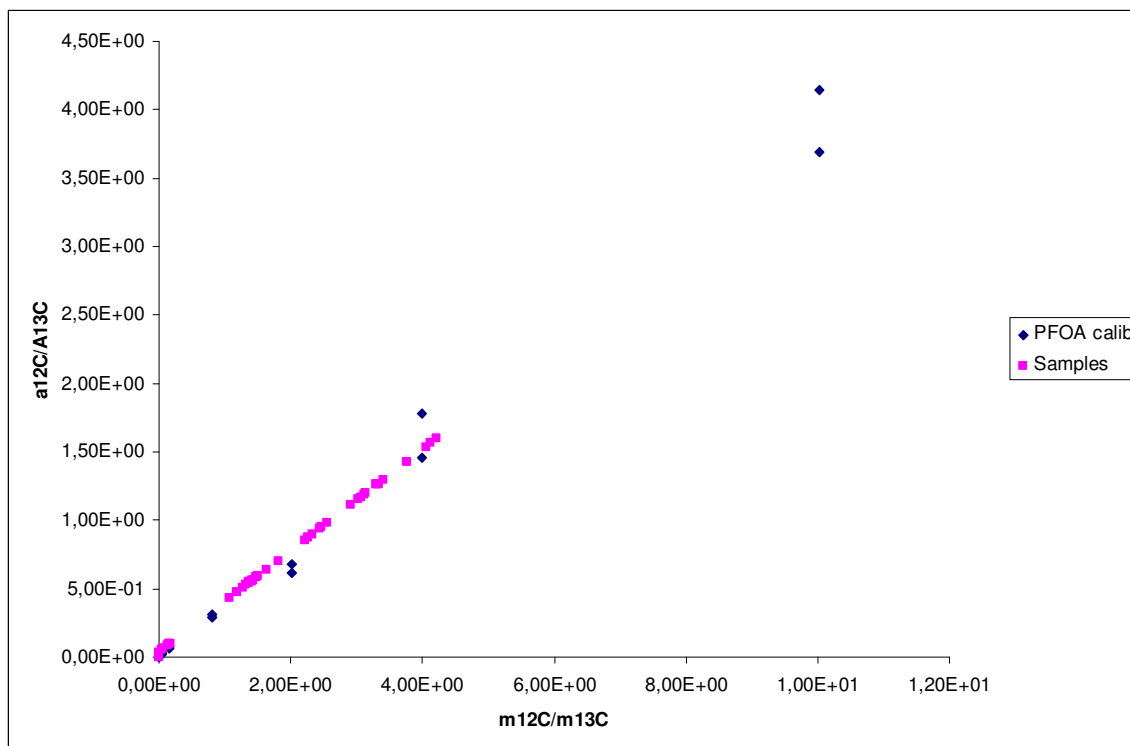


Figure S6. Calibration plot of PFOA showing responses of sample extracts relative to calibration points. Lowest samples on the calibration line are procedural blanks.

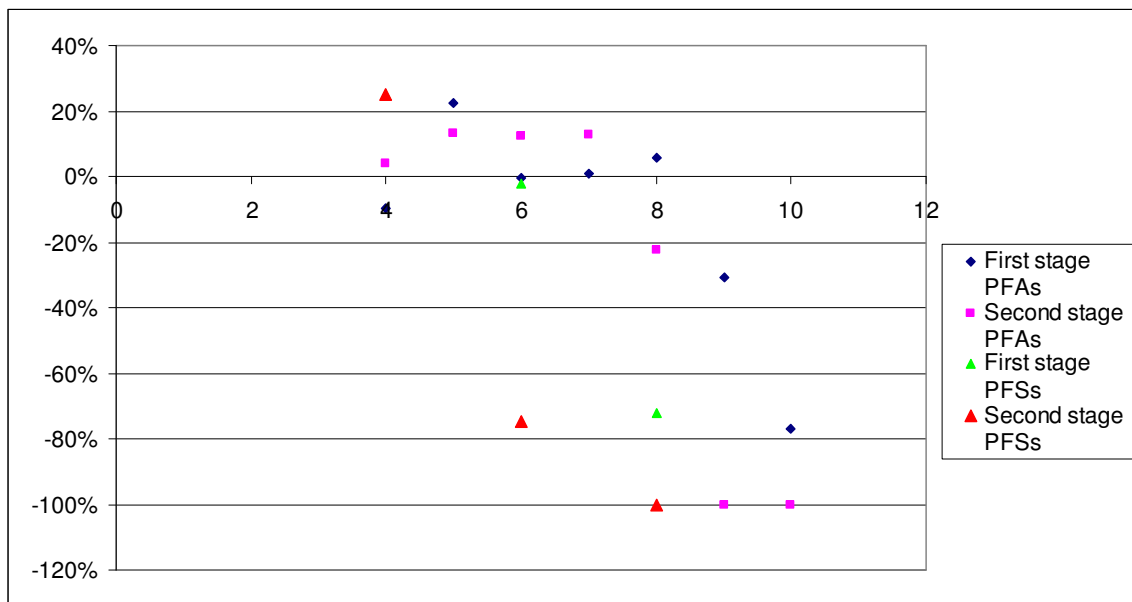


Figure S7. Carbon chain length of the perfluorocarboxylate and perfluorosulfonates vs. the removal in the first (lead) GAC treatment step and second (lag) treatment step.

N14A - 12C PFOS trans 1 (Unknown) 499.0/80.0 Da - sample 57 of 127 from Waternet II 1 okt.wiff
Area: 6.74e+003 counts Height: 1.31e+003 cps RT: 9.78 min

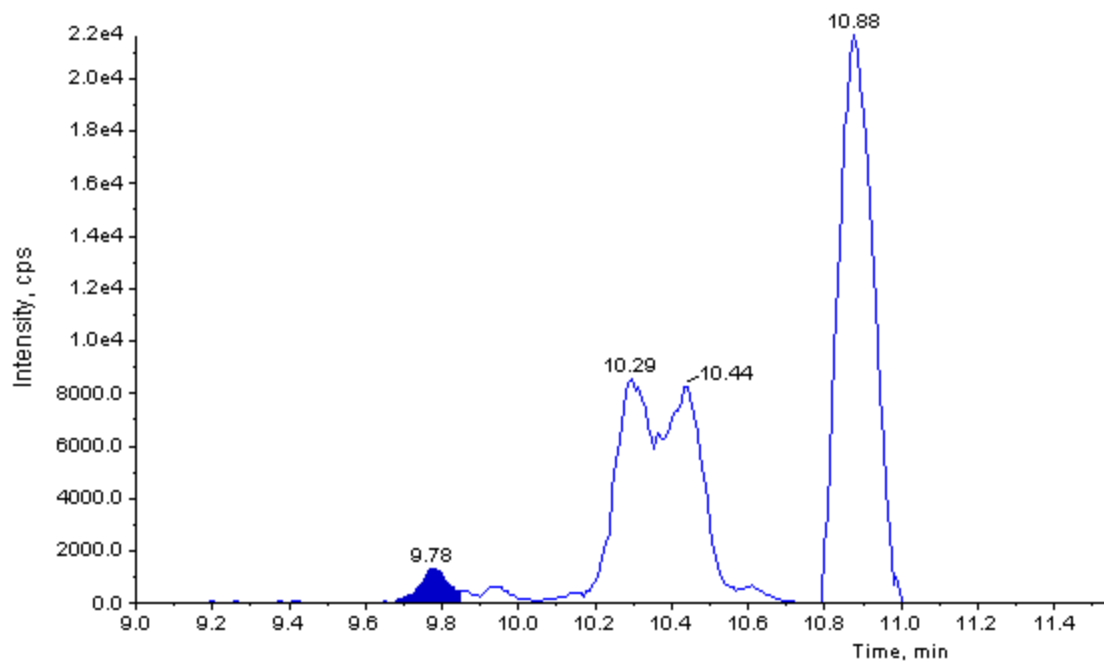


Figure S8. PFOS transition 1 chromatogram. The branched PFOS peak at retention time 9.78 was not integrated, peaks 10.29 and 10.44 were used as branched isomers and peak 10.88 the linear PFOS (corresponding to the ^{13}C labeled PFOS).

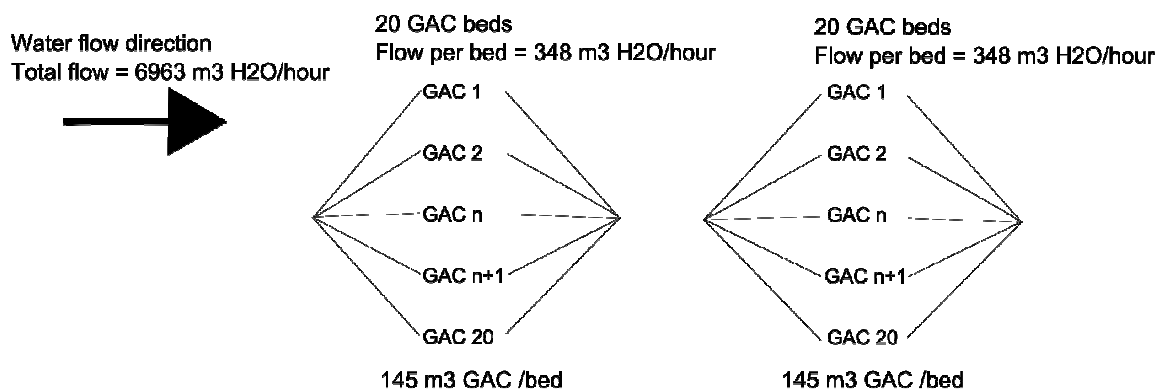


Figure S9 Scheme of the setup of the GAC filter beds in the Leiduin water treatment facility.

Table S1 Characteristics of locations sampled in the drinking water treatment processes
(locations shown in Figures S1 to S4).

Waternet code	Code in figures	Description	hydraulic retention time
Location Nieuwegein			
PNG-OW-02	A	Surface water Lekkanaal intake location	0
PNG-BB-002	B	effl. coagulation	5 h 24 min
PNG-VSF-001	C	Effl. rapid sand filtration	8 h 34 min
Location Leiduin			
PLD-SF-INF002	D	After dune passage	0
PLD-SF-EFF001	E	Effl. rapid sand filtration	0 h 45 min
PLD-OH-INF001	F	Effl. ozonation	1 h 16 min
PLD-KF-INF001	G	Infl GAC filtration	1 h 27 min
PLD-KF-006	H	Effl. First GAC filtration	1 h 58 min
PLD-KF-001	I	effl. GAC filtration	2 h 24 min
PLD-RW-004	J	Drinking water	14 h 55 min

Table S2 Recoveries of the available mass labeled internal standards, field blank concentrations and LOQs¹

	Recovery ^{a,b} 1st sampling round (January)		Recovery ^{a,b} 2nd sampling round (September)		Blank conc ^c (ng/L)	Blank stdev ^d (ng/L)	LOQ ^e (ng/L)
		Range		Range			
PFBA	52	27-89	52	9-62	1.5	0.8	9.5
PFPeA	-				<LOQ	0	0.78
PFHxA	82	67-97	65	32-65	<LOQ	0	0.78
PFHpA	-				<LOQ	0	0.78
PFOA	93	75-116	74	40-100	0.25	0.05	0.75
PFNA	82	62-104	68	36-87	<LOQ	0	0.24
PFDA	81	58-107	67	30-84	<LOQ	0	0.09
PFBS	-				<LOQ	0	0.21
PFHxS	87	73-103	65	34-67	0.05	0.05	0.55
PFOS	72	55-95	57	31-73	<LOQ	0	0.23

^a Recoveries were determined for the entire analytical procedure and method was described in detail before [4] (in the SI).

^b The first set was extracted with a lower vacuum, resulting in a smaller extraction speed (approximately 1- 2 drops per second) and in a higher recovery. The second set (September) was extracted at a higher speed (2-3 drops per second) and resulted in a lower recovery. The relatively high stdev in the table is caused by averaging of the recoveries for the Februar and September sets.

^c A total of four field blanks and three procedural blanks were analyzed

^d stdev = Standard deviation.

^e The (method) LOQ is defined as the lowest validated spike level meeting the method performance acceptability criteria LOQ (explained in the paper M&M section); LOQ was then calculated on the basis of a 250 mL sample. If the lowest achievable limit was determined by the method blank (PFBA, PFOA and PFHxS), the LOQ was defined as blank contribution + 10 x standard deviation of 3 replicates of the blanks.

Table S3 Mass transitions and retention times of perfluoroalkyl carboxylic acids.

Compound	Q1 mass	Q3 mass	Transition	Retention time
¹² C PFBA	213	169	1	2.5
¹² C PFPeA	263	219	1	3.2
¹² C PFHxA	313	269	1	4.4
	313	119	2	
¹³ C ₂ PFHxA	315	270	1	4.4
	315	119	2	
¹² C PFHpA	363	319	1	7.2
	363	169	2	
¹² C PFOA ^a	413	369	1	9.3
	413	169	2	Used for quantification
¹³ C ₄ PFOA	417	372	1	9.3
	417	169	2	
¹² C PFDA	513	469	1	12
	513	219	2	
¹³ C ₂ PFDA	515	470	1	12
	515	219	2	
¹² C PFUnA	563	519	1	12.9
	563	269	2	
¹³ C ₂ PFUnA	565	520	1	12.9
	565	269	2	
¹² C PFDoA	613	569	1	13.7
	613	319	2	
¹³ C ₂ PFDoA	615	570	1	13.7
	615	369	2	
¹² C PFTrA	663	619	1	14.4
	663	369	2	
¹² C PFTeA	713	669	1	14.9
	713	369	2	
¹² C PFHxD	813	769	1	14.9
	813	369	2	

¹² C PFHxD	913	869	1	14.9
	913	369	2	

^aTransition 413 to 169 was used for non-branched and branched isomers of PFOA.

Table S4 Mass transitions and retention times of perfluoroalkyl sulfonates.

Compound	Q1 mass	Q3 mass	Transition	Retention time
^{12}C PFBS	299	80	1	3.30
	299	99	2	
^{12}C PFHxS	399	80	1	7.32
	399	99	2	
^{12}C PFOS (K) ^a	499	80	1	10.9
	499	99	2	used for quantification
$^{13}\text{C}_4$ PFOS (Na)	503	80	1	10.9
	503	99	2	
^{12}C FOSA	498	78	1	13.2
	498	169	2	
^{12}C PFDS	599	80	1	12.9
	599	99	2	

^aTransition 499 to 99 was used for non-branched and branched isomers of PFOS.

1 **Table S5 Analytes and internal standards used**

Abbreviation	Compounds	Quantification by internal standard
PFBA	Perfluorobutanoic acid	13C4 PFBA
PFPeA	Perfluoropentanoic acid	13C4 PFBA
PFHxA	Perfluorohexanoic acid	13C2 PFHxA
PFHpA	Perfluoroheptanoic acid	13C4 PFOA
PFOA	Perfluorooctanoic acid	13C4 PFOA
PFNA	Perfluorononanoic acid	13C5 PFNA
PFDA	Perfluorodecanoic acid	13C2 PFDA
PFUnA	Perfluoroundecanoic acid	13C2 PFUnA
PFDoA	Perfluorododecanoic acid	13C2 PFDoA
PFTTrDA	Perfluorotridecanoic acid	13C2 PFDoA
PFTeDA	Perfluorotetradecanoic acid	13C2 PFDoA
PFHxD	Perfluorohexadecanoic acid	13C2 PFDoA
PFOcD	Perfluorooctanoic acid	13C2 PFDoA
PFBS	Perfluorobutane sulfonate	13C4 PFOS
PFHxS	Perfluorohexane sulfonate	13C4 PFOS
PFHpS	Perfluoroheptane sulfonate	13C4 PFOS
PFOS	Perfluorooctane sulfonate	13C4 PFOS
PFOSA	Perfluorooctane sulfonamide	13C4 PFOS
PFDS	Perfluorodecane sulfonate	13C4 PFOSA
13C4 PFBA	Perfluoro[1,2,3,4-13C] butanoic acid	
13C2 PFHxA	Perfluoro [1,2-13C] hexanoic acid	
13C4 PFOA	Perfluoro [1,2,3,4-13C] octanoic acid	
13C5 PFNA	Perfluoro [1,2,3,4,5-13C] nonanoic acid	
13C2 PFDA	Perfluoro [1,2-13C] decanoic acid	
13C2 PFUnA	Perfluoro [1,2-13C] undecanoic acid	
13C2 PFDoA	Perfluoro [1,2-13C] dodecanoic acid	
13C4 PFOS	Perfluoro [1,2,3,4-13C] octane sulfonate	
13C4 PFOSA	Perfluoro [1,2,3,4-13C] octanesulfonamide	

2

3 **Table S6 Concentrations of PFAS (ng/L) observed in the river Rhine at Lobith in the year 2009 [data from 5].**

Sampling month	PFBS	PFHxS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	ΣSum PFAS
Januar	16	2	9	6	1	4	0	3	41
Februar	9	2	9	1	0	0	2	3	26
March	3	1	9	0	0	0	2	2	17
April	6	2	10	1	0	0	1	3	23
May	27	2	16	0	0	0	0	3	48
June	10	2	13	2	1	2	0	3	33
July	15	2	28	5	0	0	2	5	57
August	50	2	13	120	0	0	0	5	190
September	25	3	14	110	1	0	2	6	161
Oktober	70	3	18	53	0	0	2	5	151
November	24	4	14	71	2	4	0	9	128
December	8	0	7	40	0	0	0	4	59
Average	21.9	2.1	13.3	34.1	0.4	0.8	0.9	4.3	77.8

7 **Table S7 Concentrations of PFOS and PFOA (ng/L) observed in the Lek canal at Nieuwegein in the period 2006 to 2008 [data from 1-3].**

Sampling date	PFOS	PFOA	Sampling date	PFOS	PFOA	Sampling date	PFOS	PFOA
1/18/2006	15	13	1/17/2007	6.8	5	2/13/2008	5	5
2/15/2006	13	13	2/14/2007	7.7	5	5/7/2008	7.6	5
3/15/2006	10	10	3/14/2007	5.5	5	7/30/2008	12	6.5
4/19/2006	10	5	4/11/2007	9.5	6.1	10/22/2008	8.9	7.8
5/10/2006	11	5.4	5/9/2007	10	11			
6/7/2006	9.8	5	6/6/2007	15	6.4			
7/5/2006	16	5.4	7/4/2007	13	5			
8/2/2006	15	5	8/1/2007	9.7	5			
8/30/2006	26	5	8/29/2007	5.5	5			
9/27/2006	8.5	6.1	9/26/2007	11	5			
10/25/2006	12	12	10/24/2007	6.7	9.6			
11/22/2006	9.3	5	11/21/2007	6.5	5			
12/20/2006	13	5	12/19/2007	5	5			

12 **Table S8 Average PFAA concentration at the effluent of three sampled young GAC beds and three sampled old GAC beds.**

	young	stdev	old	stdev
PFBA	31	1,6	31	1,5
PFPeA	1,7	0,2	1,9	0,2
PFHxA	4,6	0,1	4,8	0,1
PFHpA	4,2	0,4	4,4	0,6
PFOA L	13	0,8	11	1,3
PFNA	<LOQ		<LOQ	
PFDA	<LOQ		<LOQ	

PFBS	21	1,3	24	1,5
PFHxS	4,6	0,2	3,0	0,5
PFOS L	3,7	0,8	2,0	0,8

References

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