Supporting Information

Determination of polar organic micropollutants in surface and pore water by high-resolution sampling-direct injection-ultra high performance liquid chromatography-tandem mass spectrometry

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1. Sediment properties

Table S1. Sediment porosity determined in 8 cm long sub-cores of the 40 cm long sediment core taken directly at the HPW sampling location after the sampling event in June 2016.

Depth (cm)	Porosity
0-8	0.69
8-16	0.50
16-24	0.45
24-32	0.41
32-40	0.39

Table S2. Sediment grain size distribution measured from 1.667 kg of streambed sediment taken directly adjacent to the HPW sampling location after the sampling event in June 2016.

Mesh size (mm)	Weight (g)	Share (%)
6.3	11.1	0.67
2	75.9	4.55
1	125.2	7.51
0.63	165.6	9.93
0.18	1207.5	72.43
0.063	74.6	4.47
0.02	5.6	0.34
<0,02	1.1	0.07

2. *Vertical seepage flux in the hyporheic zone during pore water sampling*

Time series of vertical seepage fluxes (m d^{-1}) in the hyporheic zone were calculated from measured temperature depth profiles using the method proposed by McCallum et al.[1] (Figures S1). Median (inter quartile range) pore water velocities during the sampling period were determined to be 7.5 (0.7) cm h^{-1} during the June and 4.3 (0.4) cm h^{-1} during the April experiment, respectively. Note that the McCallum method provides Darcy fluxes. To obtain pore water velocities, Darcy velocities were divided by sediment porosity (0.4±0.1).

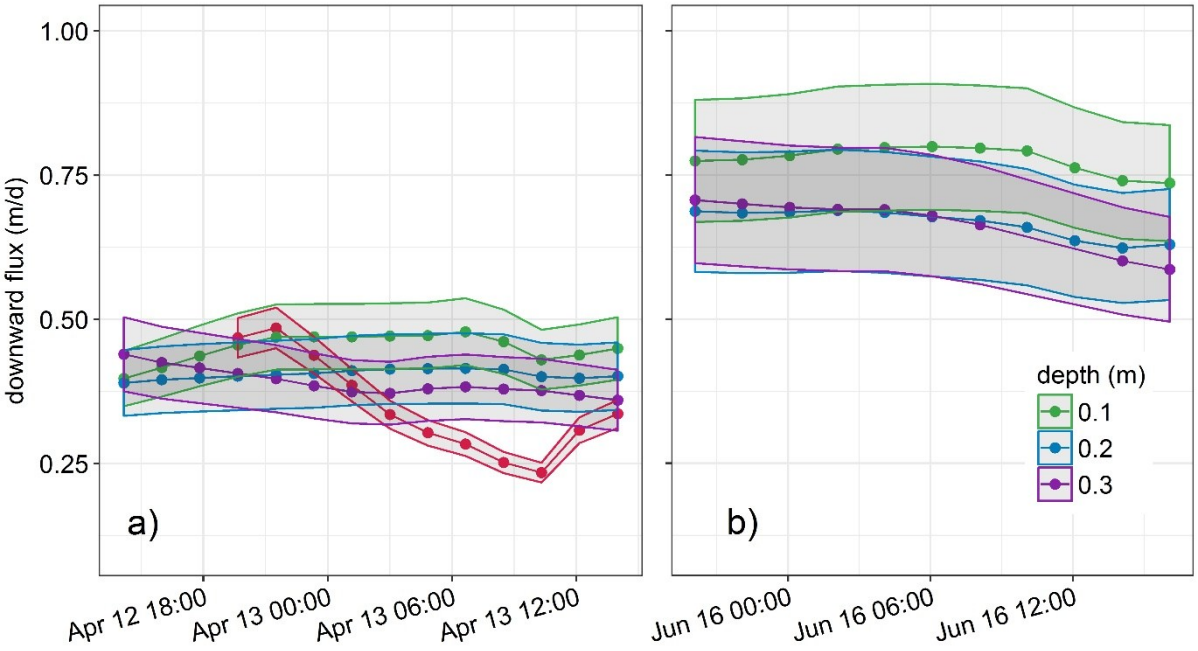

Figure S1. Time series of vertical seepage fluxes (m d^{-1}) in the hyporheic zone during the minipoint sampling period in April (a) and June (b) 2016 calculated from measured temperature depth profiles. Note that vertical seepage fluxes shown are Darcy fluxes. To obtain porewater velocities, vertical seepage fluxes were divided by sediment porosity (0.4±0.1).

3. *Temporal and spatial resolution of the modified minipoint sampler*

The temporal resolution of the modified minipoint sampler is a function of the pore water velocity (cm/h) in the hyporheic zone, sediment porosity and extracted sample volume. Assuming that the hyporheic sediment around the sampling ports of the minipoint is homogeneous and water flows to filter screened section of the minipoint from all directions, the radius (r, cm) of influence and around the sampling ports of the minipoint and thus the spatial resolution of the sampling method can conservatively be approximated via:

$$r = \left(\frac{vol.\ 3}{n\ \ 4\pi}\right)^{1/3} \quad (1)$$

in which *vol.* equals the extracted pore water volume (cm^3) and *n* the sediment porosity (Figure S2). Given a certain extracted pore water volume and sediment porosity, the minimum sampling interval (h) is determined by the residence time of pore water in the sphere of influence and hence by the pore water velocity (u, cm h^{-1}). The minimum sampling interval, i.e. the temporal resolution of the minipoint sampler, is therefore given by:

$$sampling\ interval > \frac{2r}{u} \quad (2)$$

Under the conditions found in the present study (porosity 0.4 ± 0.1, pore water velocity 7.5 and 4.3 cm h^{-1} during the June and April experiment, respectively, and extracted pore water volume of ≈ 13 ± 0.5 mL), the minimum sampling interval was determined be 30 min in the June experiment and 50 min in the April experiment.

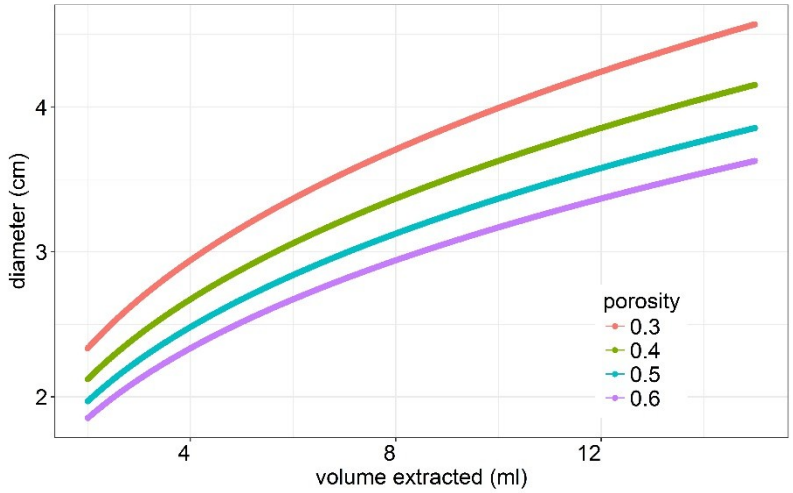

Figure S2. Diameter of a hypothetical sphere of influence in saturated porous media, as a function of extracted pore water (cm^3) and different sediment porosities typically encountered in the hyporheic zone.

4. Determination of theoretical load of metformin based on human consumption

A calculation of theoretical loads from consumption numbers of metformin was compared to loads of metformin and guanylurea calculated from the concentration time series to test whether the high concentrations of guanylurea measured in the surface water (SW) in April (in a series of 48 hourly samples) are sensible. Discharge at the sampling site was determined by Q-h rating curves, using a handhold electromagnetic current meter (MF pro, OTT Hydromet, Kempten, Germany) and a water level logger (CTD-Diver, VanEssen Instruments, Delft, the Netherlands). Hourly discharge was multiplied with the respective concentrations and summed up resulting in average loads of 0.2 mol d^{-1} metformin and 54.7 mol d^{-1} guanylurea. The river was composed by EW to 82% downstream of the outfall and metformin and guanylurea were not detected above LOQ in upstream surface water (USW). That is why the contribution of USW to the loads is neglected in this calculation. Following formula was used to calculate theoretical average daily loads (metformin and guanylurea combined) from the WWTP in 2016 (L_{WWTP}):

$$L_{WWTP} = \frac{P * D * n_{WWTP}}{365 * n} * f_{excr} * f_{rec}$$

It was assumed that the average consumption of metformin by inhabitants contributing to the WWTP (n_{WWTP}) resembles the average consumption by people insured in a German statutory health insurance (86% of the population). The annual amount of consumption was derived from the number of daily doses of metformin prescribed by German statuary health insurances in 2016 (*P*), the number of members in 2016 (*n*) and the defined daily dose of pure metformin (*D*). The daily average discharge of the WWTP during the sampling period (Q_{WWTP}, data provided by the WWTP facility) was divided by the population equivalent of waste water volume (Q_{PE}) to obtain an estimation of n_{WWTP} in this time. The portion of consumed metformin that exits the body unchanged is included as f_{excr} , while the molar portion of metformin, that passes the WWTP unchanged or is transformed into guanylurea is expressed as f_{rec}. As some values for the required parameters are reported in wide ranges in literature, a maximum and minimum value of L_{WWTP} was calculated to account for uncertainties.

Table S3. Values and respective sources used for calculation of the theoretical loads of metformin and guanylurea combined released by WWTP Münchehofe (L_{WWTP}). To account for differences of reported values, a minimum and maximum L_{WWTP} was calculated.

Parameter	Values minimum calculation		Values maximum calculation	
P [DDD]	595,100,000	[2]	595,100,000	[2]
n	71,404,631	[3]	71,404,631	[3]
D [g DDD^{-1}]	1.56	[4]	2.00	[5]
Q_{PE} [L d^{-1}]	193	[6]	167	[7]
Q_{WWTP} [L d^{-1}]	33,110,381	WWTP Münchehofe	33,110,381	WWTP Münchehofe
n_{WWTP}	170984		198,242	
f_{excr}	77%	[4]	100%	[4]
f_{rec}	30%	[8]	84%	[9]
L_{WWTP} [mol d^{-1}]	**10.9**		**58.9**	

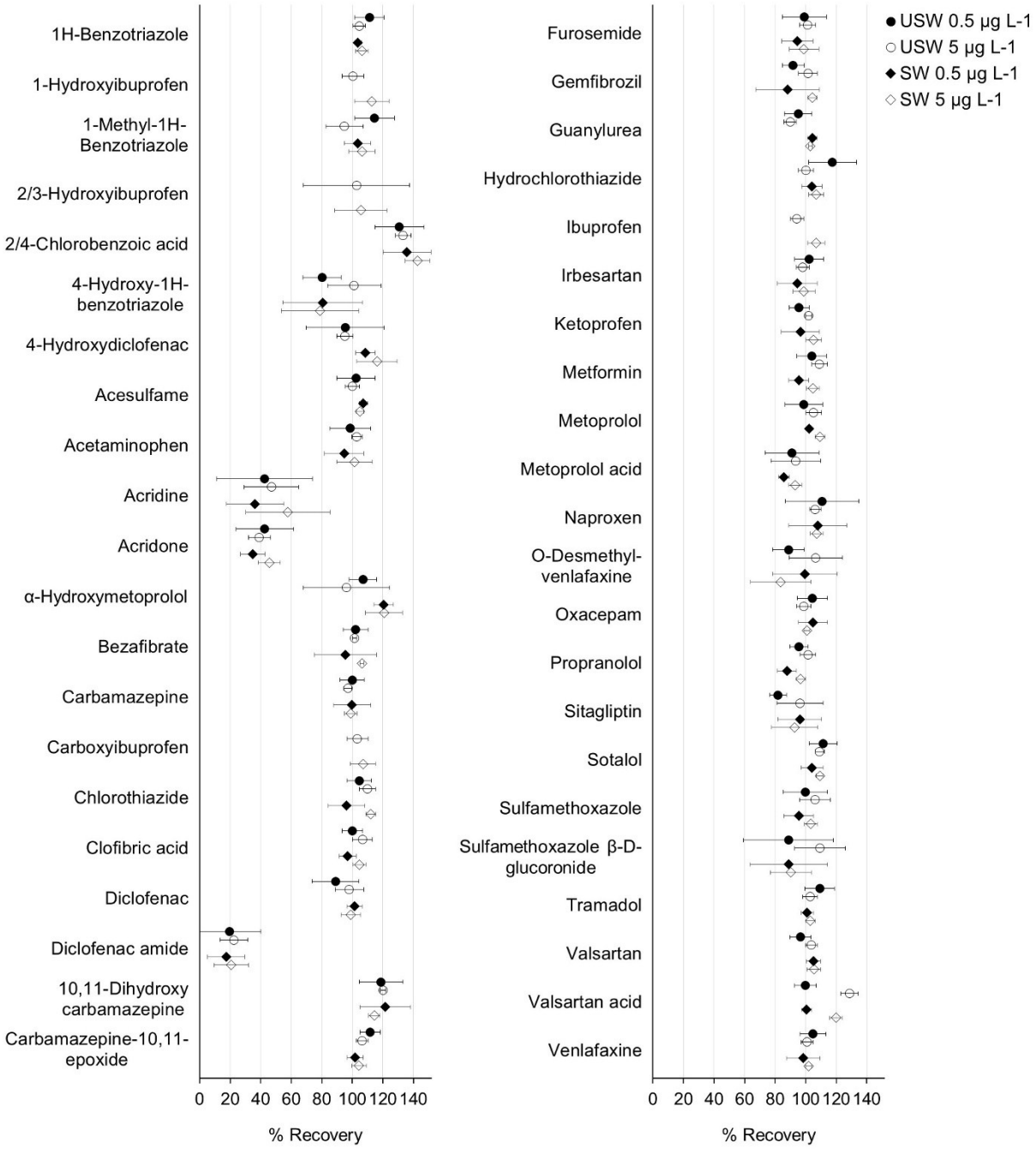

Figure S3. Results from spike recovery experiments with Erpe surface water (SW) and up-stream water (USW). Averages of % recovery in SW are displayed as diamonds and in USW as circles; error bars show % RSD. Black markers show results from the low-spike level white markers the high-spike level.

Table S4. Summary of parent compounds and transformation products (TPs) included in this study, their therapeutic class, log K_{ow} values and CAS numbers.

Chemical	Therapeutic class	Log K_{ow}[a]	CAS
Acesulfame	artificial sweetener	-0.55	55589-62-3
Acetaminophen	analgesic	0.91	103-90-3
1H-Benzotriazole	corrosion inhibitor	1.3	95-14-7
4-Hydroxy-1H-benzotriazole	TP	1	26725-51-9
Bezafibrate	lipid regulator	3.99	41859-67-0
2/4-Chlorobenzoic acid	TP	2.23	118-91-2/74-11-3
Carbamazepine	anticonvulsant	2.8	298-46-4
Carbamazepine-10,11-Epoxide	TP	2	36507-30-9
10,11-Dihydroxy carbamazepine	TP	1.41	58955-93-4
Acridine	TP	3.51	260-94-6
Acridone	TP	4.2	578-95-0
Clofibric acid	lipid regulator	2.9	882-09-7
Diclofenac	NSAID analgesic	4.3	15307-86-5
4-Hydroxydiclofenac	TP	4	64118-84-9
Diclofenac amide	TP	3.8	15362-40-0
Furosemide	diuretic	1.8	54-31-9
Gemfibrozil	lipid regulator	4.39	25812-30-0
Hydrochlorothiazide	diuretic	-0.58	58-93-5
Chlorothiazide	TP (diuretic)	-0.44	58-94-6
Ibuprofen	NSAID analgesic	3.8	15687-27-1
Carboxyibuprofen	TP	2.8	15935-54-3
1-Hydroxyibuprofen	TP	2.69	53949-53-4
2/3-Hydroxyibuprofen	TP	2.4 /2.37	51146-55-5/53949-54-5
Irbesartan	Angiotensin II receptor antagonists	5.39	138402-11-6
Ketoprofen	NSAID analgesic	3.6	22071-15-4
Metformin	antihyperglycemic agent	-0.92	657-24-9
Guanylurea	TP	-2.03	141-83-3
1-Methyl-1H-benzotriazole	corrosion inhibitor	1.42	13351-73-0
Metoprolol	β-blocker	1.8	37350-58-6
α-Hydroxymetoprolol	TP	0.84	56392-16-6
Metoprolol acid	TP	-1.2	56392-14-4
Naproxen	NSAID analgesic	3	22204-53-1
Oxazepam	antianxiety	2.92	604-75-1
Propranolol	β-blocker	2.6	525-66-6
Sitagliptin	antihyperglycemic agent	1.26	486460-32-6
Sotalol	β-blocker	-0.4	3930-20-9
Sulfamethoxazole	antibiotic	0.79	723-46-6
Sulfamethoxazole β-D-glucuronide	TP	-1.3	14365-52-7
Tramadol	opioid analgesic	2.45	27203-92-5
Valsartan	Angiotensin II receptor antagonists	4.59	137862-53-4
Valsartan cid	TP	3.18	164265-78-5
Venlafaxine	antidepressant	2.74	93413-69-5
O-Desmethylvenlafaxine	TP	2.29	93413-62-8

[a] K_{ow} values were obtained from the online platform Chemicalize (https://chemicalize.com/)

Table S5. Summary of selected method parameters: retention time (RT), electrospray ionization mode (ESI), precursor (Pre.), quantitative (Quan.) and qualitative (Qual.) product ions (m/z) and the internal standards used for quantification.

Chemical	RT	ESI	Pre.	Quan.	Qual.	Internal standard
Acesulfame	1.9	-	162.1	82.1	78.0	Acesulfame-d4
Acetaminophen	2.35	+	152.0	65.2	65.2	Acetaminophen-d4
1H-Benzotriazole	3.29	+	120.1	65.2	39.3	1H-benzotriazole-d4
4-Hydroxy-1H-benzotriazole	2.7	+	136.0	53.2	80.1	1H-benzotriazole-d4
Bezafibrate	5.41	+	362.0	316.0	139.0	Bezafibrate-d4
2/4-Chlorobenzoic acid	4.97	-	155.1	111.0	35.3	Bezafibrate-d4
Carbamazepine	4.87	+	237.1	194.1	179.1	Carbamazepine-d8
Carbamazepine-10,11-Epoxide	4.3	+	253.2	180.1	182.1	Carbamazepine-d8
10,11-Dihydroxy carbamazepine	4.11	+	271.1	180.1	210.1	Carbamazepine-d8
Acridine	4.29	+	180.1	152.1	128.1	Carbamazepine-d8
Acridone	4.64	+	196.1	167.1	178.1	Carbamazepine-d8
Clofibric acid	5.34	-	213.1	127.0	35.2	Clofibric acid-d4
Diclofenac	5.78	-	293.9	249.9	213.9	Diclofenac-13C6
4-Hydroxydiclofenac	5.26	-	312.1	230.0	265.8	Diclofenac-13C6
Diclofenac amide	5.44	+	278.0	214.0	208.1	Diclofenac-13C6
Furosemide	4.39	-	329.0	204.9	284.9	Furosemide-d5
Gemfibrozil	6.09	-	249.1	121.1	106.1	Gemfibrozil-d6
Hydrochlorothiazide	2.25	-	296.0	268.9	205.0	Hydrochlorothiazide-C13d2
Chlorothiazide	2.17	-	294.0	213.9	179.0	Hydrochlorothiazide-C13d2
Ibuprofen	5.85	-	205.2	161.0		Ibuprofen-d3
Carboxyibuprofen	4.8	-	235.1	73.1	190.9	Carboxyibuprofen-d3
1-Hydroxyibuprofen	4.99	-	221.1	159.1		Ibuprofen-d3
2/3-Hydroxyibuprofen	4.83	-	221.1	177.0		Ibuprofen-d3
Irbesartan	5.48	-	427.2	193.1	399.1	Irbesartan-d6
Ketoprofen	5.24	+	255.1	209.1	77.1	Ketoprofen-13Cd3
Metformin	0.56	+	130.1	71.2	68.1	Metformin-d6
Guanylurea	0.49	+	103.1	60.2		Guanylurea-15N4
1-Methyl-1H-benzotriazole	3.59	+	134.1	77.1	51.2	1H-benzotriazole-d4
Metoprolol	3.11	+	268.2	133.1	77.1	Metoprolol-d7
α-Hydroxymetoprolol	2.4	+	284.2	105.1	91.1	Metoprolol acid-d5
Metoprolol acid	2.5	+	268.1	191.0	145.1	Metoprolol acid-d5
Naproxen	5.35	+	231.2	170.1	153.1	Naproxen-d3
Oxazepam	5.1	+	287.1	241.0	104.1	Oxazepam-d5
Propranolol	3.79	+	260.2	116.2	155.1	Propranolol-d7
Sitagliptin	4.2	+	408.0	174.0	193.0	Venlafaxine-d6
Sotalol	1.75	+	273.1	133.1	213.0	Sotalol-d6
Sulfamethoxazole	3.26	+	254.0	92.1	108.1	Sulfamethoxazole-d4
Sulfamethoxazole β-D-glucuronide	2.84	+	430.1	156.0	92.1	Sulfamethoxazole-d4
Tramadol	3.09	+	264.2	58.2	72.3	Tramadol-d6
Valsartan	5.53	-	434.3	350.1	179.1	Valsartan-d3
Valsartan cid	4.46	-	265.1	165.1	193.1	Valsartan-d3
Venlafaxine	3.68	+	278.2	58.2	121.1	Venlafaxine-d6
O-Desmethylvenlafaxine	2.99	+	264.2	58.2	246.1	Venlafaxine-d6

Table S6. Fortification levels used for spike/recovery experiments, and calibration curve parameters (weighting, correlation coefficient, dynamic range).

Target	Spike/recovery experiment		Calibration curve			Instrumental precision	
	Low spike (µg L^{-1})	**High spike (µg L^{-1})**	**Weight**	**r^2**	**Concentration range (µg L^{-1})**	**Intra-day (%RSD)**	**Inter-day (%RSD)**
10,11-Dihydroxy carbamazepine	0.54	5.36	1/X	0.9989	0.21-11.08	4.61	6.13
1H-Benzotriazole	1.00	9.95	1/X	0.9998	0.04-20.56	2.69	2.74
1-Hydroxyibuprofen	0.50	4.95	1/X	0.9972	0.2-10.23	19.94	12.24
1-Methyl-1H-Benzotriazole	0.98	9.77	1/X	0.9967	0.04-20.18	4.43	6.06
2/3-Hydroxyibuprofen	0.99	9.91	1/X	0.9923	0.39-20.48	14.38	15.08
2/4-Chlorobenzoic acid	1.06	10.56	1/X	0.9984	0.04-21.81	7.73	9.07
4-Hydroxy-1H-benzotriazole	0.51	5.12	1/X	0.9936	0.05-10.57	13.75	13.95
4-Hydroxydiclofenac	0.13	1.25	1/X	0.9939	0.05-2.59	7.64	16.47
Acesulfame	0.95	9.50	1/X	0.9951	0.04-19.63	3.48	2.00
Acetaminophen	0.50	5.03	1/X	0.9973	0.02-10.39	4.75	5.61
Acridine	0.61	6.12	1/X	0.9973	0.06-12.65	3.07	1.86
Acridone	0.43	4.31	1/X	0.9991	0.02-8.89	4.73	5.69
Bezafibrate	0.52	5.23	1/X	0.9980	0.02-10.81	3.59	2.86
Carbamazepine	0.49	4.93	1/X	0.9920	0.02-10.18	2.72	6.64
Carbamazepine-10,11-epoxide	0.51	5.05	1/X^2	0.9923	0.02-10.44	6.14	7.11
Carboxyibuprofen	0.51	5.15	1/X	0.9956	0.52-26.61	19.76	10.82
Chlorothiazide	0.52	5.21	1/X	0.9986	0.02-10.75	6.24	17.92
Clofibric acid	0.52	5.18	1/X	0.9979	0.05-10.71	1.46	5.07
Diclofenac	0.51	5.05	1/X	0.9987	0.05-10.44	11.03	5.97
Diclofenac amide	0.55	5.52	none	0.9985	0.02-11.4	2.34	5.24
Furosemide	0.50	4.97	1/X	0.9985	0.05-10.27	8.35	5.93
Gemfibrozil	0.51	5.11	1/X	0.9973	0.05-10.56	2.83	7.40
Guanylurea	0.51	5.12	1/X	0.9999	0.2-208.45	1.13	1.49
Hydrochlorothiazide	0.50	5.03	1/X	0.9973	0.02-10.39	5.02	5.70
Ibuprofen	0.52	5.18	1/X	0.9966	0.52-10.7	24.03	12.32
Irbesartan	0.99	9.89	1/X	0.9977	0.04-20.43	2.42	2.73
Ketoprofen	0.50	4.97	1/X	0.9993	0.02-10.28	1.77	3.07
Metformin	0.51	5.13	1/X	0.9909	0.05-10.6	3.10	3.71
Metoprolol	0.51	5.05	1/X	0.9987	0.02-26.11	5.81	4.20
Metoprolol acid	0.51	5.13	1/X	0.9965	0.02-10.6	3.33	5.28
Naproxen	0.51	5.05	1/X	0.9979	0.2-10.44	12.87	11.09
O-Desmethylvenlafaxine	0.50	4.99	1/X	0.9937	0.02-10.31	4.85	4.83
Oxazepam	0.52	5.21	1/X	0.9995	0.02-10.76	5.35	1.72
Propranolol	0.49	4.89	1/X	0.9994	0.02-10.1	5.23	6.50
Sitagliptin	0.50	5.03	1/X	0.9983	0.02-10.39	2.69	9.94
Sotalol	0.50	4.99	1/X	0.9994	0.02-25.81	4.45	7.36
Sulfamethoxazole	0.50	5.00	1/X	0.9997	0.02-10.32	5.22	2.65
Sulfamethoxazole β-D-glucuronide	0.50	5.02	1/X	0.9975	0.2-10.36	3.22	15.71
Tramadol	0.50	4.98	1/X	0.9993	0.02-10.28	2.48	2.26
Valsartan	0.99	9.92	1/X	0.9992	0.04-51.24	4.85	11.43
Valsartan acid	0.50	4.96	none	0.9999	0.2-25.61	9.66	7.86
Venlafaxine	0.49	4.86	1/X	0.9995	0.02-10.03	2.03	3.28
α-Hydroxymetoprolol	0.52	5.18	1/X	0.9874	0.05-10.71	3.61	18.27

Table S7. Results from spike recovery experiments with Erpe SW and USW at spike levels 0.5 and 5 μg L^{-1}. Mean % recovery (N=5) and respective % RSDs are displayed.

	SW 0.5	% RSD	SW 5	% RSD	USW 0.5	% RSD	USW 5	% RSD
10,11-Dihydroxy carbamazepine	121.6	16.5	114.4	3.5	118.9	14.2	120.2	1.8
1H-Benzotriazole	103.7	2.4	106.3	4.1	111.2	9.7	104.5	4.0
1-Hydroxyibuprofen	133.4	34.5	112.8	11.2	103.6	24.5	100.4	7.0
1-Methyl-1H-Benzotriazole	103.4	8.6	106.3	8.5	114.7	13.1	94.9	12.2
2/3-Hydroxyibuprofen	132.9	31.5	105.6	17.1	122.2	20.3	102.7	34.8
2/4-Chlorobenzoic acid	135.9	15.8	142.8	8.0	130.9	16.1	133.4	5.1
4-Hydroxy-1H-benzotriazole	80.6	26.1	79.0	25.4	80.2	12.5	101.3	17.4
4-Hydroxydiclofenac	108.5	6.5	116.2	13.2	95.3	25.6	95.2	5.2
Acesulfame	107.2	2.7	105.1	2.5	102.4	12.6	100.0	4.6
Acetaminophen	94.6	13.0	101.6	11.7	98.6	13.4	103.0	3.3
Acridine	36.3	18.8	57.9	27.6	42.5	31.3	47.0	17.7
Acridone	34.7	8.1	45.6	7.3	42.6	18.9	39.2	7.2
Bezafibrate	95.5	20.4	106.3	1.3	102.3	8.1	101.4	1.4
Carbamazepine	99.8	12.2	98.9	4.2	99.9	7.8	97.1	2.6
Carbamazepine-10,11-epoxide	102.0	5.3	104.4	4.7	111.8	6.7	106.4	3.9
Carboxyibuprofen	49.3	57.6	107.0	8.2	83.6	14.2	103.4	6.8
Chlorothiazide	96.2	11.9	112.1	3.2	104.5	7.9	109.9	5.3
Clofibric acid	97.0	5.6	104.7	4.2	100.2	6.7	106.6	6.5
Diclofenac	101.6	4.9	98.9	6.4	89.0	15.3	98.1	9.2
Diclofenac amide	17.4	12.3	20.6	11.4	19.6	20.3	22.5	9.2
Furosemide	94.5	10.2	99.0	9.8	99.2	14.4	101.4	5.3
Gemfibrozil	88.2	20.7	104.4	2.8	91.8	7.2	101.5	6.3
Guanylurea	104.3	3.1	103.1	1.2	95.2	9.0	89.9	4.0
Hydrochlorothiazide	104.2	6.7	106.8	4.9	117.5	15.7	100.2	4.8
Ibuprofen	84.1	54.5	106.8	5.7	133.2	31.2	94.4	4.3
Irbesartan	94.4	13.1	98.9	7.3	102.4	9.5	98.0	4.2
Ketoprofen	96.5	12.4	105.3	5.2	95.8	6.5	101.9	2.2
Metformin	95.5	6.4	104.8	4.2	104.0	9.7	109.2	5.2
Metoprolol	102.2	1.7	109.3	3.3	98.8	12.5	105.2	5.1
Metoprolol acid	85.7	3.6	93.2	4.1	91.0	17.6	93.6	16.3
Naproxen	108.0	19.1	107.3	4.4	110.8	24.0	106.3	3.6
O-Desmethylvenlafaxine	99.5	21.2	83.7	19.6	88.8	10.4	106.6	17.5
Oxazepam	104.8	9.6	100.8	1.9	104.6	9.9	98.8	4.5
Propranolol	87.8	6.2	96.8	3.0	95.6	6.1	101.5	5.1
Sitagliptin	96.2	14.3	92.8	15.1	82.0	5.4	96.3	15.3
Sotalol	104.2	7.3	109.2	2.3	111.5	9.2	109.1	3.0
Sulfamethoxazole	95.5	9.6	103.3	4.3	100.0	14.5	106.1	10.0
Sulfamethoxazole β-D-glucuronide	88.9	25.4	90.4	13.5	88.8	29.5	109.4	16.6
Tramadol	101.0	4.1	103.2	3.1	109.3	9.7	103.0	4.7
Valsartan	105.1	4.5	105.3	4.3	96.5	6.7	103.8	3.9
Valsartan acid	100.5	3.2	119.9	4.1	99.8	7.1	128.7	5.7
Venlafaxine	98.4	10.8	102.0	2.2	104.7	8.6	100.9	4.0
α-Hydroxymetoprolol	120.5	6.3	120.8	12.2	107.0	9.0	96.2	28.2

Table S8. Results from spike recovery experiments with MQ, TW and HPW at spike levels 0.5 and 5 µg L^{-1}. Mean % recovery (N=5; HPW: N=3) and respective % RSDs are displayed.

	MQ 0.5	% RSD	MQ 5	% RSD	TW 0.5	% RSD	TW 5	% RSD	HPW 0.5	% RSD
10,11-Dihydroxy carbamazepine	116.3	10.4	109.0	15.5	126.5	10.0	124.0	3.5	131.4	19.0
1H-Benzotriazole	107.9	9.0	109.8	3.8	119.1	8.4	104.5	4.8	102.7	6.6
1-Hydroxyibuprofen	282.0	46.7	364.3	24.3	159.3	36.0	140.1	7.7	141.9	19.2
1-Methyl-1H-Benzotriazole	107.0	12.0	107.0	9.5	112.4	28.4	102.8	9.4	112.5	14.9
2/3-Hydroxyibuprofen	405.0	46.2	388.5	24.2	153.4	27.2	119.3	13.0	104.2	41.3
2/4-Chlorobenzoic acid	184.1	15.8	201.6	11.4	145.9	10.7	180.5	46.0	145.9	18.6
4-Hydroxy-1H-benzotriazole	91.6	40.3	135.5	69.8	73.3	29.4	73.6	34.9	83.6	25.4
4-Hydroxydiclofenac	n.d. [a]	n.d.	73.1	64.0	133.4	14.2	86.2	8.8	65.8	29.2
Acesulfame	101.8	8.1	108.5	3.2	105.2	6.2	102.8	2.5	94.9	6.2
Acetaminophen	102.0	9.7	107.8	4.0	113.7	6.2	108.0	2.4	106.4	4.0
Acridine	56.6	13.2	82.1	16.1	32.5	30.6	39.9	33.4	37.2	29.2
Acridone	34.7	9.3	41.9	12.0	34.5	19.6	36.5	3.7	40.8	7.1
Bezafibrate	99.2	9.7	106.7	6.8	108.2	13.5	108.6	2.2	106.1	5.1
Carbamazepine	99.6	8.6	101.0	11.4	112.4	6.8	99.3	5.5	86.1	46.2
Carbamazepine-10,11-epoxide	114.0	16.5	108.3	18.7	94.7	31.9	95.2	29.9	104.6	7.4
Carboxyibuprofen	74.0	30.8	128.8	20.2	124.2	58.3	108.0	9.1	58.5	0.7
Chlorothiazide	106.6	10.0	114.7	2.3	113.0	6.8	111.9	8.0	91.9	17.0
Clofibric acid	95.0	18.2	108.8	6.9	113.1	4.6	108.0	4.0	85.3	14.9
Diclofenac	n.d.	n.d.	n.d.	n.d.	107.2	6.9	99.6	5.9	n.d.	n.d.
Diclofenac amide	n.d.	n.d.	n.d.	n.d.	33.3	36.2	20.5	9.9	22.9	5.2
Furosemide	91.4	14.3	102.1	7.0	106.9	14.3	105.7	10.0	115.5	8.9
Gemfibrozil	103.7	22.9	91.9	15.8	97.0	11.0	108.8	5.9	98.1	16.3
Guanylurea	6.2	43.7	82.5	3.5	159.2	11.9	95.8	3.4	98.6	8.2
Hydrochlorothiazide	93.7	16.0	105.7	6.3	98.6	20.8	102.7	4.9	93.0	11.6
Ibuprofen	145.7	4.1	111.6	21.0	124.9	14.4	94.4	4.3	106.2	6.3
Irbesartan	90.0	8.1	100.9	5.4	106.8	10.3	98.0	4.2	99.7	5.1
Ketoprofen	92.1	14.4	106.2	4.4	95.8	6.5	101.9	2.2	89.0	6.1
Metformin	97.8	5.3	106.3	10.1	104.0	9.7	109.2	5.2	115.3	10.2
Metoprolol	93.0	11.8	107.5	2.3	98.8	12.5	105.2	5.1	101.5	12.9
Metoprolol acid	96.1	34.6	98.2	8.1	91.0	17.6	93.6	16.3	90.9	5.6
Naproxen	n.d.	n.d.	102.6	4.7	110.8	24.0	106.3	3.6	88.8	25.5
O-Desmethylvenlafaxine	87.5	21.1	97.6	16.7	88.8	10.4	106.6	17.5	94.4	12.7
Oxazepam	99.0	12.4	103.4	4.4	104.6	9.9	98.8	4.5	108.1	5.2
Propranolol	95.6	12.0	99.3	2.4	95.6	6.1	101.5	5.1	109.5	6.2
Sitagliptin	72.0	19.3	92.8	15.1	82.0	5.4	96.3	15.3	85.1	23.6
Sotalol	99.1	12.0	109.2	2.3	111.5	9.2	109.1	3.0	104.3	9.6
Sulfamethoxazole	97.9	10.7	103.3	4.3	100.0	14.5	106.1	10.0	100.6	4.7
Sulfamethoxazole β-D-glucuronide	121.8	44.0	90.4	13.5	88.8	29.5	109.4	16.6	98.5	37.3
Tramadol	105.6	9.0	103.2	3.1	109.3	9.7	103.0	4.7	102.4	10.7
Valsartan	87.0	20.1	105.3	4.3	96.5	6.7	103.8	3.9	99.7	4.4
Valsartan acid	181.7	7.9	119.9	4.1	99.8	7.1	128.7	5.7	84.5	8.6
Venlafaxine	99.5	7.9	102.0	2.2	104.7	8.6	100.9	4.0	109.5	11.6
α-Hydroxymetoprolol	143.1	13.3	146.6	6.9	139.4	22.3	132.1	15.2	131.9	26.5

[a] n.d. data not determined due to poor signal intensity

Table S9. Average concentration and concentration span (Min., Max.) of micropollutants and transformation products in HPW from 10, 20 and 30 cm depth, SW and USW from the River Erpe. HPW and SW samples were taken in April over the course of 24 h while USW was collected as grab sample.

	SW (N=24)			HPW 10 cm (N=24)			HPW 20 cm (N=24)			HPW 30 cm (N=24)			USW
	Avg	Min.	Max.	**Avg**	Min.	Max.	**Avg**	Min.	Max.	**Avg**	Min.	Max.	
10,11-Dihydroxy carbamazepine	**3.07**	1.41	5.52	**3.05**	2.57	3.70	**3.00**	2.43	3.58	**2.99**	2.56	3.59	0.18
1H-Benzotriazole	**3.85**	2.00	6.26	**4.29**	3.88	4.85	**4.86**	3.63	5.50	**5.35**	3.57	6.59	<0.126
1-Hydroxyibuprofen	**0.45**	n.f.	1.47	**0.45**	n.f.	1.56	**0.37**	n.f.	0.96	**0.43**	n.f.	0.96	n.f.
1-Methyl-1H-Benzotriazole	**0.11**	<0.12	0.24	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	n.f.	n.f.
2/3-Hydroxyibuprofen	**1.37**	<0.66	4.86	**1.45**	n.f.	4.43	**0.91**	n.f.	3.22	**1.36**	n.f.	3.59	n.f.
2/4-Chlorobenzoic acid	**0.10**	n.f.	0.23	**0.15**	n.f.	<0.31	**0.17**	n.f.	0.32	**0.13**	n.f.	<0.31	n.f.
4-Hydroxy-1H-benzotriazole	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	n.f.	n.f.
4-Hydroxydiclofenac	**1.72**	0.76	2.82	**0.59**	0.16	1.21	**0.37**	0.12	0.62	**0.31**	<0.02	0.91	<0.02
Acesulfame	**8.50**	5.20	13.45	**1.26**	0.52	2.82	**2.69**	1.92	4.46	**2.10**	1.54	2.61	0.64
Acetaminophen	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	<0.37	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	n.f.	n.f.
Acridine	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	n.f.	n.f.
Acridone	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	n.f.	n.f.
Bezafibrate	**0.74**	0.37	1.04	**0.49**	0.42	0.72	**0.51**	0.36	0.69	**0.45**	0.30	0.58	n.f.
Carbamazepine	**1.64**	0.76	2.42	**1.25**	1.11	1.40	**1.25**	1.08	1.49	**1.25**	1.04	1.59	0.12
Carbamazepine-10,11-epoxide	**1.22**	0.40	2.10	**0.07**	0.05	0.11	**0.08**	0.04	0.14	**0.07**	<0.37	0.11	n.f.
Carboxyibuprofen	**n.f.**	n.f.	n.f.	**0.39**	n.f.	<1.66	**0.46**	n.f.	<1.66	**0.51**	n.f.	2.36	n.f.
Chlorothiazide	**0.12**	<0.10	0.18	**0.30**	0.15	0.51	**0.37**	0.22	0.59	**0.43**	0.15	1.04	n.f.
Clofibric acid	**0.02**	n.f.	<0.07	**0.05**	n.f.	0.10	**0.04**	n.f.	0.07	**0.04**	n.f.	<0.07	n.f.
Diclofenac	**4.82**	2.57	7.04	**4.22**	2.11	9.52	**4.00**	1.84	8.63	**3.98**	2.10	11.31	n.f.
Diclofenac amide	**0.03**	n.f.	0.08	**0.09**	n.f.	0.44	**0.08**	n.f.	0.47	**0.06**	n.f.	0.22	n.f.
Furosemide	**0.37**	n.f.	0.73	**0.19**	n.f.	<0.57	**0.17**	n.f.	<0.57	**0.17**	n.f.	<0.57	n.f.
Gemfibrozil	**n.f.**	n.f.	n.f.	**0.02**	n.f.	<0.07	**0.02**	n.f.	<0.07	**0.02**	n.f.	<0.07	n.f.
Guanylurea	**153**	85	222	**17**	15	23	**63**	53	71	**50**	39	59	n.f.
Hydrochlorothiazide	**6.2**	3.3	8.8	**6.2**	3.7	11.0	**6.2**	3.9	9.1	**6.1**	3.7	8.6	n.f.
Ibuprofen	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	<1.57	**n.f.**	n.f.	<1.57	**n.f.**	n.f.	n.f.	n.f.
Irbesartan	**1.77**	1.03	2.55	**1.13**	0.86	1.52	**1.17**	0.85	1.51	**1.11**	0.71	1.74	<0.05
Ketoprofen	**0.12**	n.f.	<0.21	**0.16**	n.f.	0.34	**0.15**	n.f.	0.23	**0.16**	n.f.	0.23	n.f.
Metformin	**1.00**	0.55	1.66	**0.42**	<0.47	0.58	**0.56**	<0.47	0.78	**0.67**	<0.47	0.80	<0.46
Metoprolol	**5.48**	2.95	8.42	**0.28**	0.21	0.47	**0.59**	0.34	0.71	**0.59**	0.44	0.75	n.f.
Metoprolol acid	**0.28**	0.14	0.45	**0.86**	0.68	1.52	**0.85**	0.66	0.99	**0.84**	0.60	1.02	<0.1
Naproxen	**0.18**	n.f.	0.62	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	n.f.	**n.f.**	n.f.	n.f.	n.f.
O-Desmethylvenlafaxine	**1.64**	0.81	2.65	**1.16**	0.82	1.56	**1.12**	n.f.	1.54	**1.14**	0.72	1.69	<0.03
Oxazepam	**0.05**	n.f.	0.10	**0.04**	n.f.	0.09	**0.04**	n.f.	0.10	**0.04**	n.f.	0.08	n.f.
Propranolol	**0.05**	<0.06	0.09	**0.03**	n.f.	<0.06	**0.03**	n.f.	<0.06	**0.03**	n.f.	0.07	n.f.
Sitagliptin	**5.09**	1.63	7.69	**3.39**	2.82	4.69	**3.17**	0.02	4.40	**3.15**	2.55	4.37	n.f.

Sotalol	**0.23**	0.13	0.30	**0.12**	0.10	0.13	**0.13**	0.10	0.16	**0.13**	0.10	0.15	n.f.
Sulfamethoxazole	**0.08**	<0.05	0.14	**0.08**	<0.06	0.12	**0.08**	n.f.	0.14	**0.08**	<0.06	0.14	n.f.
Sulfamethoxazole β-D-glucuronide	**0.29**	n.f.	<0.46	**0.24**	n.f.	<0.78	**0.26**	n.f.	<0.78	**0.24**	n.f.	<0.78	n.f.
Tramadol	**0.91**	0.50	1.43	**0.81**	0.70	1.00	**0.83**	0.71	0.97	**0.83**	0.69	0.96	<0.11
Valsartan	**37.4**	20.8	54.3	**8.2**	2.9	12.5	**4.4**	2.0	7.9	**9.9**	3.7	13.9	n.f.
Valsartan acid	**2.3**	0.8	4.5	**22.2**	15.7	30.0	**24.4**	18.2	32.1	**25.0**	16.8	30.4	1.8
Venlafaxine	**0.49**	0.29	0.74	**0.48**	0.42	0.61	**0.49**	0.39	0.58	**0.49**	0.42	0.57	n.f.
α-Hydroxymetoprolol	**0.54**	<0.46	1.15	**0.11**	n.f.	<0.62	**0.20**	n.f.	<0.62	**0.11**	n.f.	<0.62	n.f.

[a]n.f. below detection limit

Table S10. Method detection and quantification limits (in µg L^{-1}) in water collected upstream and downstream of a waste water treatment plant and in sediment pore water.

Target	Downstream Water		Upstream Water		Pore Water	
	MDL	**MQL**	**MDL**	**MQL**	**MDL**	**MQL**
10,11-Dihydroxy carbamazepine	0.02	0.088	0.013	0.064	0.014	0.069
1H-Benzotriazole	0.005	0.114	0.1	0.1	0.014	0.144
1-Hydroxyibuprofen	0.189	0.631	0.259	0.864	0.326	1.086
1-Methyl-1H-Benzotriazole	0.018	0.099	0.015	0.089	0.019	0.101
2/3-Hydroxyibuprofen	0.529	1.956	0.985	3.476	0.629	2.290
2/4-Chlorobenzoic acid	0.04	0.181	0.032	0.154	0.059	0.245
4-Hydroxy-1H-benzotriazole	0.091	0.314	0.072	0.250	0.108	0.370
4-Hydroxydiclofenac	0.015	0.05	0.005	0.005	0.004	0.004
Acesulfame	0.018	0.088	0.002	0.036	0.002	0.036
Acetaminophen	0.07	0.249	0.039	0.146	0.084	0.294
Acridine	0.043	0.141	0.033	0.106	0.035	0.114
Acridone	0.041	0.152	0.01	0.050	0.096	0.335
Bezafibrate	0.024	0.094	0.022	0.087	0.020	0.079
Carbamazepine	0.025	0.025	0.018	0.018	0.005	0.044
Carbamazepine-10,11-epoxide	0.006	0.03	0.002	0.017	0.006	0.029
Carboxyibuprofen	0.351	1.306	0.338	1.261	0.358	1.329
Chlorothiazide	0.019	0.082	0.008	0.044	0.015	0.067
Clofibric acid	0.004	0.056	0.001	0.046	0.004	0.055
Diclofenac	0.107	0.383	0.111	0.395	0.121	0.428
Diclofenac amide	0.031	0.091	0.033	0.096	0.043	0.133
Furosemide	0.005	0.198	0.003	0.189	0.081	0.452
Gemfibrozil	0.011	0.04	0.006	0.022	0.017	0.060
Guanylurea	0.329	1.298	0.004	0.213	0.069	0.433
Hydrochlorothiazide	0.044	0.151	0.044	0.151	0.067	0.228
Ibuprofen	0.33	1.194	0.347	1.250	0.349	1.257
Irbesartan	0.008	0.029	0.009	0.033	0.019	0.067
Ketoprofen	0.047	0.169	0.049	0.176	0.050	0.178
Metformin	0.119	0.394	0.11	0.364	0.114	0.378
Metoprolol	0.006	0.085	0.004	0.079	0.023	0.142
Metoprolol acid	0.014	0.06	0.016	0.066	0.017	0.069
Naproxen	0.064	0.253	0.07	0.273	0.080	0.308
O-Desmethylvenlafaxine	0.017	0.063	0.017	0.063	0.006	0.027
Oxazepam	0.006	0.032	0.008	0.039	0.009	0.041
Propranolol	0.007	0.044	0.002	0.030	0.008	0.047
Sitagliptin	0.01	0.03	0.006	0.016	0.008	0.021
Sotalol	0.017	0.092	0.003	0.046	0.001	0.041
Sulfamethoxazole	0.01	0.047	0.009	0.042	0.009	0.043
Sulfamethoxazole β-D-glucuronide	0.187	0.623	0.096	0.317	0.111	0.367
Tramadol	0.003	0.098	0.002	0.093	0.004	0.102
Valsartan	0.049	0.049	0.049	0.049	0.009	0.115
Valsartan acid	0.114	0.372	0.107	0.350	0.188	0.619
Venlafaxine	0.01	0.01	0.007	0.007	0.008	0.008
α-Hydroxymetoprolol	0.067	0.365	0.041	0.278	0.107	0.498

Table S11. Method detection and quantification limits (in µg L^{-1}) in tap water and Milli-Q-water.

Target	Tap Water		Milli-Q-Water	
	MDL	**MQL**	**MDL**	**MQL**
10,11-Dihydroxy carbamazepine	0.003	0.029	0.003	0.031
1H-Benzotriazole	0.007	0.122	0.003	0.109
1-Hydroxyibuprofen	0.276	0.919	0.376	1.252
1-Methyl-1H-Benzotriazole	0.017	0.092	0.004	0.050
2/3-Hydroxyibuprofen	0.383	1.469	1.094	3.840
2/4-Chlorobenzoic acid	0.061	0.253	0.074	0.295
4-Hydroxy-1H-benzotriazole	0.100	0.346	0.068	0.239
4-Hydroxydiclofenac	0.001	0.003	1.304	4.346
Acesulfame	0.003	0.038	0.002	0.036
Acetaminophen	0.030	0.116	0.026	0.100
Acridine	0.023	0.075	0.024	0.078
Acridone	0.008	0.043	0.016	0.070
Bezafibrate	0.009	0.043	0.011	0.049
Carbamazepine	0.008	0.008	0.002	0.002
Carbamazepine-10,11-epoxide	0.001	0.012	0.002	0.016
Carboxyibuprofen	0.282	1.077	0.514	1.848
Chlorothiazide	0.009	0.048	0.014	0.064
Clofibric acid	0.000	0.045	0.000	0.045
Diclofenac	0.119	0.422	n.d.	n.d.
Diclofenac amide	0.029	0.084	n.d.	n.d.
Furosemide	0.016	0.235	0.047	0.336
Gemfibrozil	0.399	1.332	0.296	0.990
Guanylurea	0.108	0.562	0.062	0.408
Hydrochlorothiazide	0.024	0.084	0.021	0.075
Ibuprofen	0.212	0.801	0.823	2.838
Irbesartan	0.009	0.033	0.006	0.023
Ketoprofen	0.051	0.183	0.090	0.314
Metformin	0.110	0.364	0.154	0.511
Metoprolol	0.019	0.129	0.019	0.130
Metoprolol acid	0.017	0.068	0.011	0.048
Naproxen	0.074	0.288	0.522	1.781
O-Desmethylvenlafaxine	0.002	0.014	0.001	0.011
Oxazepam	0.009	0.039	0.002	0.018
Propranolol	0.004	0.035	0.045	0.172
Sitagliptin	0.007	0.017	0.008	0.021
Sotalol	0.001	0.041	0.002	0.042
Sulfamethoxazole	0.007	0.036	0.016	0.065
Sulfamethoxazole β-D-glucuronide	0.164	0.545	0.108	0.359
Tramadol	0.007	0.111	0.013	0.131
Valsartan	0.055	0.055	0.002	0.093
Valsartan acid	0.097	0.316	0.161	0.529
Venlafaxine	0.009	0.009	0.014	0.014
α-Hydroxymetoprolol	0.005	0.159	0.002	0.149

Table S12. Consistency (%RSD) of the calibration curve standards across 3 batches (N=9) and of a QC standard that was analyzed every 15 samples (N=18). Concentration levels range from 1 (lowest) to 7 (highest) missing standard levels were below LOD.

Target	Calibration curve (%RSD)							QC Standard (%RSD)
	Level 1	**Level 2**	**Level 3**	**Level 4**	**Level 5**	**Level 6**	**Level 7**	
10,11-Dihydroxy carbamazepine	16.25	8.18	5.88	3.45	1.82	2.60	2.46	4.61
1H-Benzotriazole	23.15	19.21	13.97	14.24	7.82	8.79	6.04	2.69
1-Hydroxyibuprofen			20.78	21.47	16.16	5.27	6.84	19.94
1-Methyl-1H-Benzotriazole	19.27	18.90	20.15	8.52	6.20	5.94	6.50	4.43
2/3-Hydroxyibuprofen				22.76	23.70	9.58	8.03	14.38
2/4-Chlorobenzoic acid		16.66	19.05	10.68	6.87	6.36	7.04	7.73
4-Hydroxy-1H-benzotriazole			25.91	16.56	10.88	10.50	7.69	13.75
4-Hydroxydiclofenac	19.85	18.18	8.85	2.99	3.43	1.78	1.45	7.64
Acesulfame	29.74	8.37	12.85	4.57	2.36	2.23	0.62	3.48
Acetaminophen		23.03	6.87	8.85	5.79	4.54	3.56	4.75
Acridine	16.60	15.99	16.43	6.67	5.15	5.88	4.77	3.07
Acridone		29.56	24.16	18.85	9.02	6.56	6.07	4.73
Bezafibrate	23.23	21.22	8.59	2.91	4.32	3.46	3.30	3.59
Carbamazepine	26.51	14.55	14.41	12.57	12.17	6.21	6.45	2.72
Carbamazepine-10,11-epoxide				22.61	13.26	10.36	8.11	6.14
Carboxyibuprofen	24.11	15.90	8.86	5.45	6.52	5.40	5.42	19.76
Chlorothiazide		20.42	13.86	9.86	5.29	3.08	2.64	6.24
Clofibric acid		17.15	9.51	15.27	8.79	5.68	3.57	1.46
Diclofenac	21.86	17.09	16.34	8.40	8.11	7.33	6.54	11.03
Diclofenac amide	25.56	25.59	12.78	17.88	7.08	8.13	4.82	2.34
Furosemide	33.48	13.53	9.27	5.83	4.92	4.28	4.10	8.35
Gemfibrozil		26.62	19.26	18.34	7.12	6.44	5.93	2.83
Guanylurea		10.35	10.82	10.51	7.07	2.52	2.08	1.13
Hydrochlorothiazide			8.81	4.35	2.77	1.28	1.44	5.02
Ibuprofen	40.16	21.85	17.18	10.40	5.32	5.97	5.62	24.03
Irbesartan			15.19	10.80	15.18	8.63	1.87	2.42
Ketoprofen	29.86	6.09	9.53	7.22	3.54	2.53	2.66	1.77
Metformin	19.50	19.79	8.80	5.03	2.24	2.16	2.55	3.10
Metoprolol			3.93	4.35	3.99	2.00	1.77	5.81
Metoprolol acid	20.21	17.35	13.87	6.87	6.26	2.42	2.68	3.33
Naproxen	41.94	22.34	18.52	5.04	5.62	4.73	3.49	12.87
O-Desmethylvenlafaxine			11.73	15.61	8.78	3.78	2.80	4.85
Oxazepam	20.55	5.77	8.88	7.09	7.19	7.17	5.24	5.35
Propranolol	18.86	13.13	6.90	4.17	3.67	3.02	2.83	5.23
Sitagliptin	14.94	18.93	8.74	6.27	5.93	2.24	2.65	2.69
Sotalol	29.34	21.62	10.52	6.26	4.95	4.66	5.37	4.45
Sulfamethoxazole	33.66	24.19	8.76	8.25	6.34	3.68	2.91	5.22
Sulfamethoxazole β-D-glucuronide			31.95	32.03	12.65	10.22	11.35	3.22
Tramadol	29.96	11.23	9.03	9.24	6.91	6.06	6.71	2.48
Valsartan	26.07	9.30	8.08	2.86	2.33	1.64	3.39	4.85
Valsartan acid	29.41	26.73	19.34	7.67	6.67	3.04	4.29	9.66
Venlafaxine	20.73	32.88	16.08	16.30	16.39	5.72	6.62	2.03
α-Hydroxymetoprolol	28.34	8.94	4.63	3.13	2.61	1.73	1.51	3.61

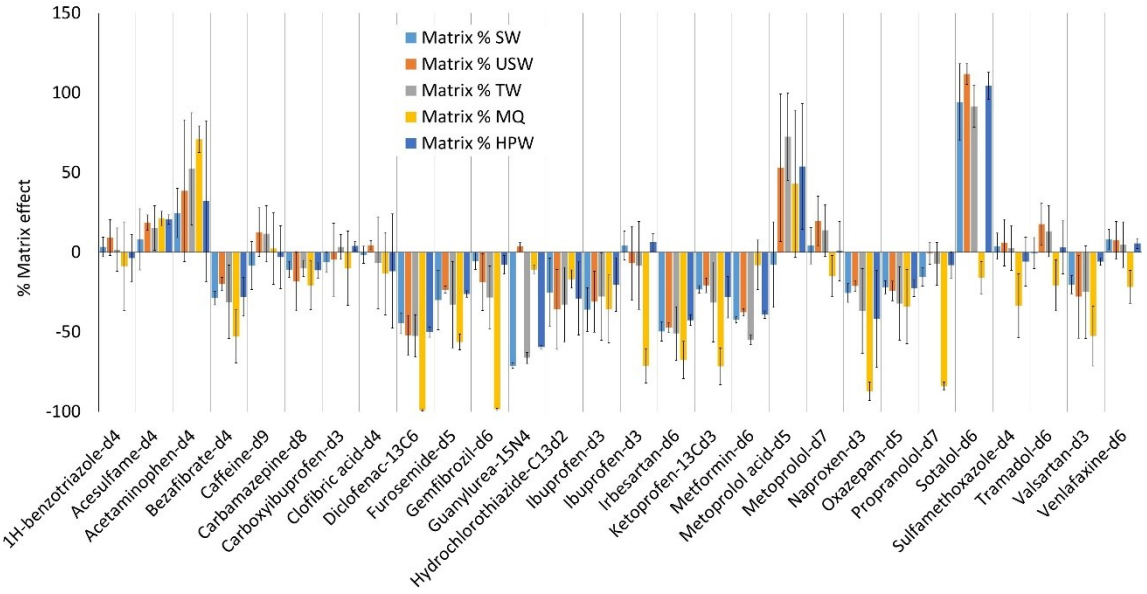

Figure S4: Matrix effects of Erpe surface water (SW), Erpe surface water upstream of the WWTP (USW), tap water (TW), Mili-Q water (MQ) and Erpe hyporheic pore water (HPW) on isotopically labelled internal standards. Percentage deviation of quantitative ion intensities from calibration standards, error bars indicate % RSD of N=5 measurements.

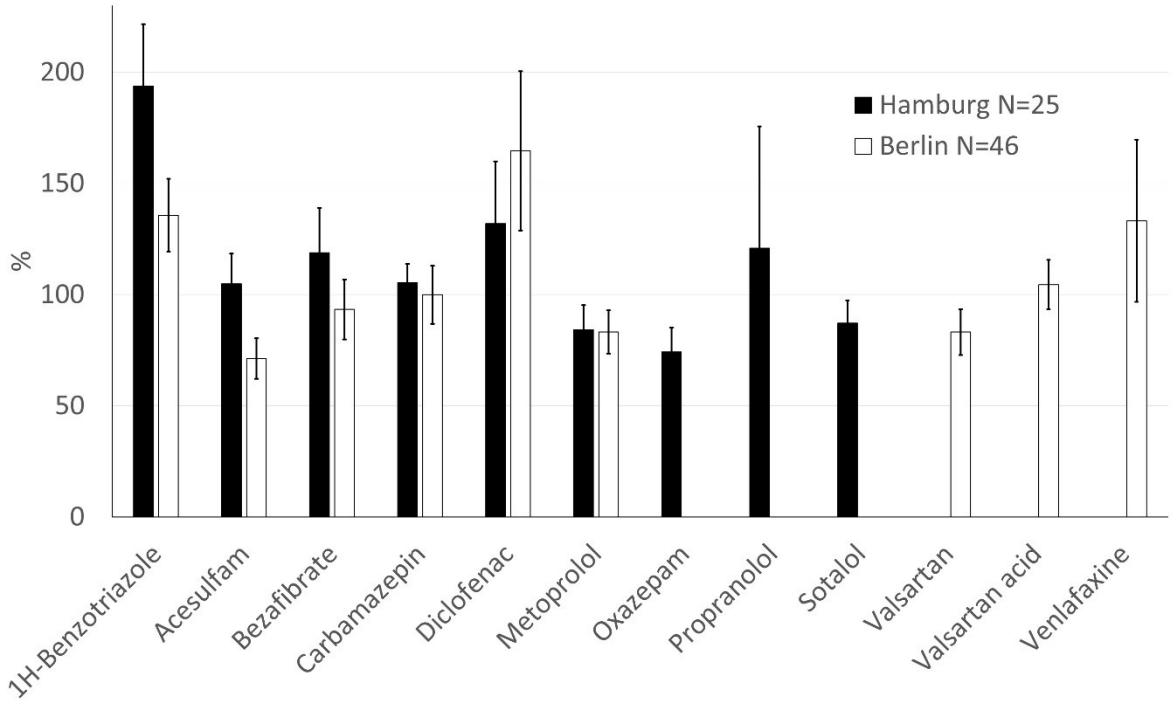

Figure S5. Results from an inter-laboratory method comparison. Bars show average % deviation ±SD of concentrations reported by the Institute for Hygiene and Environment (Hamburg; black bars) and by the Technical University Berlin (TU Berlin; white bars) from data generated with our method (i.e. perfect agreement with our method is 100%).

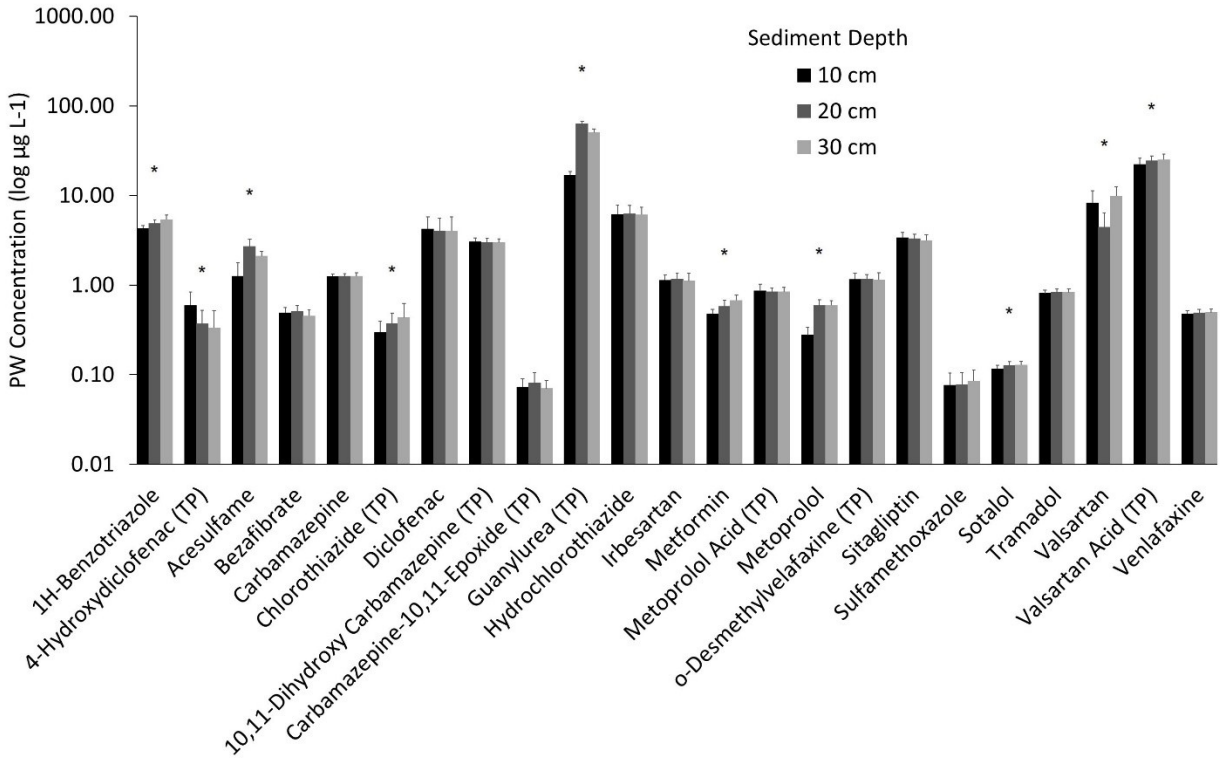

Figure S6: Average HPW concentrations ±SD of selected pharmaceuticals in three different sediment depths downstream of a WWTP. Samples were taken hourly for one day (N=24). * indicates a significant difference of the means (two-way ANOVA, $P < 0.05$).

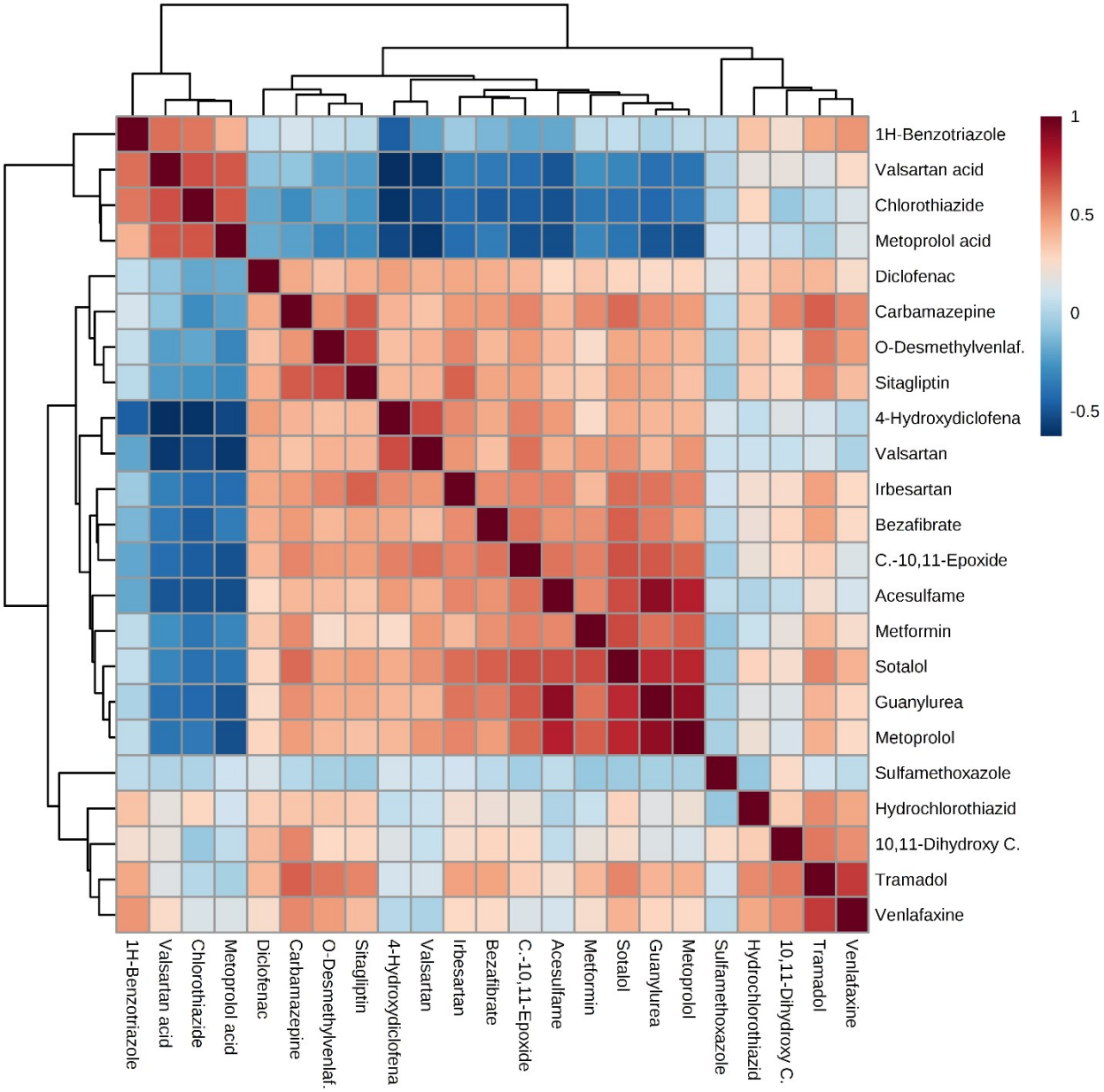

Figure S7: Correlation matrix visualizing overall correlations between different polar organic micropollutants (average concentrations of all April samples from surface water and hyporheic pore water-Table S9) using Spearman's rank correlation and cube root transformed data.

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