Supporting Information for

QUANTIFYING DIFFUSE AND POINT INPUTS OF PERFLUOROALKYL ACIDS IN A NON-INDUSTRIAL RIVER CATCHMENT

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1. Additional Information on Materials and Methods

1.1. Materials

Reference and isotopically labeled PFAA standards were all purchased from Wellington Laboratories (Ontario, Canada). Acesulfame K (analytical purity) was obtained from Supelco (Sigma-Adrich, Buchs, Switzerland). Methanol (suprasolv grade), water (Lichrosolv), and tert-butylmethylether (MTBE, analytical grade) were purchased from Merck (Darmstadt, Germany). Ammonium hydroxide (NH_4OH, <25% in water), sodium acetate (NaAc), ammonium acetate (NH_4Ac), and acetic acid were obtained from Fluka (Sigma-Adrich).

1.2. Study Area

Table S1: Contribution of sealed and natural surfaces to the study catchment areas.

	type of area	area (km^2)	fraction
total catchment	sealed area stormwater sewer	0.49	25%
	sealed area combined sewer	1.44	75%
	total sealed area	1.93	33%
	natural area	3.96	67%
	total area	**5.89**	
C1: rural	sealed area stormwater sewer	0.10	3%
	natural area	2.93	97%
	total area	3.04	
C2: urban (excl. C1)	sealed area stormwater sewer	0.39	28%
	natural area	1.02	72%
	total area	1.41	
WWTP (all combined sewer areas)	sealed area catchment 1	0.52	36%
	sealed area catchment 2	0.64	45%
	sealed area catchment 3	0.05	3%
	sealed area outside catchment	0.23	16%
	total sealed area	1.44	
C3 (excl. C1, C2 and WWTP)	natural area	0.01	100%
	total area	0.01	

Combined Sewer Overflows (CSO): Besides the CSO located lext to the WWTP, additional ones were located in C1 and C2, however, they were not active during sampling. The activity of the CSO in C1 was not monitored directly but checked by measuring a wastewater marker (acesulfame[1]). Due to these measurements, it was concluded that the CSO in C1 was not active during all sampling (Figure S7 and Table S11). A second CSO is located in C2, but it discharges the waste- and stormwater into a river outside of the catchment when it is activated. This overflow was automatically monitored but no activity was seen during sampling.

1.3. FIELD SAMPLING

Automated Sampling: ISCO samplers collect river water with a squeeze pump over a long polypropylene tube that is fixed in the river bed. The end of the tube is connected to a metal sieve (10 mm pore size), which hinders larger participles from entering the tube. The sampled water is collected in consecutive order in one of 24 sampling bottles, which are located inside the sampler. These samples were regularly transferred into polypropylene sampling bottles. 10 ml of methanol was used to wash the surface of the sampling bottle in order to avoid losses of PFAAs due to adsorption. These 10 ml of methanol were added to the corresponding storage bottle.

In order to avoid cross-contamination the following measures were taken: (i) After the sampling bottles were emptied, they were washed with methanol and clean water. (ii) Just before river water was collected, the sampling tube was washed three times with river water.

Level-Discharge Calibration: Each river sampling location was equipped with a pressure conductor (750 Area Velocity Module, Teledyne ISCO) to measure the water level in 5 min intervals. The water level-discharge relationship was determined with NaCl dilution experiments.[2] The data was fitted with a second order polynomial equation. The results are displayed in Table S2 and Figure S1.

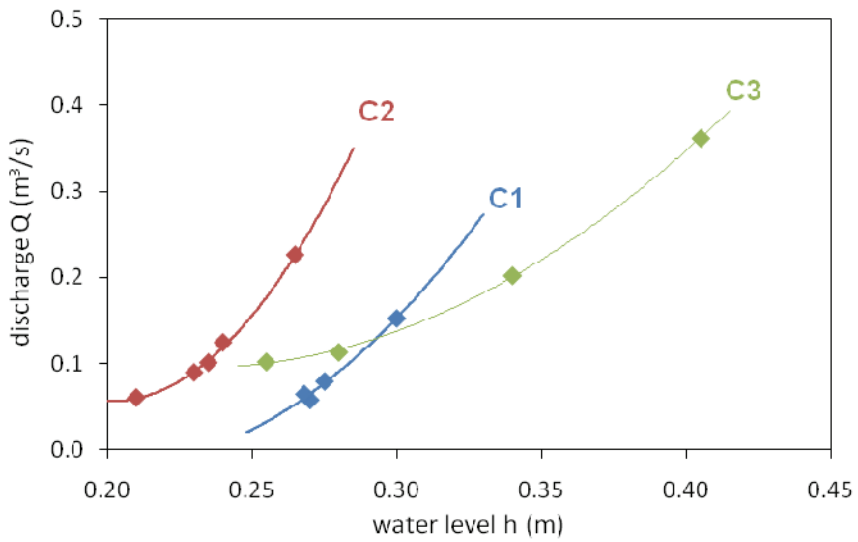

Figure S1: Graphical display of the water level-discharge polynomial relationship for locations C1 (blue), C2 (red), and C3 (green)

Table S2: Results of the water level-discharge calibration with polynomial fit.

	catchment C1		catchmen C2		catchmen C3	
	water level h (m)	discharge Q (m^3/s)	water level h (m)	discharge Q (m^3/s)	water level h (m)	discharge Q (m^3/s)
experiment 1	0.300	0.153	0.265	0.226	0.405	0.362
experiment 2	0.275	0.079	0.240	0.124	0.340	0.202
experiment 3	0.270	0.058	0.230	0.089	0.280	0.113
experiment 4	0.268	0.064	0.210	0.060	0.255	0.102
experiment 5			0.235	0.100		
a_0 (m^3/s)	0.7120		1.7521		0.5576	
a_1 (m^2/s)	-7.2091		-16.8610		-4.0256	
a_2 (m/s)	17.8190		41.9030		8.7514	
R^2	0.987		0.997		0.999	
SD (m^3/s)	0.01		0.005		0.024	

polynomial equation: $Q = a_0 + a_1 \times h + a_2 \times h^2$

SD: standard deviation

Additional samples: Wastewater effluent, rainwater, drinking water and stormwater sewer grab samples were taken for the two sampling periods. 0.25-L wastewater effluent flow-proportional daily mixed samples were provided by the WWTP together with the 15-min interval effluent discharge data. Rainfall was collected at one location in C2. The rain intensity was measured by the WWTP and by the local environmental agency (rain gauge outside catchment). Drinking water of the town consisted of 76% groundwater from the region, 15% lake water from Lake Zürich and 9% of a local spring. For every component, one sample was taken directly at the water plant (0.5 L each). Stormwater sewer grab samples were taken at the outflow to the river during the rain events. These samples are not representative of all stormwater sewers, as there were many different sewers and due to limited resources, not all could be sampled. Additionally, no discharge measurements were available for sewers outlets.

Table S3: Overview on all the samples collected for this study.

			number of samples	
	type of sample	**volume**	**SP1**	**SP2**
catchment 1[a]		0.5 L	12	9
catchment 2[a]	2 hours mixed samples (time proportional)	0.5 L	11	10
catchment 3[a]		0.5 L	12	9
wastewater	24 h mixed samples (volume proportional)	0.25 L	3	3
rain	total rain (collected in fractions)	dependent on rain	3	3
stormwater	grab samples	ca. 0.5 L	8	
drinking water	grab samples of every source	0.5 L	3	

[a] not all samples initially collected were analyzed in the lab due to limited resources

1.4. Analytical Procedure

The water samples were analyzed for 13 PFAAs, including 10 PFCAs from perfluorobutanoate (PFBA) to perfluorotridecanoate (PFTrA), three PFSAs, and acesulfame. All analytes are listed in Table S4.

PFAAs: For the sample preparation, the unfiltered samples were acidified to a pH of 5 with acetic acid and a mix of isotope-labeled internal standards was added (see Table S4). The samples were left for an hour in order to equilibrate between dissolved and particulate phase as well as sample bottle walls. The weak anion exchange (WAX) SPE cartridges (Waters Corporation, Milford, MA, USA) were cleaned with methanol and conditioned with water prior to use. Samples were then passed through the cartridge at a flow rate of approx. 3 mL/min. The loaded cartridges were cleaned with 25 mM sodium acetate (pH 4.2) and dried. Ten milliliters of methanol, which were prior used to extract the sample bottle walls, were passed through the cartridge and were discarded. Finally, the analytes were eluted in 4 mL of 1 % ammonium hydroxide in MTBE/methanol (9:1) containing all PFAAs. The eluate was further concentrated under a gentle stream of nitrogen to 0.5 mL and 0.5 mL of water was added.

Instrumental analyses were all performed using liquid chromatography-tandem mass spectrometry (LC-MS/MS) methods on a 1290 series LC connected to a 6460 triple quadrupole MS from Agilent Technologies Inc. (Santa Clara, CA, USA). The concentrated sample (10 µL) was injected onto a ZORBAX RRHD Eclipse Plus C18 column (50 × 2.1 mm, 1.8 µm particle size; Agilent Technologies Inc.), which was heated to 60 °C. The mobile phase consisted of 2.5 mM ammonium acetate in (A) water and (B) methanol. The flow rate was 0.4 mL/min and a gradient was applied (0 min, A: 90%; 0.5 min, A: 90%; 1.5 min A: 45%; 7.0 min, A: 10%). MS/MS parameters were as follows: drying gas temperature at 250°C, sheath gas temperature at 300°C, capillary voltage at -2000 V. The compounds specific parameters are listed in Table S4. Quantification was performed with internal standard normalized external calibration.

Acesulfame: Acesulfame was not extracted prior to instrumental analysis. A subsample (0.5 mL) of every surface water sample was filtered through a 0.2 µm Nylon filter (ISO-Disc, Supelco, Bellefonte, PA, USA) and 15 µL of the sample was injected on a ZORBAX Eclipse XDB-C18 column (100 × 2.1 mm, 1.8 µm particle size, Agilent Technologies Inc.) which was heated to 55°C. The mobile phase consisted of (A) 1.5 mM acetic acid and 0.15 mM triethylamine in water and (B) methanol. The flow rate was 0.5 mL/min and a gradient was applied (0 min, A: 95%; 0.2 min, A: 95%; 2.0 min A: 75%). MS/MS parameters were as follows: drying gas temperature at 325°C, sheath gas temperature at 250°C, capillary voltage at -2000 V. Acesulfame was quantified with standard addition with four different standards.

Quality assurance: Spike and recovery experiments were conducted with river water samples. After spiking with native standards, the bulk water solutions were left for an hour to equilibrate. Absolute recoveries were all satisfying (65-128%). Recoveries of internal standards for all analyzed samples were also sufficient (82-106%). The relative standard deviation of parallel samples were between 4-11%, see Table S5.

Table S4: List of all analyzed PFAAs and isotopically labeled internal standards with MS parameter.

chemical name	abbrevia-tion	molecular weight	quantifier transition	CE [V]	qualifier transition	CE [V]	used internal standard
			target analytes				
perfluorobutanoic acid	PFBA	214.04	213→169	1	-		$^{13}C_4$ PFBA
perfluoropentanoic acid	PFPA	264.05	263→219	1	-		$^{13}C_2$ PFHxA
perflurorohexanoic acid	PFHxA	314.05	313→269	1	313→119	10	$^{13}C_2$ PFHxA
perfluroheptanoic acid	PFHpA	364.06	363→319	4	363→169	15	$^{13}C_4$ PFOA
perfluotooctanoic acid	PFOA	414.07	413→369	4	413→169	15	$^{13}C_4$ PFOA
perfluorononanoic acid	PFNA	464.08	463→419	5	463→169	15	$^{13}C_2$ PFDA
perfluorodecanoic acid	PFDA	514.09	513→469	5	513→219	15	$^{13}C_2$ PFDA
perfluoroundecanoic acid	PFUnA	564.09	563→519	5	563→169	15	$^{13}C_2$ PFDA
perfluorododecanoic acid	PFDoA	614.10	613→569	5	-		$^{13}C_2$ PFDA
perfluorotridecanoic acid	PFTrA	664.11	663→619	5	-		$^{13}C_2$ PFDA
perfluorobutane sulfonate[a]	PFBS	338.19	299→80	40	299→99	40	$^{18}O_2$ PFHxS
perfluorohexane sulfonate[b]	PFHxS	422.10	399→80	50	399→99	50	$^{18}O_2$ PFHxS
perfluorooctane sulfonate[b]	PFOS	522.11	499→80	55	499→99	55	$^{13}C_4$ PFOS
acesulfame[a]	ACE	201.24	162→82	10	162→78	36	-
			mass labeled internal standards				
$^{13}C_4$-perfluotobutanoic acid	$^{13}C_4$ PFBA	218.01	217→172	1	-		
$^{13}C_2$-perfluotohexanoic acid	$^{13}C_2$ PFHxA	316.04	315→270	1	-		
$^{13}C_4$-perfluotooctanoic acid	$^{13}C_4$ PFOA	418.04	417→372	4	417→169	15	
$^{13}C_2$-perfluorodecanoic acid	$^{13}C_2$ PFDA	516.07	515→470	5	515→219	15	
$^{18}O_2$-perfluorohexane sulfonate[b]	$^{18}O_2$ PFHxS	426.10	403→84	50	403→103	50	
$^{13}C_4$-perfluorooctane sulfonate[b]	$^{13}C_4$ PFOS	526.08	503→80	55	503→99	55	

[a]potassium salt, [b] sodium salt, CE: collision energy

Table S5: Absolute and relative standard recoveries and relative standard deviation

Analyte	RSD (n=6)	absolute recovery (n=3)	IS recovery (n=86)	relative recovery (n=3)
PFBA	13%	65%	82%	80%
PFPA	6%	114%		114%
PFHxA	5%	112%	100%	112%
PFHpA	9%	116%		110%
PFOA	9%	128%	106%	121%
PFNA	6%	102%		97%
PFDA	10%	114%	94%	121%
PFUnA	11%	80%		85%
PFDoA	5%	72%		77%
PFTrA	6%	66%		70%
PFTeA	7%	69%		74%
PFBS	10%	105%		122%
PFHxS	4%	96%	86%	112%
PFOS	9%	94%	95%	99%

RSD: relative standard deviation; IS: internal standard

Table S6: Method and field blank values in ng/L with the average blank and the blank level with security factor (three times standard deviation.

	blank level (ng/L)												
	PFBA	**PFPA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUnA**	**PFDoA**	**PFTrA**	**PFBS**	**PFHxS**	**PFOS**
blank 1	*0.007*	0.017	0.020	*0.007*	0.040	*0.007*	0.011	*0.007*	*0.007*	*0.007*	*0.006*	*0.006*	0.039
blank 2	0.015	0.029	0.018	*0.007*	0.038	*0.007*	0.045	*0.007*	*0.007*	*0.007*	0.016	*0.006*	0.166
blank 3	0.017	0.012	0.017	*0.007*	0.038	*0.007*	0.013	*0.007*	*0.007*	*0.007*	*0.006*	*0.006*	0.148
blank 4	0.023	0.011	0.017	0.020	0.041	*0.007*	*0.007*	*0.007*	*0.007*	*0.007*	*0.006*	0.011	0.128
blank 5	*0.007*	*0.007*	0.013	*0.007*	*0.007*	*0.007*	*0.007*	*0.007*	*0.007*	*0.007*	*0.006*	0.010	0.011
blank 6	*0.007*	*0.007*	0.007	0.045	0.095	*0.007*	*0.007*	*0.007*	*0.007*	*0.007*	*0.006*	0.229[a]	1.280[a]
blank 7	*0.007*	*0.007*	0.030	0.030	0.030	*0.007*	0.045	0.021	*0.007*	*0.007*	*0.006*	0.017	0.363
blank 8	*0.007*	*0.007*	0.042	0.047	0.012	*0.007*	0.043	*0.007*	*0.007*	*0.007*	*0.006*	0.023	0.129
field blank 1	0.021	0.013	0.018	0.018	0.050	*0.007*	*0.007*	*0.007*	*0.007*	*0.007*	*0.006*	0.065	0.796[a]
field blank 2	*0.007*	*0.007*	0.033	0.029	0.052	*0.007*	0.017	*0.007*	*0.007*	*0.007*	*0.006*	0.028	0.182
field blank 3	*0.007*	*0.007*	0.004	*0.007*	0.012	*0.007*	*0.007*	*0.007*	*0.007*	*0.007*	*0.006*	0.022	0.017
average blank	**0.011**	**0.011**	**0.020**	**0.020**	**0.038**	**0.007**	**0.019**	**0.008**	**0.007**	**0.007**	**0.007**	**0.019**	**0.131**
blank + 3×SD	**0.030**	**0.031**	**0.054**	**0.066**	**0.111**	**0.007**	**0.069**	**0.021**	**0.007**	**0.007**	**0.016**	**0.073**	**0.456**

SD standard deviation

[a] these blank values were treated seperatly and the samples of these two batches were only reported when above the specific values. This was done in order not to discriminate a major part of the results.

italic numbers show blank which were below LOD (were set equal to 1/2 LOD)

Table S7: Limit of quantification (LOQ) and limit of detection (LOD) for all PFAAs

	(ng/L)													
	PFBA	**PFPA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUnA**	**PFDoA**	**PFTrA**	**PFBS**	**PFHxS**	**PFOS**	**ACE**
LOQ	**0.044**	**0.044**	**0.054**	**0.066**	**0.11**	**0.044**	**0.069**	**0.044**	**0.044**	**0.044**	**0.038**	**0.073**	**0.46**	**5.0**
MQL	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.038	0.038	0.042	5.0
LOD	0.013	0.013	0.013	0.013	0.013	0.013	0.013	0.013	0.013	0.013	0.011	0.011	0.013	1.5

LOQ: limit of quantification, defined by either by blank level or quantification limit of method
MQL: method quantification limit
LOD: limit of detection, 3 × standard deviation of noise

1.5. Mass Balance Calculations

To calculate the mass balance the following assumptions were made:

1. The rain intensity was homogeneous over the whole study area. This assumption is supported by the fact that the rain gauge within and another one outside the study area detected the same rain amount. Additionally, the area is very small with 6 km^2.
2. PFAA are conserved in the water phase during the whole period. It is assumed that there was no adsorption on soil, sediment, and sludge. This assumption is reasonable for shorter-chain PFCAs up to ten carbons as well as PFBS and PFHxS. It is known that PFOS and longer-chain PFCAs (11 to 13 carbons) have higher sorption affinities.[3] Additionally, it is assumed that there is no degradation in the WWTP and surface water, as these compounds are considered recalcitrant.
3. The load measured in C1 and C2 are considered as strictly diffuse inputs. CSO1 was not active during the sampling period.

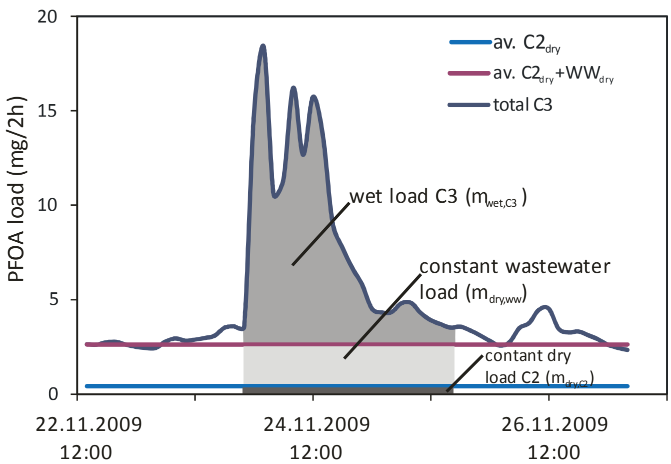

Figure S2: Load calculation with the example of PFOA loads in catchment 3

4. Dry loads (usual wastewater load and dry diffuse loads) are assumed to be constant and present in the same amount during wet weather (see Figure S2).
5. CSO3 water volume was considered to be the difference between water volume from C2 plus wastewater effluent and C3. The load of the CSO is calculated with the wet weather wastewater effluent concentration, so it is assumed that no degradation or production of

PFAAs (from precursor substances) occurs in the wastewater treatment plant. A second scenario uses the assumption that additional PFAAs are generated in the WWTP with 100% increase, so that CSO concentrations are half the wastewater effluent concentrations.

Table S8: Equations for the mass balance calculation.

description	abbr.	equation	legend	comments
load calculations for river catchments and wastewater effluents				
total load river catchment x		$m_{tot,Cx} = \sum_{i=1}^{n_{tot}} c_{Cx,i} \times V_{Cx,i}$	$m_{tot,Cx}$.....total load in catchment x during the whole sampling period (mg) Cx..........catchment x (1,2, or 3) $c_{Cx,i}$.........concentration at catchment x for time period i (mg/m^3) $V_{Cx,i}$........water discharge in two hours (m^3) n_{tot}.........total number of two hour (or 24 hour for wastewater) sampling periods	interpolated concentrations for missing data points
average dry load river catchment x	**i,ii,iii**	$\bar{\dot{m}}_{dry,Cx} = \frac{\sum_{i=1}^{n_{dry}} c_{Cx,i} \times V_{Cx,i}}{t_{dry}}$	$\bar{\dot{m}}_{dry,Cx}$....average mass flow in catchment x during dry weather, when discharge was not elevated (mg/h) n_{dry}........total number of two hour sampling periods during dry weather t_{dry}.........total time of dry weather (h)	
wet load river catchment x	**I,II,III**	$m_{wet,Cx} = m_{tot,Cx} - \bar{\dot{m}}_{dry,Cx} \times t_{tot}$	$m_{wet,Cx}$....load in catchment x during wet weather (mg) t_{tot}.........total time of sampling period (h)	
total wastewater load		$m_{tot,ww} = \sum_{i=1}^{n_{tot}} c_{ww,i} \times V_{ww,i}$	$m_{tot,ww}$......total wastewater load during sampling period (mg) $c_{ww,i}$.......wastewater concentration as 24 hours composite sample (mg/m^3) $V_{ww,i}$......wastewater effluent discharge in 24 hours (m^3)	
average dry wastewater load	**iv**	$\bar{\dot{m}}_{dry,ww} = \frac{\sum_{i=1}^{n_{dry}} c_{ww,i} \times V_{ww,i}}{t_{dry}}$	$\bar{\dot{m}}_{dry,ww}$...average wastewater mass flow during dry weather (mg/h)	
wet weather load wastewater treatment plant	**IV**	$m_{wet,ww} = m_{tot,ww} - \bar{\dot{m}}_{dry,ww} \times t_{tot}$	$m_{wet,ww}$...additional wastewater load during wet weather (mg)	

Table S8 (continued)

description	abbr.	equation	legend	comments
load calculations for the combined sewer overflow (CSO3)				
water volume CSO3		$V_{CSO3} = V_{C3} - (V_{C2} + V_{WW})$ $V_x = \sum_{i=1}^{n_a} V_{x,i}$	V_{CSO3}.......volume of water which is drained by the CSO3 (m^3) V_x..........volume of water at C2, C3 or WW (m^3) $V_{x,i}$.........water discharge in C2, C3 or WW in time period i(m^3) n_a...........total number of sampling periods when CSO active	only calculated for period when CSO3 was active
total load of CSO3	**V**	$m_{CSO3} = V_{CSO3} \times \bar{c}_{ww,wet}$	m_{CSO3}.......total load CSO3 (mg) $\bar{c}_{ww,wet}$..........average wastewater effluent concentration during wet weather period (mg/m^3)	
source calculations				
S1. rain				
volume of rain per catchment x		$V_{rain,Cx} = V_{tot,Cx} - \bar{Q}_{dry,Cx} \times t_{tot}$ $V_{tot,Cx} = \sum_{i=1}^{n_{tot}} V_{Cx,i}$ $\bar{Q}_{dry,Cx} = \frac{\sum_{i=1}^{n_{dry}} V_{x,i}}{t_{dry}}$	$V_{rain,Cx}$......volume of rain (m^3) $V_{tot,Cx}$.........volume of water in catchment x during the whole sampling period (m^3) $\bar{Q}_{dry,Cx}$........average flow rate in catchment x during dry weather period (m^3/h) $V_{Cx,i}$.........volume of water in catchment x (m^3)	
rain load per catchment x	**S1.1** **S1.2**	$m_{rain,Cx} = V_{rain,Cx} \times c_{rain}$	$m_{rain,Cx}$......rain load for catchment 1 or 2 (mg) C_{rain}.........concentration of rain (mg/m^3)	
volume of rain in combined sewers (WWTP and CSO3)		$V_{rain,CS} = V_{tot,CS} - \bar{Q}_{dry,ww} \times t_{tot}$ $V_{tot,CS} = \left(\sum_{i=1}^{n_{tot}} V_{ww,i}\right) + V_{CSO3}$ $\bar{Q}_{dry,ww} = \frac{\sum_{i=1}^{n_{dry}} V_{ww,i}}{t_{dry}}$	$V_{rain,CS}$......volume of rain in combined sewers (m^3) $V_{tot,CS}$........volume of water in combined sewers during the whole sampling period (m^3) $\bar{Q}_{dry,ww}$........average volume of water in WW (treatment plant) during dry weather (m^3/h)	
rain load in combined sewers	**S1.3**	$m_{rain,CS} = V_{rain,CS} \times c_{rain}$	$m_{rain,CS}$......rain load in combined sewers (mg)	

Table S8 (continued)

description	abbr.	equation	legend	comments
S2. 'stormwater mobilized' (dry deposition and outdoor use of PFAA products)				
stormwater mobilized load catchment C1,C2	**S2.1** **S2.2**	$m_{SW,Cx} = m_{wet,Cx} - m_{rain,Cx}$	$m_{SW,Cx}$.....stormwater load in catchment 1 or 2 (mg)	stormwater is defined as all what is mobilized from surfaces (dry deposition and outdoor use of products)
stormwater mobilized load combined sewers	**S3.2**	$m_{SW,CS} = m_{wet,ww} + m_{CSO3} - m_{rain,CS}$	$m_{SW,Cx}$.....stormwater load in wastewater (mg)	
S4. drinking water				
loads in WWTP due to drinking water	**S4**	$m_{DW} = c_{DW} \times \bar{Q}_{dry,ww} \times t_{wet}$	m_{DW}.......drinking water load during the wet weather (mg) t_{wet}.........total time of wet weather (h)	same as during dry weather
S3. indoor use of PFAA products				
loads due to indoor use	**S3**	$m_{ID} = \bar{\bar{m}}_{dry,ww} \times t_{wet} - m_{DW}$	m_{ID}.........indoor use loads during wet weather (mg)	same as during dry weather

2. Additional Information on Results

2.1. Hydrological Results

Table S9: Water loads in river catchment and WWTP during the whole sampling period and during rain.

	total $water_{112h}$ (m^3)	dry weather $background_{112h}$ (m^3)	additional water volume during $rain_{44h}$ (m^3)	theoretical rain (area × rain intensity) (m^3)	runoff coefficient[a] (-)
sampling period 1 (November 22-27, 2009: 112h)					
C1	41'000	22'000	19'000 ± 1'000	52'000	**0.37**
C2	62'000	35'000	27'000 ± 2'000	76'000	**0.36**
C2 (without C1)	21'000		8'000 ± 2'000	24'000	**0.34**
WWTP effluent	24'000	17'000[b]	6'600 ± 300	25'000 (WWTP effluent + CSO)	**0.47** (WWTP effluent + CSO)
CSO	5'000	0	5'000 ± 1'000		
C3 total watershed	93'000	55'000	39'000 ± 2'000	100'000	**0.45**
sampling period 2 (December 21-25, 2009: 82h)					
	total $water_{82h}$ (m^3)	dry weather $background_{82h}$ (m^3)	additional water volume during $rain_{40h}$ (m^3)	theoretical rain (area × rain intensity) (m^3)	runoff coefficient[a] (-)
C1	14'000	12'000	1'700 ± 300	27'000	**0.06**
C2	22'000	20'000	2'400 ± 600	40'000	**0.06**
C2 (without C1)	8'000		700 ± 700	13'000	**0.06**
WWTP effluent	16'000	11'000[b]	3'900 ± 200	13'000 (WWTP effluent + CSO)	**0.36** (WWTP effluent + CSO)
CSO	700	0	700 ± 400		
C3 total watershed	39'000	31'000	7'000 ± 1'000	53'000	**0.13**

CSO: combined sewer overflow
WWTP: wastewater treatment plant
[a] runoff coefficient: ratio between rain water load river and theoretical rain load
[b] shows the usual water volume processed by the WWTP

2.2. PFAA AND ACESULFAME CONCENTRATIONS

Table S10: Overview on the average and median concentration of all sample groups.

		Concentration (ng/L)												
		PFBA	**PFPA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUnA**	**PFDoA**	**PFTrA**	**PFBS**	**PFHxS**	**PFOS**
C1-SP1	**average**	**0.28**	**0.14**	**0.18**	**0.15**	**0.43**	**0.08**	**0.08**	**0.04**	**0.07**	**0.10**	**0.17**	**0.30**	**1.13**
	median	0.23	0.13	0.17	0.13	0.37	0.05	0.05	0.02	0.07	0.10	0.16	0.26	0.53
	min	0.15	0.07	0.07	<0.05	0.16	<0.04	<0.05	<0.04	<0.04	ND	0.12	0.19	0.15
	max	0.71	0.27	0.39	0.36	1.07	0.23	0.37	0.14	0.17	0.20	0.24	0.49	4.15
	>LOQ	12/12	12/12	12/12	10/12	12/12	10/12	7/12	5/12	9/12	9/12	12/12	12/12	8/12
C1-SP2	**average**	**0.21**	**0.13**	**0.15**	**0.12**	**0.26**	**0.04**	**0.04**	**0.02**	**0.03**	**0.02**	**0.11**	**0.30**	**0.69**
	median	0.15	0.11	0.13	0.09	0.22	0.02	0.02	0.02	0.02	0.02	0.12	0.29	0.38
	min	0.08	0.07	0.08	0.06	0.10	<0.04	<0.05	<0.04	<0.04	ND	<0.03	0.20	0.15
	max	0.63	0.28	0.32	0.30	0.66	0.15	0.20	0.06	0.07	0.04	0.18	0.43	3.04
	>LOQ	9/9	9/9	9/9	9/9	9/9	3/9	1/9	2/9	2/9	1/9	8/9	9/9	5/9
C2-SP1	**average**	**0.41**	**0.25**	**0.34**	**0.35**	**1.07**	**0.16**	**0.18**	**0.14**	**0.14**	**0.13**	**0.38**	**0.32**	**1.33**
	median	0.31	0.21	0.28	0.29	0.86	0.13	0.15	0.11	0.11	0.15	0.35	0.32	1.21
	min	0.24	0.17	0.21	0.21	0.63	0.04	<0.05	<0.04	0.04	<0.04	0.28	0.28	0.43
	max	0.96	0.37	0.56	0.57	1.62	0.30	0.38	0.35	0.33	0.32	0.56	0.39	2.32
	>LOQ	11/11	11/11	11/11	11/11	11/11	11/11	11/11	7/11	11/11	7/11	11/11	11/11	11/11
C2-SP2	**average**	**0.48**	**0.28**	**0.37**	**0.31**	**1.01**	**0.12**	**0.10**	**0.03**	**0.06**	**0.07**	**0.34**	**0.36**	**1.42**
	median	0.43	0.25	0.33	0.30	0.99	0.09	0.06	0.02	0.06	0.07	0.33	0.35	0.88
	min	0.25	0.17	0.21	0.17	0.54	0.05	<0.05	<0.04	<0.04	ND	0.27	0.08	0.50
	max	0.83	0.52	0.61	0.54	1.52	0.25	0.34	0.07	0.14	0.17	0.54	0.86	6.01
	>LOQ	10/10	10/10	10/10	10/10	10/10	10/10	9/10	3/10	7/10	7/10	10/10	10/10	8/10
C3-SP1	**average**	**0.64**	**0.64**	**1.07**	**0.74**	**3.21**	**0.29**	**0.48**	**0.22**	**0.07**	**0.03**	**0.74**	**0.77**	**2.34**
	median	0.63	0.62	1.05	0.71	3.22	0.25	0.44	0.30	0.05	0.02	0.74	0.71	2.40
	min	0.41	0.41	0.71	0.57	2.28	0.19	0.24	0.02	<0.04	<0.04	0.57	0.50	0.52
	max	1.02	0.88	1.40	0.98	4.58	0.41	0.79	0.38	0.16	0.07	0.85	1.18	6.64
	>LOQ	12/12	12/12	12/12	12/12	12/12	12/12	12/12	12/12	8/12	4/12	12/12	12/12	11/12
C3-SP2	**average**	**0.83**	**0.68**	**1.34**	**0.78**	**3.45**	**0.33**	**0.60**	**0.05**	**0.04**	**0.02**	**0.82**	**0.79**	**2.99**
	median	0.76	0.68	1.50	0.84	3.45	0.28	0.47	0.05	0.02	0.02	0.88	0.80	2.15
	min	0.50	0.46	0.87	0.58	2.37	0.24	0.44	0.02	<0.04	ND	0.55	0.50	1.57
	max	1.41	0.89	1.72	1.00	4.74	0.47	0.91	0.09	0.10	0.06	0.98	1.00	6.09
	>LOQ	9/9	9/9	9/9	9/9	7/9	3/9	1/9	7/9	4/9	2/9	9/9	9/9	9/9
rain	**average**	**0.79**	**0.11**	**0.42**	**0.21**	**0.75**	**0.21**	**0.24**	**0.14**	**0.13**	**0.11**	**0.26**	**0.13**	**0.85**
	median	0.57	0.08	0.43	0.22	0.78	0.21	0.24	0.14	0.09	0.08	0.18	0.13	0.65
	min	0.32	0.05	0.15	0.07	0.37	0.07	0.13	0.06	0.05	<0.04	0.02	<0.11	0.23
	max	1.72	0.23	0.68	0.36	0.92	0.36	0.39	0.25	0.39	0.37	0.70	0.15	1.96
	>LOQ	6/6	6/6	6/6	6/6	6/6	6/6	6/6	6/6	6/6	4/6	6/6	4/6	4/6
storm-water	**average**	**1.45**	**0.73**	**0.98**	**0.94**	**2.29**	**0.39**	**0.43**	**0.15**	**0.10**	**0.03**	**2.69**	**0.44**	**2.20**
	median	1.19	0.51	0.72	0.62	1.53	0.28	0.40	0.11	0.11	0.02	0.48	0.33	2.32
	min	0.48	0.28	0.18	0.08	0.19	0.02	<0.05	<0.04	ND	<0.04	0.14	0.11	0.65
	max	4.33	1.62	2.60	2.86	5.89	1.35	1.25	0.41	0.23	0.07	17.58	0.96	4.20
	>LOQ	8/8	8/8	8/8	8/8	8/8	8/8	7/8	6/8	6/8	5/8	8/8	8/8	7/8
waste-water	**average**	**1.39**	**1.14**	**2.52**	**1.48**	**6.52**	**0.65**	**1.35**	**0.08**	**0.02**	**0.02**	**1.24**	**1.60**	**4.57**
	median	1.40	1.06	2.40	1.51	6.46	0.62	1.33	0.08	0.02	0.02	1.26	1.56	4.60
	min	1.09	0.84	1.88	1.22	5.38	0.55	0.96	0.04	<0.04	ND	0.49	1.01	2.90
	max	1.65	1.47	3.37	1.71	8.13	0.82	1.78	0.11	0.05	0.02	1.78	2.14	6.07
	>LOQ	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10
drinking water	groundwater	0.11	0.02	0.12	0.26	1.69	0.02	ND	ND	0.02	0.02	0.88	0.36	0.01
	source	0.02	ND	<0.050	0.02	0.08	0.02	0.02	0.04	0.02	ND	0.02	0.03	ND
	lake water	0.33	0.39	0.73	0.33	1.17	0.15	0.12	0.04	0.02	0.02	0.32	0.96	2.65
	average[a]	**0.16**	**0.11**	**0.27**	**0.27**	**1.48**	**0.05**	**0.04**	**0.01**	**0.02**	**0.02**	**0.70**	**0.49**	**0.67**

[a] weighted average

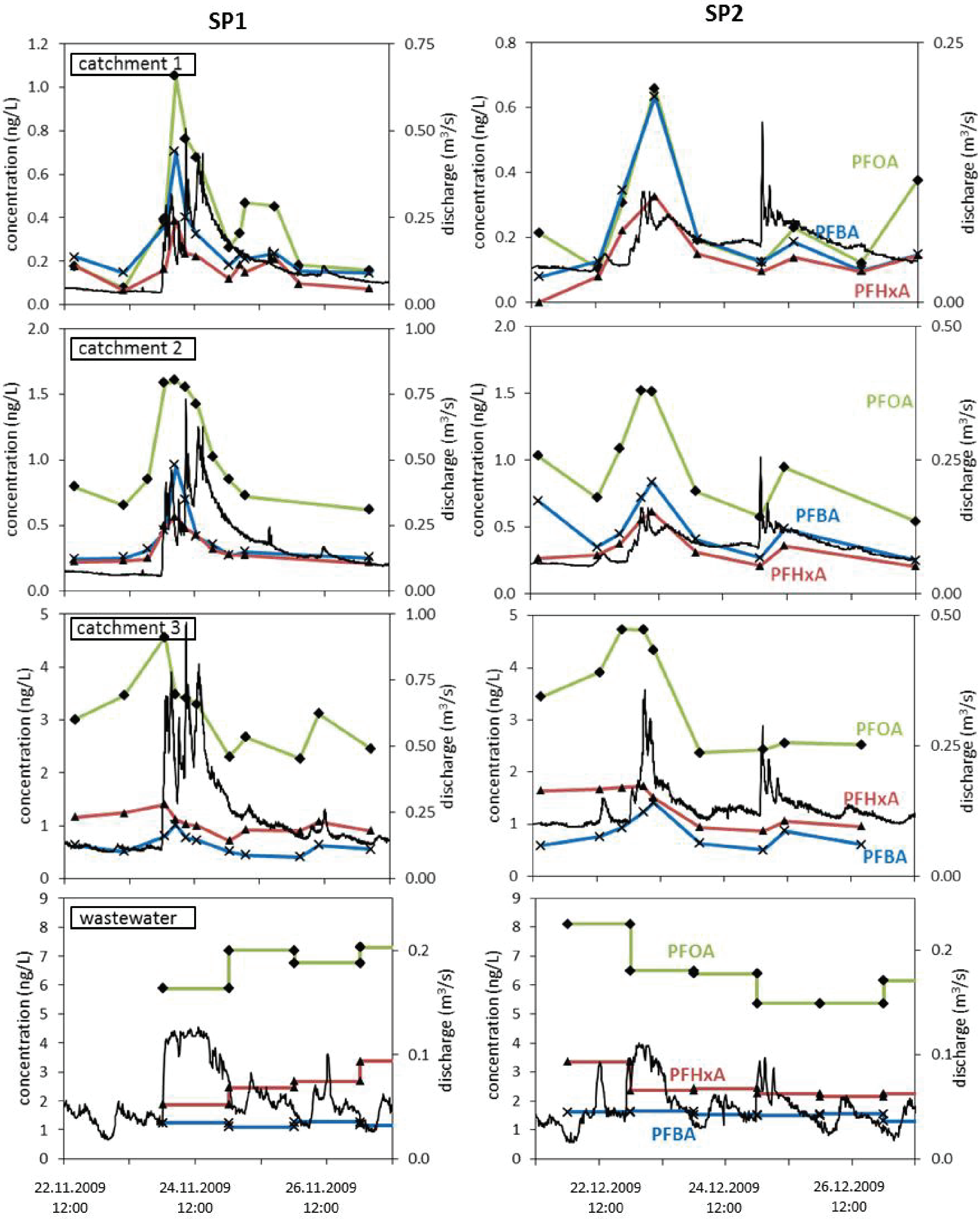

Figure S3: Concentration profiles for PFBA (blue), PFHxA (red), and PFOA (green) for catchments 1-3 and wastewater effluent combined with the discharge of the corresponding catchment (black).

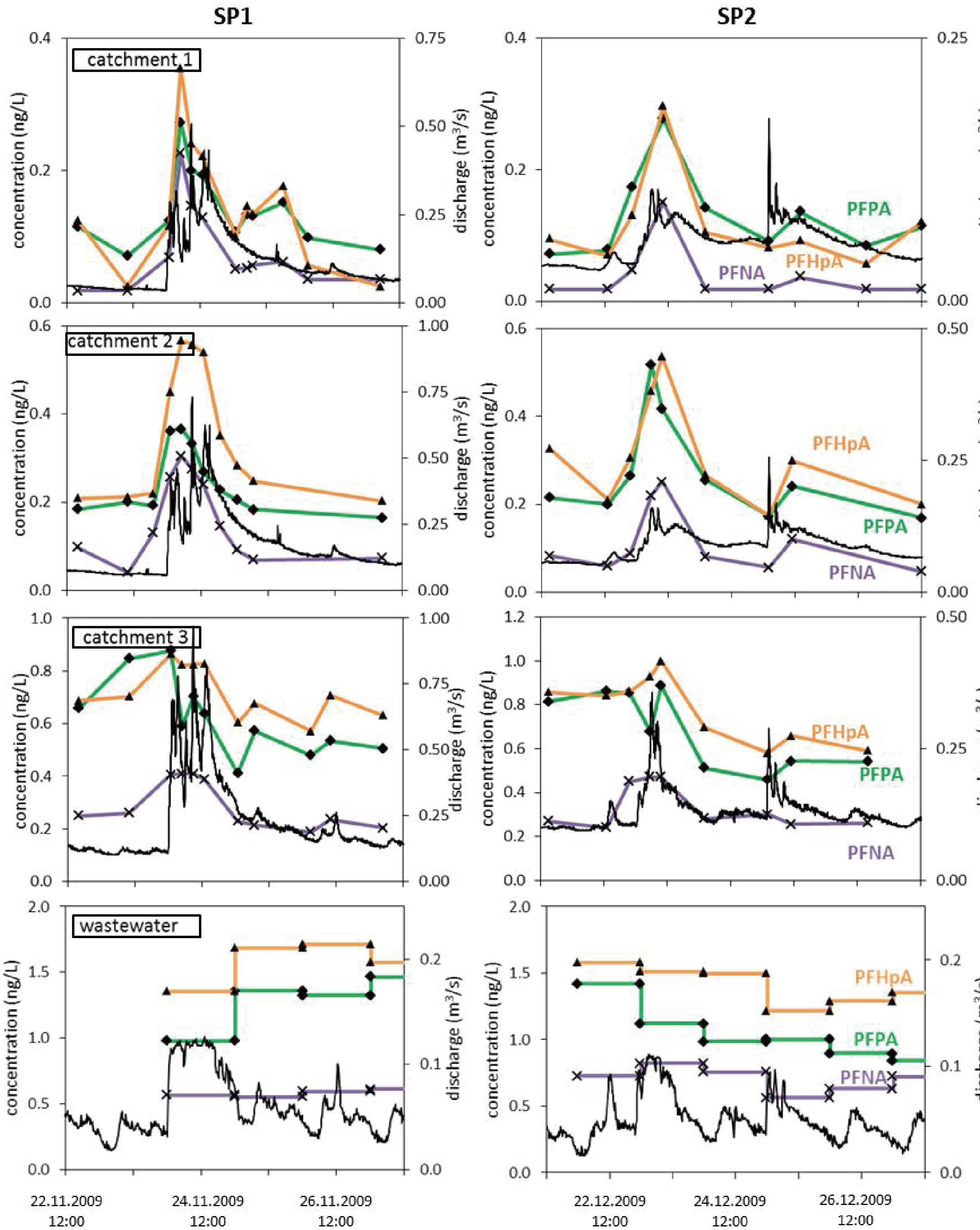

Figure S4: Concentration profiles for PFPA (green), PFHpA (orange), and PFNA (purple) for catchments 1-3 and wastewater effluent combined with the discharge of the corresponding catchment (black).

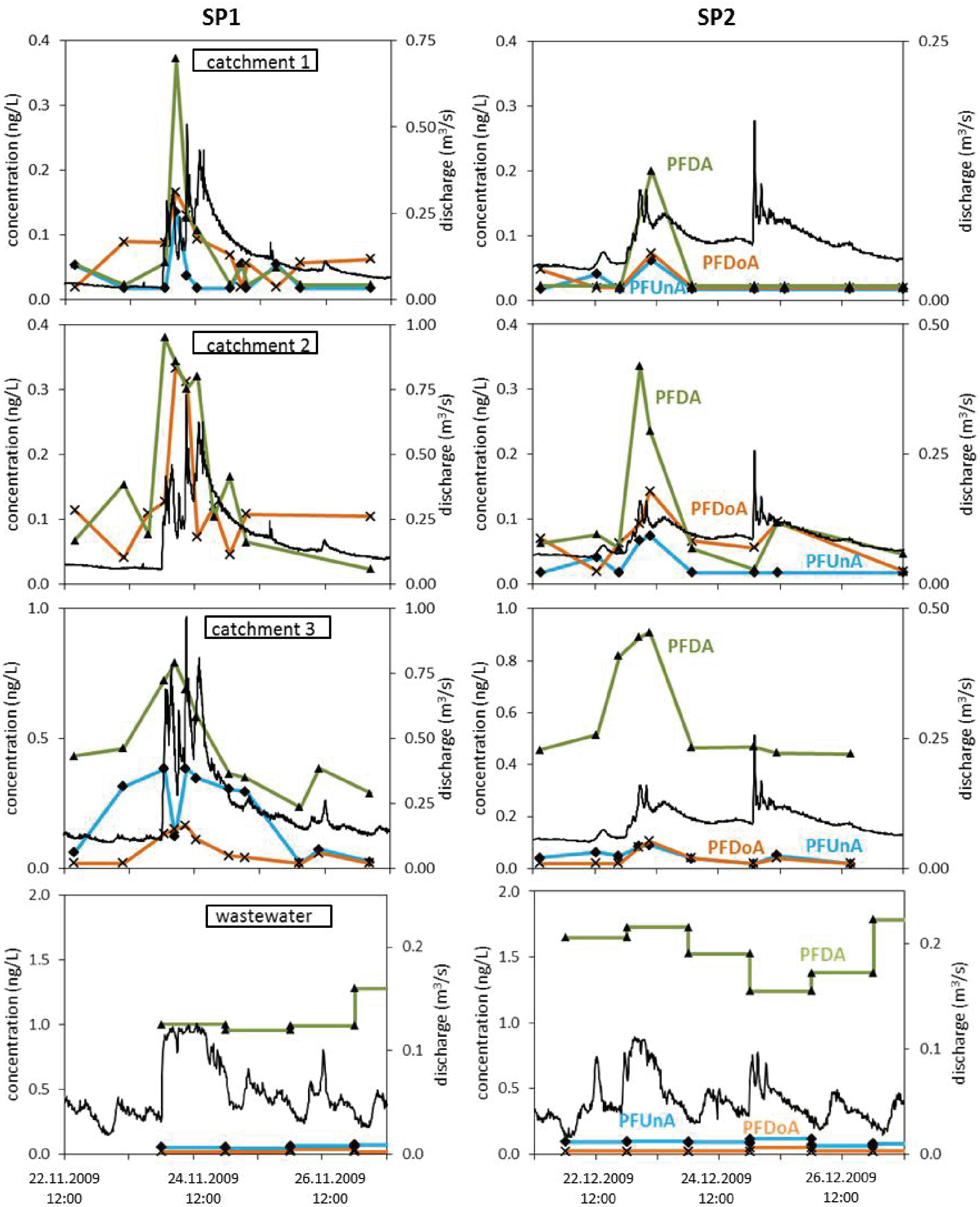

Figure S5: Concentration profiles for PFDA (green), PFUnA (blue), and PFDoA (orange) for catchments 1-3 and wastewater effluent combined with the discharge of the corresponding catchment (black).

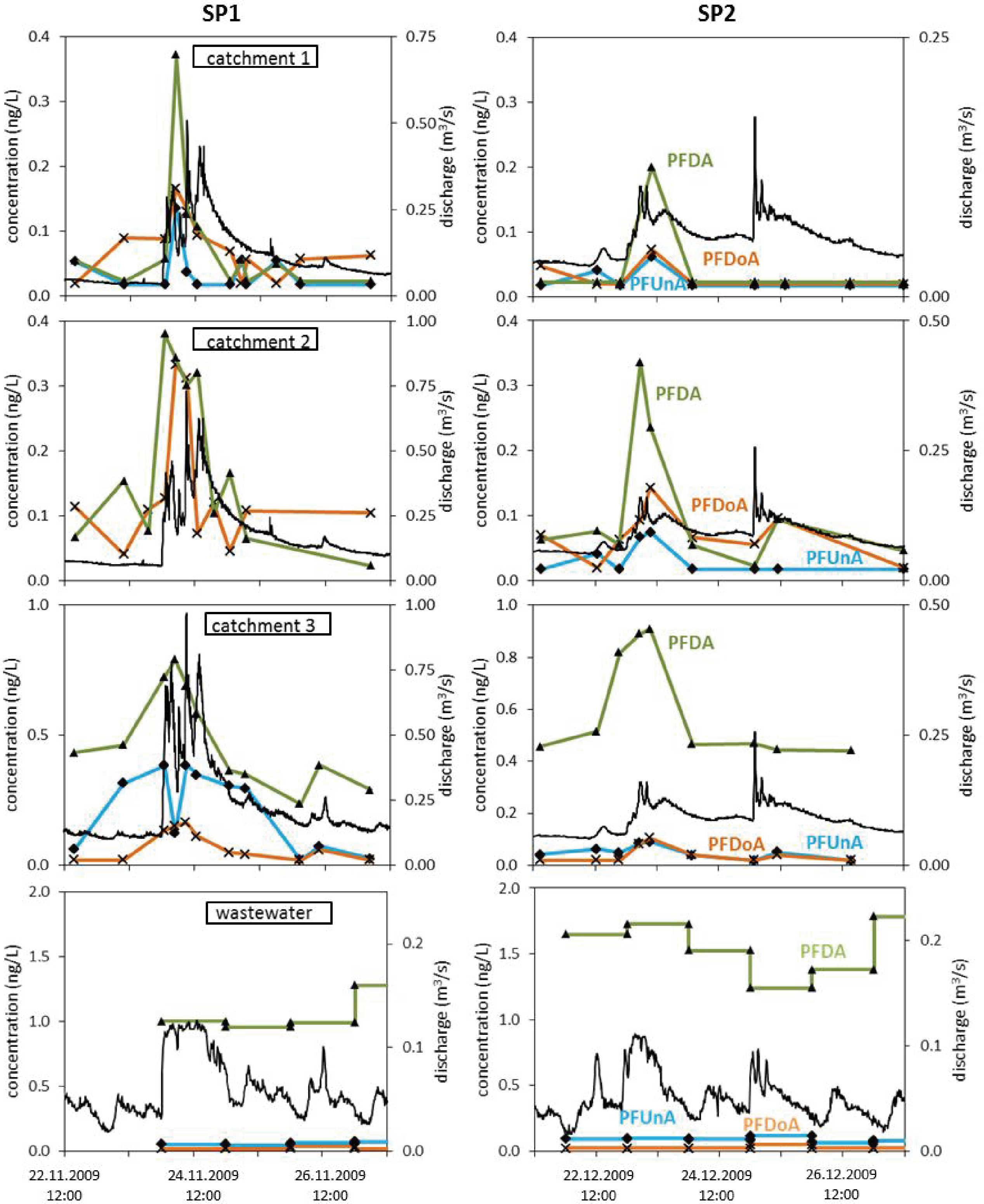

Figure S6: Concentration profiles for PFBS (blue), PFHxS (pink), and PFOS (red) for catchments 1-3 and wastewater effluent combined with the discharge of the corresponding catchment (black).

Table S11: Overview on acesulfame concentrations in river and wastewater.

	concentration (ng/L)					
	average	median	SD	min	max	>LOQ
C1-SP1	7.5	6.6	5.5	<5.0	14.8	4/8
C1-SP2	<5.0					0/9
C2-SP1	63	40	50.3	32	173	7/7
C2-SP2	53	47	25.4	32	103	10/10
C3-SP1	4843	3798	1554	2883	6611	5/5
C3-SP2	10459	9636	3498	5233	15423	9/9
wastewater	14933					2/2
stormwater	120	81	121	28	288	4/4

SD: standard deviation

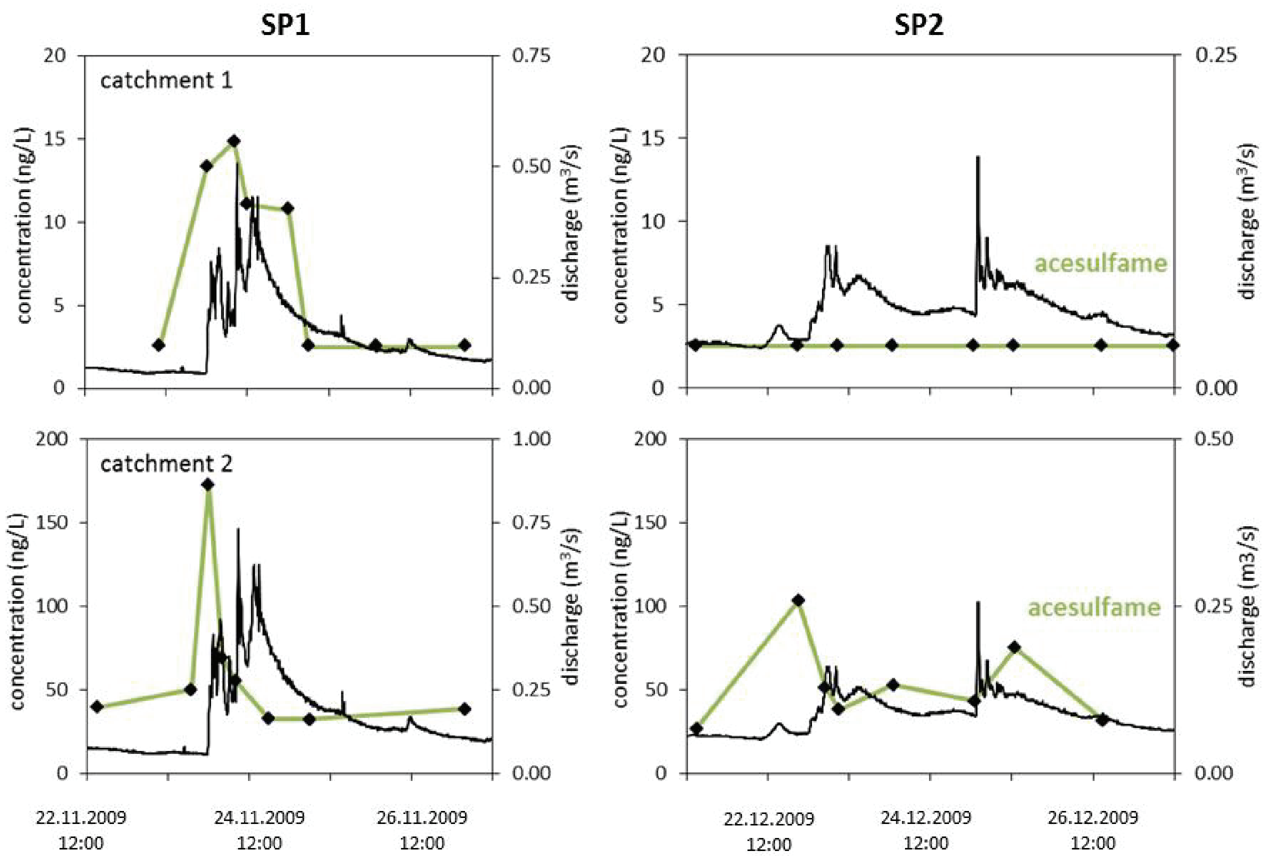

Figure S7: Acesulfame concentration dynamic for catchment 1 and 2 for both sampling periods.

Comment to the acesulfame results:

Although there seems to be concentration increase of acesulfame during rainfall in C1 and C2 this is very little in comparison to what is discharged from the WWTP. Especially C1 seems to have a considerable increase, but the total load is equivalent to emissions of only a few people. It is therefore reasonable to conclude that CSO 1 in catchment 1 was not active during sampling.

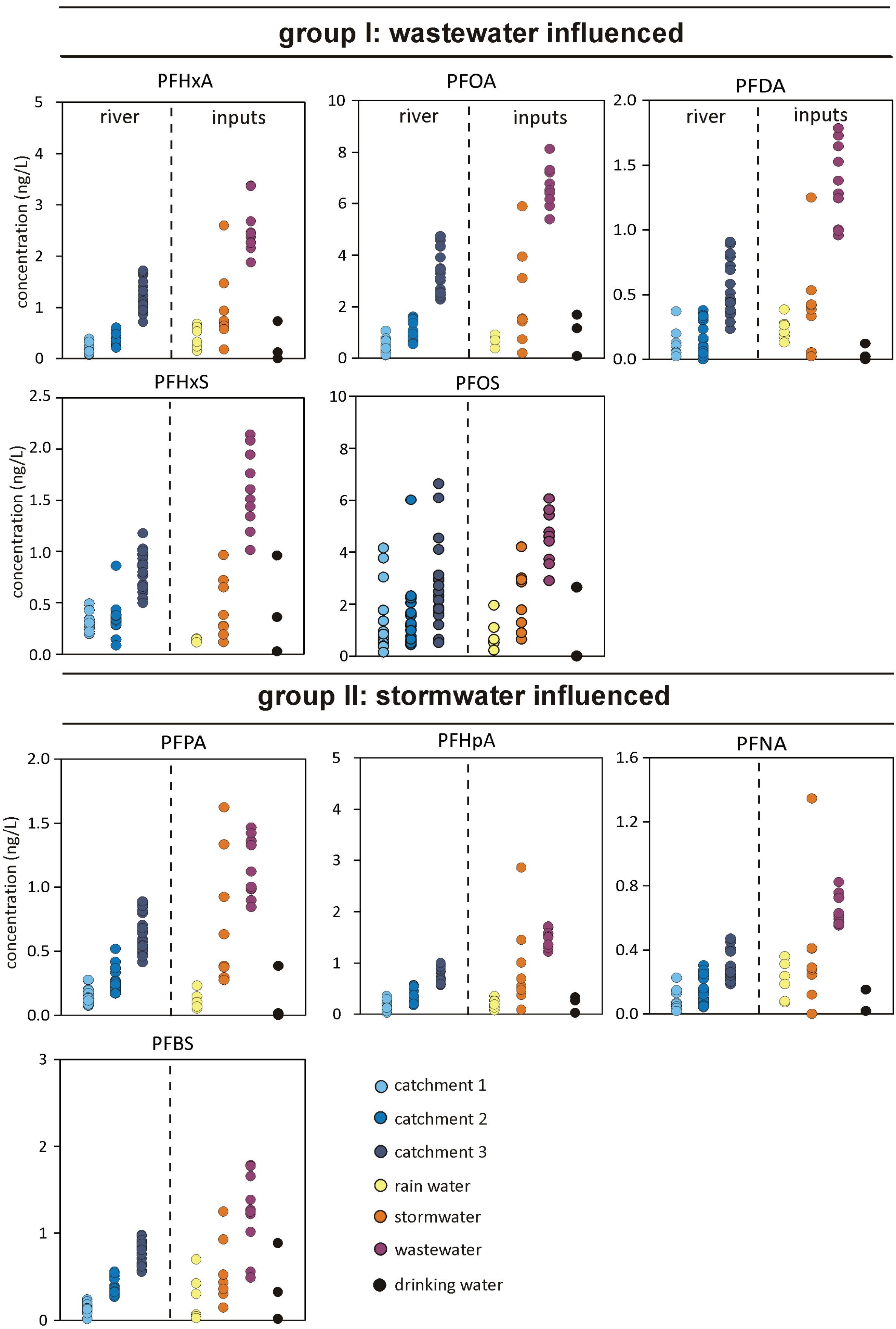

Figure S8: Concentrations of all measured samples for all PFAAs, from left to right: C1, C2, C3, rain, stormwater, wastewater effluent and drinking water. PFAAs were arranged in three groups, which have similar relative concentrations.

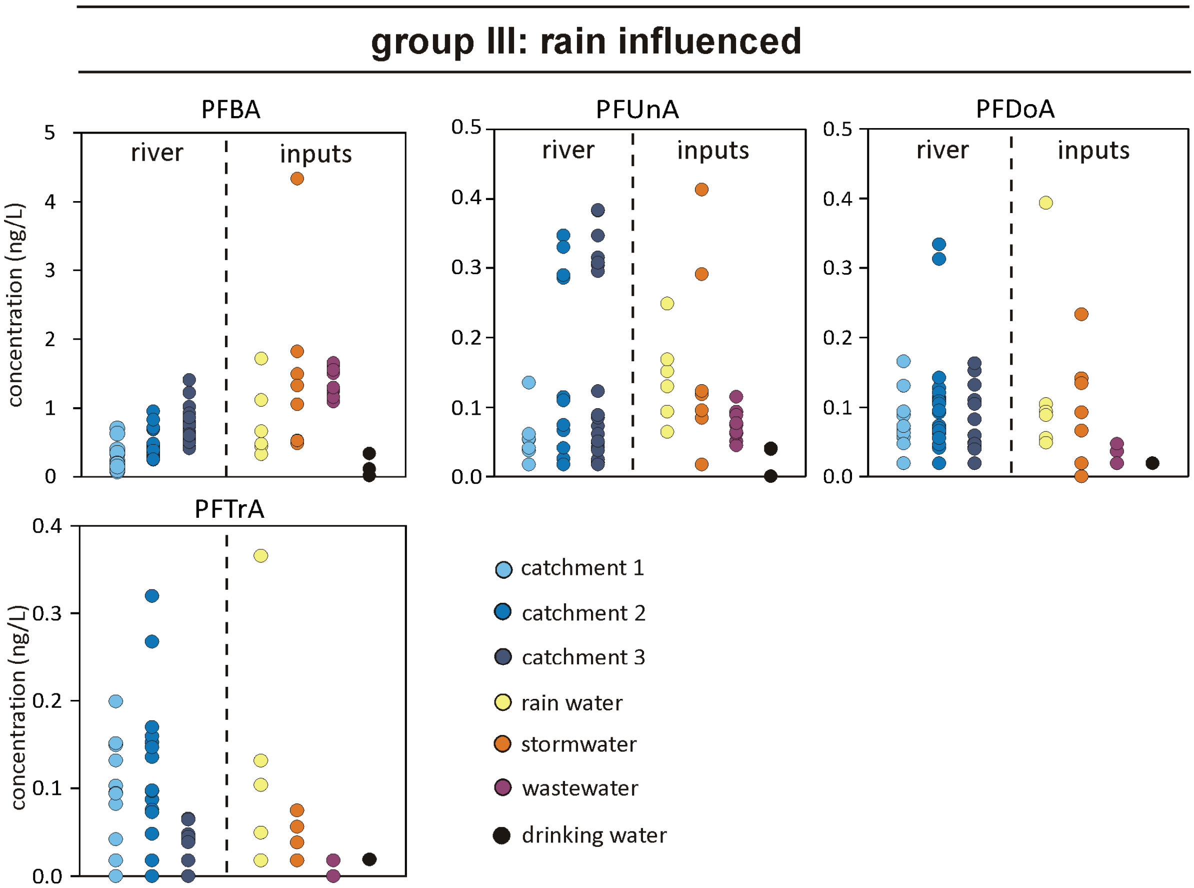

Figure S8 (continued)

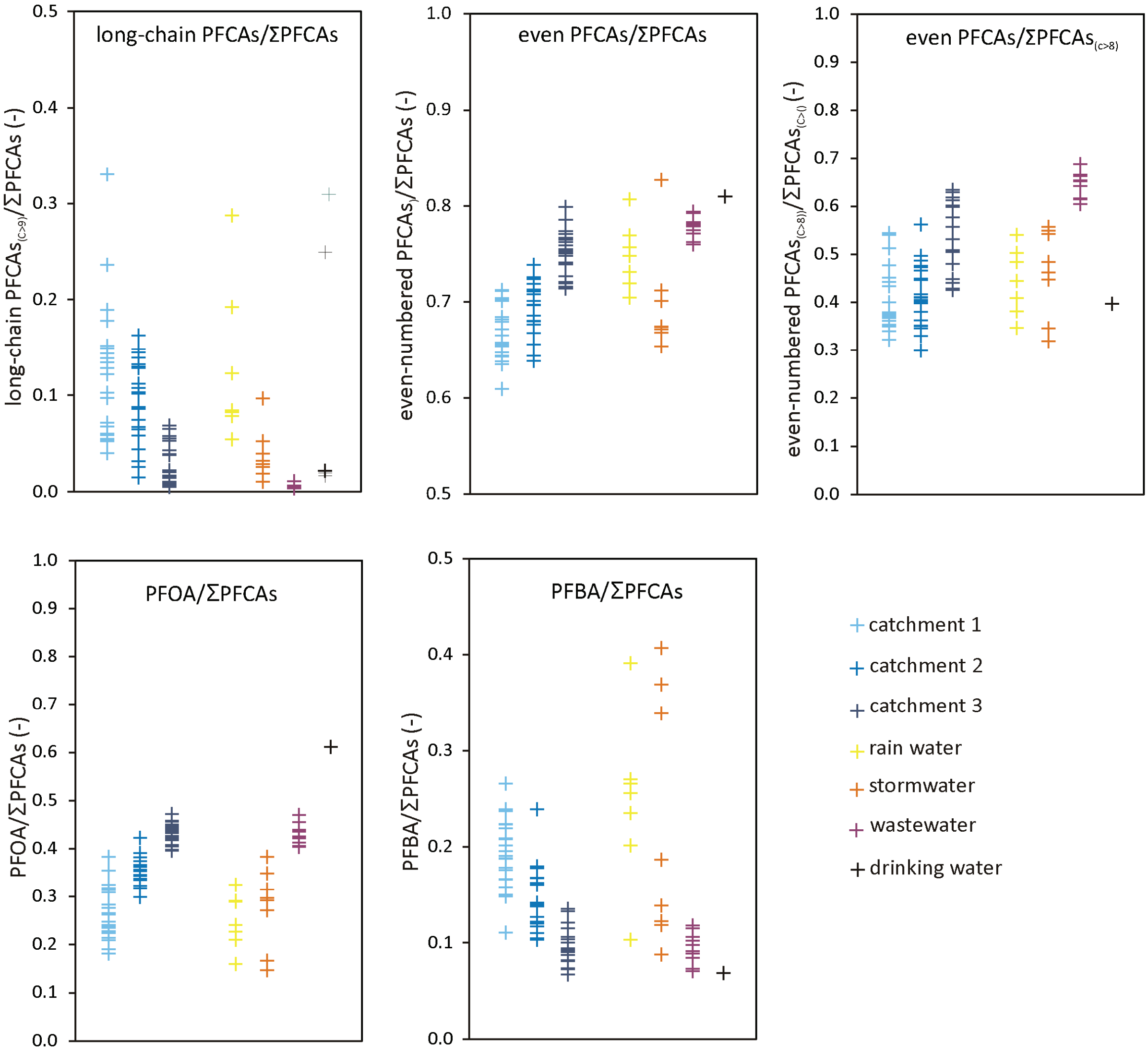

Figure S9: Relative composition of all analyzed samples.

2.3. MASS BALANCE RESULTS

Table S12: PFAA loads during rain event (sampling period 2) and during dry weather as well as the attributed sources to the rain loads.

	total loads$_{40h}$ (mg)									
	PFBA	**PFPA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFBS**	**PFHxS**	**PFOS**
					dry loads					
i. catchment 1	0.8 ± 0.2	0.6 ± 0.2	0.6 ± 0.2	0.5 ± 0.1	**1.0 ± 0.2**	0.13 ± 0.03	0.15 ± 0.04	0.8 ± 0.2	1.3 ± 0.3	1.7 ± 0.4
ii. catchment 2 (includes i)	3.6 ± 0.9	1.9 ± 0.5	2.3 ± 0.6	2.2 ± 0.6	**7.1 ± 1.8**	0.7 ± 0.2	0.5 ± 0.1	2.9 ± 0.7	2.3 ± 0.7	5.9 ± 1.5
iii. catchment 3 (includes ii/iv)	10 ± 2	9 ± 2	17 ± 4	12 ± 3	**45 ± 11**	5 ± 1	8 ± 2	11 ± 3	11 ± 3	29 ± 7
iv. wastewater	9 ± 2	6 ± 2	13 ± 4	8 ± 2	**33 ± 10**	4 ± 1	8 ± 2	7 ± 2	8 ± 2	28 ± 8
Sum ii + iv	12 ± 3	8 ± 2	15 ± 4	10 ± 3	**40 ± 11**	4.6 ± 1.3	9 ± 2	10 ± 3	11 ± 3	34 ± 10
					rain loads					
I. catchment 1	2.2 ± 0.2	0.9 ± 0.1	1.1 ± 0.1	0.9 ± 0.1	**2 ± 0**	0.49 ± 0.04	0.6 ± 0.1	0.2 ± 0.1	1.1 ± 0.1	2.7 ± 0.3
II. catchment 2 (includes I)	3 ± 0	2.2 ± 0.3	3 ± 0	2 ± 0	**7 ± 1**	1.2 ± 0.1	1.4 ± 0.1	2 ± 0	1.8 ± 0.2	5 ± 1
III. catchment 3 (includes II/IV/V)	13 ± 1	7 ± 1	15 ± 2	8 ± 1	**42 ± 5**	4 ± 1	9 ± 1	7 ± 1	6 ± 1	57 ± 5
IV. wastewater	7 ± 3	6 ± 2	14 ± 4	8 ± 2	**38 ± 11**	4 ± 1	9 ± 3	5 ± 2	2 ± 2	27 ± 9
V. CSO	1.2 ± 0.7	0.8 ± 0.5	2 ± 1	1.1 ± 0.6	**5 ± 3**	0.5 ± 0.3	1.1 ± 0.6	1.0 ± 0.5	1.0 ± 0.6	4 ± 2
Sum II + IV + V	12 ± 4	9 ± 3	19 ± 6	11 ± 3	**50 ± 14**	6 ± 2	11 ± 3	8 ± 3	5 ± 3	36 ± 12
diffuse loads (ii + II))	**29%**	**24%**	**16%**	**22%**	**15%**	**18%**	**10%**	**27%**	**27%**	**16%**
point loads (iv + IV + V)	**71%**	**76%**	**84%**	**78%**	**85%**	**82%**	**90%**	**73%**	**73%**	**84%**
	load per source$_{40h}$ (mg)									
	PFBA	**PFPA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFBS**	**PFHxS**	**PFOS**
					catchment 1: rural					
S1.1. rain	0.7 ± 0.2	0.10 ± 0.02	0.5 ± 0.1	0.3 ± 0.1	**1.6 ± 0.4**	0.3 ± 0.1	0.6 ± 0.1	0.17 ± 0.04	0.2 ± 0.1	0.6 ± 0.1
S2.1. 'stormwater mobilized' (I -S1.1)	1.5 ± 0.3	0.8 ± 0.1	0.6 ± 0.2	0.6 ± 0.1	**0.6 ± 0.4**	0.1 ± 0.1	0.03 ± 0.15	0.02 ± 0.07	0.9 ± 0.1	2.2 ± 0.3
					catchment 2: urban					
S1.2. rain	0.3 ± 0.3	0.0 ± 0.0	0.2 ± 0.2	0.1 ± 0.1	**1 ± 1**	0.1 ± 0.1	0.2 ± 0.2	0.1 ± 0.1	0.1 ± 0.1	0 ± 0
S2.2. 'stormwater mobilized' (II - I - S1.2)	0.9 ± 0.5	1.3 ± 0.3	1.8 ± 0.4	1.3 ± 0.3	**4 ± 1**	0.6 ± 0.2	0.6 ± 0.3	1.7 ± 0.3	0.7 ± 0.3	2 ± 1
					wastewater					
S1.3. rain	1.9 ± 0.3	0.27 ± 0.04	1.4 ± 0.2	0.7 ± 0.1	**4 ± 1**	1.0 ± 0.2	1.5 ± 0.3	0.5 ± 0.1	0.6 ± 0.1	1.6 ± 0.3
S2.3. 'stormwater mobilized' CS (IV+V-S1.3)	6 ± 3	7 ± 2	6 ± 5	8 ± 3	**39 ± 12**	4 ± 1	8 ± 3	6 ± 2	2 ± 2	30 ± 9
S3. indoor use (iv - S4)	8 ± 3	5 ± 2	12 ± 4	6 ± 2	**25 ± 11**	3.7 ± 1.2	8 ± 2	3 ± 2	6 ± 2	25 ± 8
S4. drinking water	0.8 ± 0.1	0.4 ± 0.1	1.1 ± 0.2	1.4 ± 0.2	**8 ± 1**	0.22 ± 0.03	0.15 ± 0.02	4.1 ± 0.6	2.4 ± 0.4	2.3 ± 0.4

CSO: combined sewer overflow; CS: combined sewers

Table S13: PFAA loads during rain event (sampling period 1) and during dry weather as well as the attributed sources to the rain loads with the scenario that additional PFAAs are generated during wastewater treatment. The parameters which are influence by this assumption are highlighted in blue.

	total loads$_{44h}$ (mg)									
	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS
average dry loads										
i. catchment 1	1.4 ±0.4	0.7 ±0.2	0.8 ±0.2	0.5 ±0.1	**1.6 ±0.4**	0.3 ±0.1	0.3 ±0.1	1.2 ±0.3	1.8 ±0.4	1.5 ±0.4
ii. catchment 2 (includes i)	3.6 ±0.9	2.4 ±0.6	3.1 ±0.8	2.9 ±0.7	**9 ±2**	1.1 ±0.3	0.9 ±0.2	4 ±1	3.6 ±0.9	14 ±3
iii. catchment 3 (includes ii/iv)	12 ±3	15 ±3	22 ±6	13 ±4	**61 ±16**	5 ±1	8 ±2	14 ±4	16 ±5	48 ±12
iv. wastewater	8 ±1	9 ±1	19 ±2	11 ±1	**49 ±11**	4.0 ±0.5	7 ±1	10 ±1	12 ±2	26 ±3
Sum ii + iv	12 ±2	12 ±2	23 ±3	14 ±2	**58 ±13**	5 ±1	8 ±1	14 ±2	16 ±2	40 ±7
rain loads										
I. catchment 1	7.3 ±0.5	3.8 ±0.3	5.0 ±0.3	4.7 ±0.3	**14 ±1**	2.5 ±0.2	2.4 ±0.2	3.8 ±0.3	6.6 ±0.5	26 ±2
II. catchment 2 (includes I)	14 ±1	8.1 ±0.6	12 ±1	14 ±1	**38 ±3**	6.1 ±0.5	7.5 ±0.6	13 ±1	8.8 ±0.7	37 ±3
III. catchment 3 (includes II/IV/V)	28 ±3	21 ±2	36 ±4	31 ±3	**123 ±11**	15 ±1	23 ±2	27 ±2	22 ±2	73 ±8
IV. wastewater	8 ±2	5 ±2	8 ±4	8 ±3	**36 ±6**	4 ±1	6 ±2	-3 ±1	8 ±2	22 ±7
V. CSO	3 ±1	3 ±1	5 ±1	4 ±1	**16 ±4**	1 ±0	2 ±1	1 ±0	4 ±1	8 ±2
Sum II + IV + V	25 ±4	16 ±3	26 ±6	26 ±5	**91 ±13**	11 ±2	16 ±3	12 ±3	20 ±4	68 ±13
total loads										
diffuse loads (ii + II))	**48%**	**37%**	**32%**	**41%**	**32%**	**45%**	**35%**	**67%**	**34%**	**47%**
point loads (iv + IV + V)	**52%**	**63%**	**68%**	**59%**	**68%**	**55%**	**65%**	**33%**	**66%**	**53%**

	load per source$_{44h}$ (mg)									
	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS
catchment 1: rural										
S1.1. rain	11 ±2	1.3 ±0.2	4.6 ±0.7	2.3 ±0.4	**9 ±1**	2.4 ±0.4	3.7 ±0.6	2.4 ±0.4	2.0 ±0.3	15 ±2
S2.1. 'stormwater mobilized' (I -S1.1)	-3.3 ±2.3	2.5 ±0.5	0.3 ±1.1	2.4 ±0.7	**5 ±2**	0.2 ±0.6	-1.3 ±0.8	1.3 ±0.7	4.6 ±0.8	11 ±4
catchment 2: urban										
S1.2. rain	4.5 ±1.3	0.6 ±0.2	2.0 ±0.6	1.0 ±0.3	**4 ±1**	1.0 ±0.3	1.6 ±0.5	1.0 ±0.3	0.9 ±0.2	6 ±2
S2.2. 'stormwater mobilized' (II - I - S1.2)	2.5 ±1.8	3.7 ±0.7	5.2 ±1.1	7.8 ±1.1	**21 ±3**	2.5 ±0.6	3.5 ±0.8	8.7 ±1.1	1.4 ±0.9	4 ±4
wastewater										
S1.3. rain	6 ±1	0.8 ±0.1	2.8 ±0.5	1.4 ±0.3	**5 ±1**	1.4 ±0.3	2.3 ±0.4	1.5 ±0.3	1.2 ±0.2	9 ±2
S2.3. 'stormwater mobilized' CS (IV+V-S1.3)	5 ±4	7 ±3	11 ±6	11 ±4	**47 ±11**	4 ±2	6 ±3	-3 ±2	10 ±4	22 ±11
S3. indoor use (iv - S4)	7 ±1	9 ±1	18 ±3	10 ±2	**39 ±12**	4 ±1	7 ±1	5 ±2	9 ±2	23 ±4
S4. drinking water	0.9 ±0.1	0.4 ±0.1	1.4 ±0.2	1.7 ±0.3	**10 ±2**	0.26 ±0.04	0.18 ±0.03	4.9 ±0.8	2.9 ±0.4	2.8 ±0.4

CSO: combined sewer overflow; CS: combined sewers

3. Supporting References

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(3) Higgins, C. P.; Luthy, R. G., Sorption of perfluorinated surfactants on sediments. *Environ. Sci. Technol.* **2006,** *40*, (23), 7251-7256.