Supporting information

Assessment of the breakthrough of micropollutants in full-scale granular activated carbon adsorbers by rapid small-scale column tests and a novel pilot-scale sampling approach

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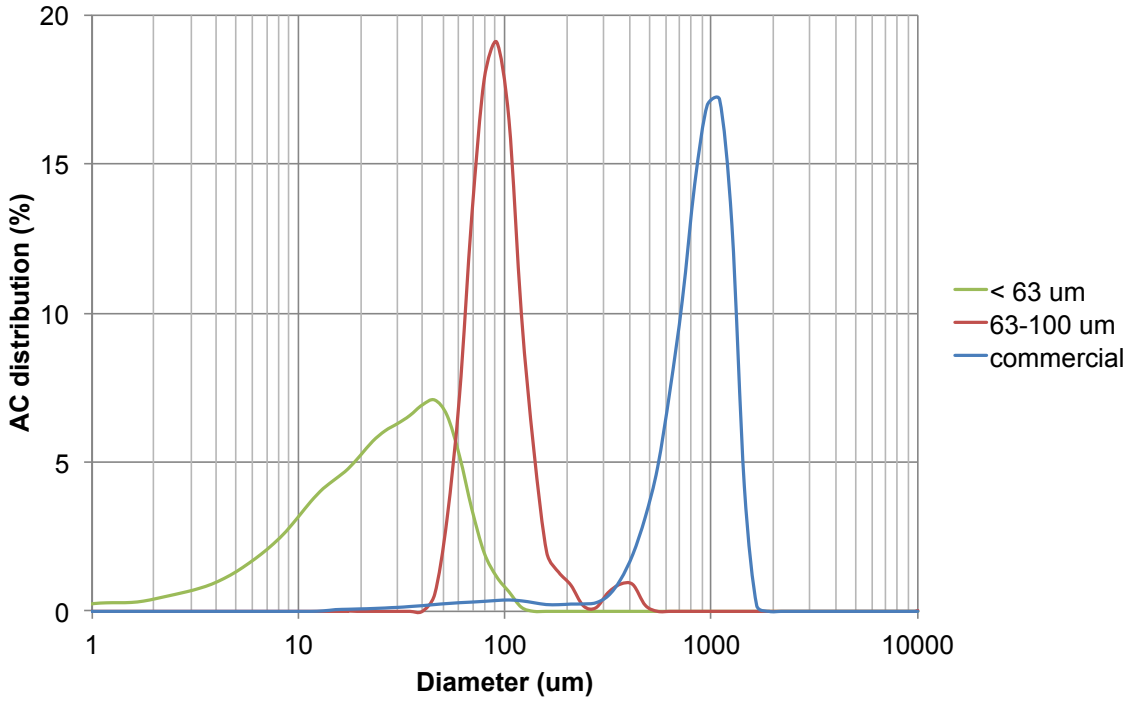

Figure S1: Particle size distribution of Calgon Filtrasorb® 400 (Chemviron) granular activated carbon and powdered activated carbon (after crushing and sieving). The commercial activated carbon particles were ground and separated with two sieves. The green curve represents the fraction < 63 µm, the red line represents the fraction 63 - 100 µm and the blue curve is the particle size distribution of the non-ground activated carbon.

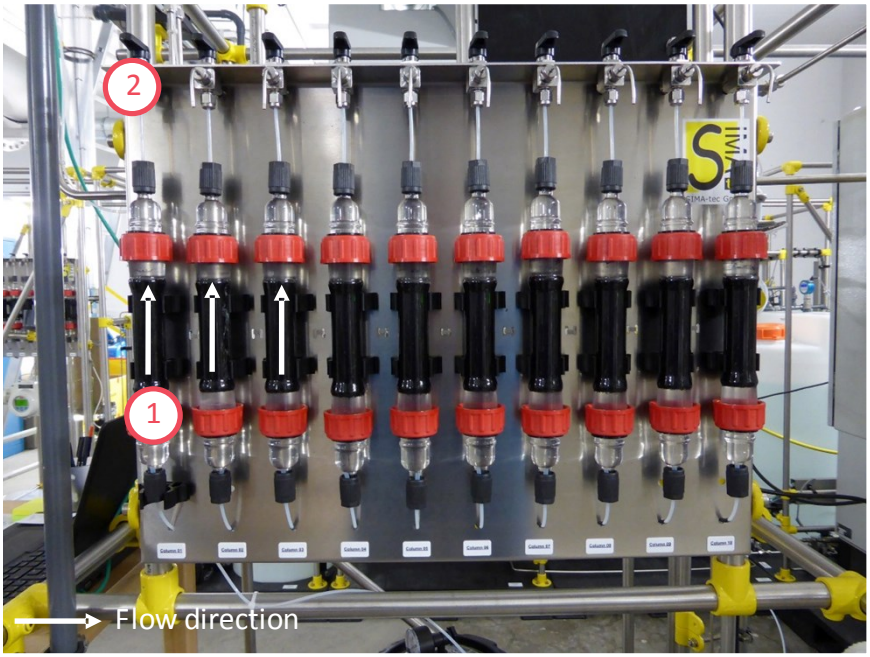

Figure S2. Pilot- scale system with 10 GAC columns in series (1) glass columns filled with GAC, (2) sampling points located after each column (length: 10 x 10 cm, diameter: 2.4 cm).

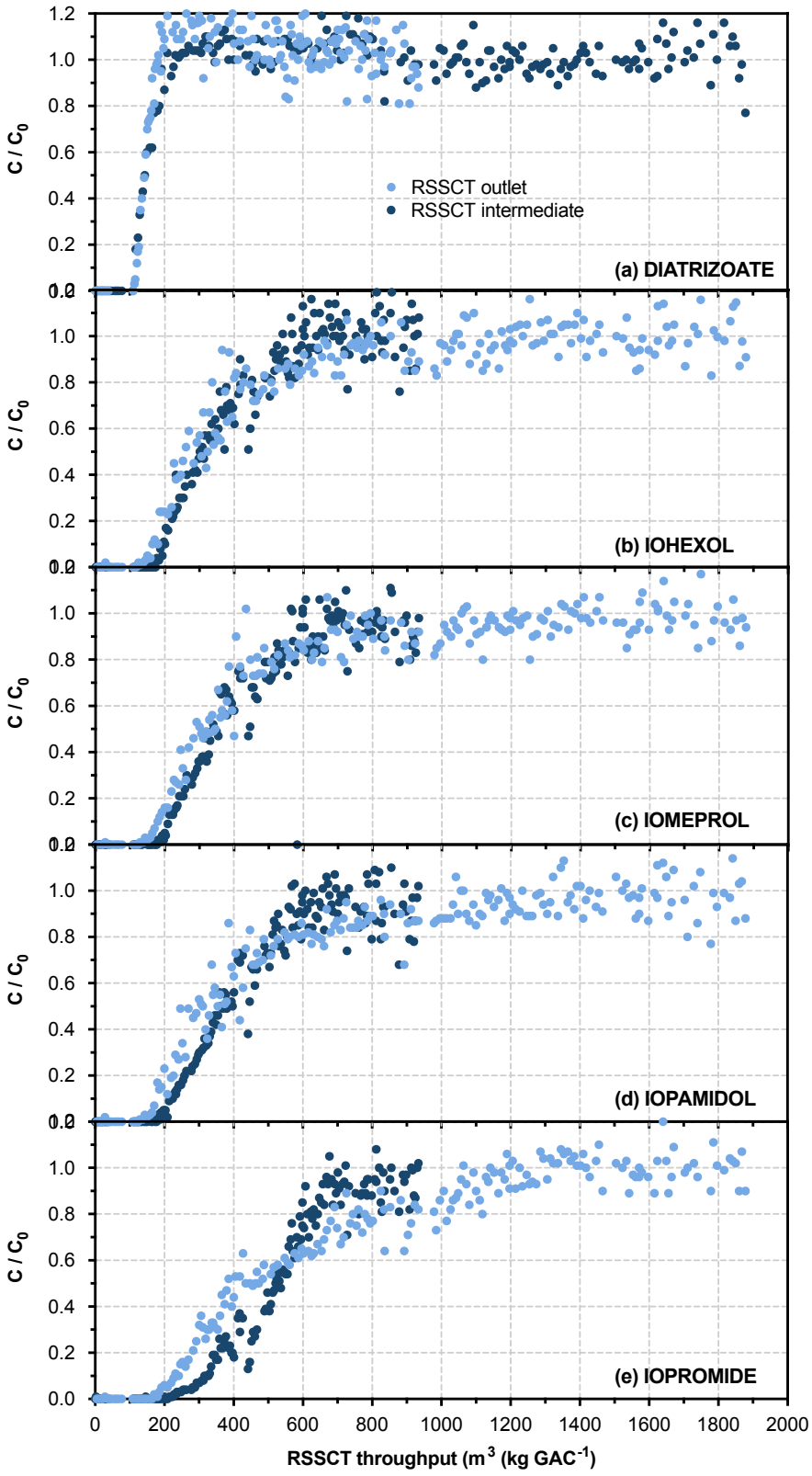

Figure S3. RSSCT breakthrough curves for five X-ray contrast media: (a) diatrizoate, (b) iohexol, (c) iomeprol, (d) iopamidol and (e) iopromide (raw data, not corrected with the fouling index). Light blue circles and dark blue circles represent intermediate and outlet sampling points, respectively.

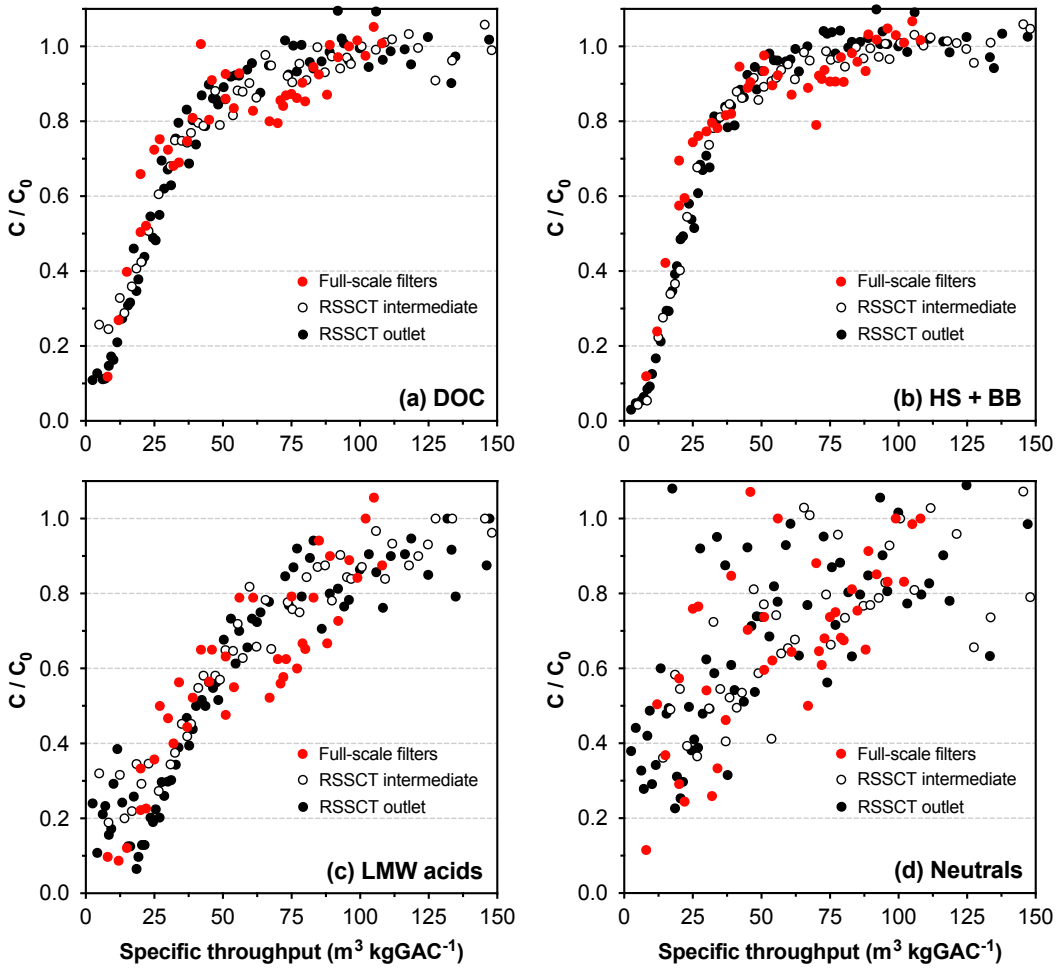

Figure S4. RSSCT breakthrough curves for (a) DOC and DOM constituents (b) humic substances and building block, (c) low molecular weight neutrals and (d) neutrals.

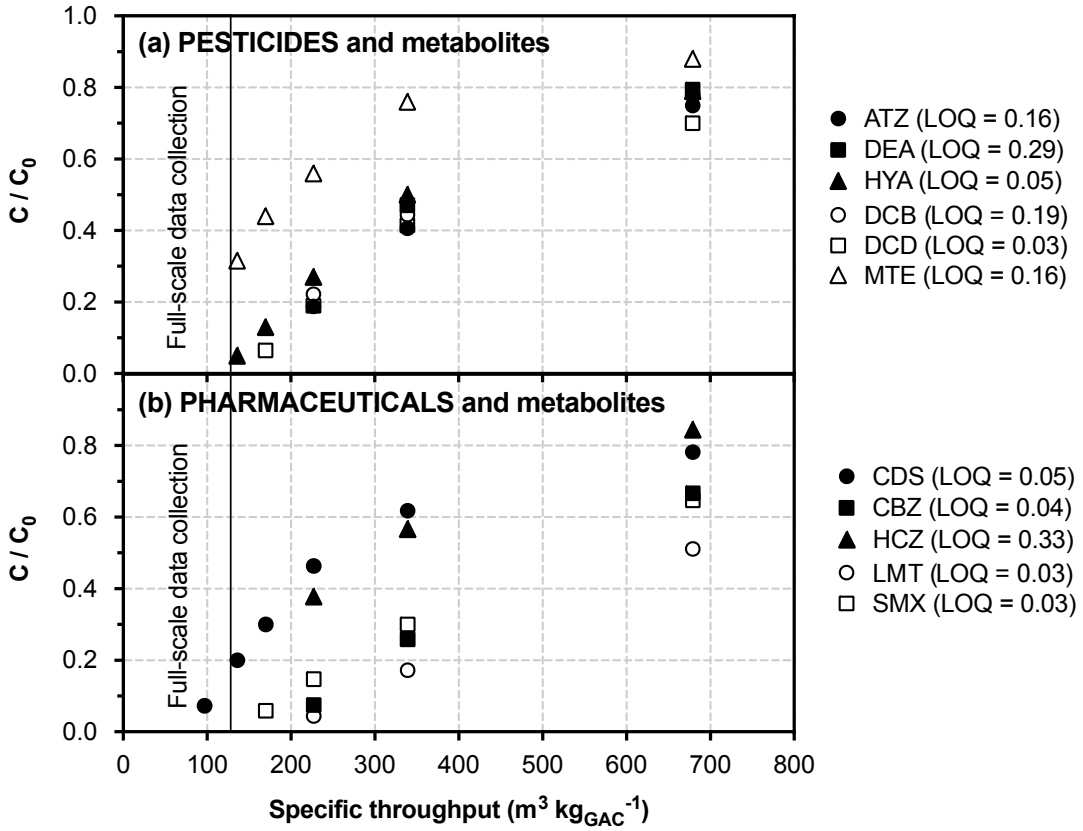

Figure S5. Breakthrough curves determined with method 2 in the pilot-scale GAC system for (a) 6 pesticides and metabolites (ATZ: atrazine; DEA: desethylatrazine; HYA: hydroxyatrazine, DCB: 2,6-dichlorobenzamide; DCD: desphenylchloridazon; MTE: metolachlor ESA) and (b) 4 pharmaceuticals and one metabolite (CDS: candesartan; CBZ: carbamazepine; HCZ: dihydroxycarbamazepine; LMT: lamotrigine; SMX: sulfamethoxazole) occurring in Hardwald groundwater. LOQs in the legends are achievable c/c_0 values and not concentrations.

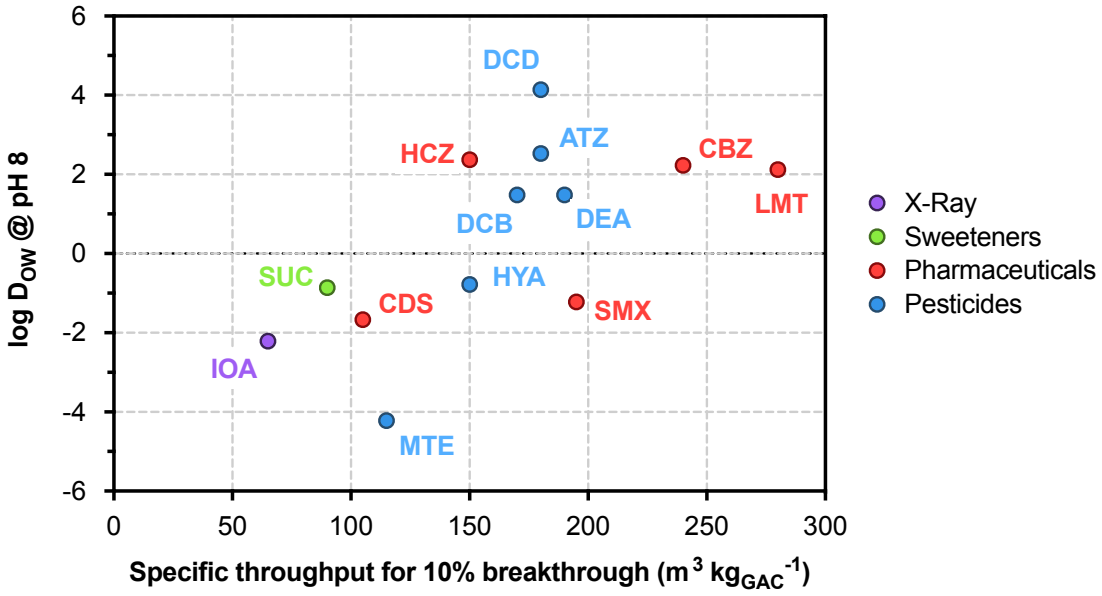

Figure S6. Comparison of specific throughput at 10% breakthrough obtained with pilot-scale GAC columns (method 2) for 11 compounds not detected after full-scale adsorbers (iopamidol and sucralose were added for comparison) with log D_{OW} values at pH 8.

53 Table S1. Water quality parameters of Hardwald groundwater used for RSSCT, pilot-scale GAC

54 column test and in the full-scale plant.

Parameters	RSSCT	Pilot-scale GAC column test	Full-scale GAC adsorber
pH	8.05 ± 0.10	7.65 ± 0.05	7.65 ± 0.20
Temperature (°C)	12.0 ± 0.5	15.0 ± 2.0	13.2 ± 3.0
DOC[(1)] (mgC/L^{-1})	0.49 ± 0.05	0.37 ± 0.02	0.46± 0.06

55 [(1)] DOC was determined with LC-OCD analyzer developed by DOC-Labor (Huber et al., 2011)

Table S2. Concentrations and characteristics of the 20 selected compounds spiked to Hardwald groundwater (HGW) for the RSSCT. log D_{OW} represents the partition coefficient of the compounds at pH 8.

Category	Compound	Concentration (ng L^{-1})	log D_{OW} (@ pH 8)[(1)]	MW (g mol^{-1})
X-ray contrast media	Iohexol (IOH)	3208 ± 367	-3.13	821.14
	Iomeprol (IOM)	3342 ± 282	-2.45	777.09
	Iopamidol (IOA)	3274 ± 303	-2.21	777.09
	Iopromide (IOP)	3252 ± 285	-1.89	791.11
	Diatrizoate (DTZ)	3345 ± 414	-0.77	613.91
Sweeteners	Sucralose (SUC)	350 ± 42	-0.86	397.63
Pesticides	Deisopropylatrazine (DIA)	51 ± 6	1.23	173.60
	Desethylatrazine (DEA)	48 ± 7	1.48	187.63
	2,6-Dichlorobenzamide (DCB)	57 ± 8	1.48	190.03
	Simazine (SIM)	32 ± 16	2.20	201.66
	Atrazine (ATZ)	49 ± 9	2.53	215.68
	Diuron (DIU)	51 ± 6	2.70	233.09
	Metolachlor (MET)	55 ± 20	3.36	283.79
Pharmaceuticals	Atenolol (ATN)	51 ± 14	-1.42	266.43
	Sulfamethoxazole (SMX)	59 ± 11	-1.22	253.28
	Metoprolol (MET)	76 ± 30	0.54	267.36
	Diclofenac (DCF)	52 ± 12	1.06	296.15
	Carbamazepine (CBZ)	60 ± 15	2.23	236.27
Industrial compounds	Benzotriazole (BZT)	267 ± 35	1.54	119.12
	5-Methylbenzotriazole (MBZ)	303 ± 34	1.83	133.15

[(1)] calculated with Advanced Chemistry Development (https://ilab.acdlabs.com/iLab2/).

62 Table S3. Physical properties of the Calgon Filtrasorb® 400 granular activated carbon.

Parameter	Value
Mean Particle Diameter (μm)	1’000
Apparent Density (kg m^{-3})	450
BET Surface Area (m^2 g^{-1})	1’050
DFT Micropore Volume (0-2 nm) (cm^3 g^{-1})	0.382
DFT Mesopore Volume (2-36 nm) (cm^3 g^{-1})	0.203

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64 Table S4. Limit of quantification and internal standard used for the 20 selected compounds spiked

65 to Hardwald groundwater (HGW) for the RSSCT.

Category	Compound	LOQ[(1)] (ng L^{-1})	Internal Standard
X-ray contrast media	Iohexol (IOH)	5 – 100	Iohexol-d5
	Iomeprol (IOM)	5 – 100	Iomeprol-d3
	Iopamidol (IOA)	5 – 100	Iopamidol-d3
	Iopromide (IOP)	5 – 100	Iopromide-d3
	Diatrizoate (DTZ)	10 – 100	Diatrizoate-d6
Sweeteners	Sucralose (SUC)	50 – 100	Sucralose-d6
Pesticides	Deisopropylatrazine (DIA)	1 – 10	Deisopropylatrazine-d5
	Desethylatrazine (DEA)	1 – 5	Desethylatrazine-15N3
	2,6-Dichlorobenzamide (DCB)	1 – 5	2,6-Dichlorobenzamide-3,4,5-d3
	Simazine (SIM)	1 - 10	Simazine-d5
	Atrazine (ATZ)	1	Atrazin-d5
	Diuron (DIU)	1 – 5	Diuron-d6
	Metolachlor (MET)	1 – 5	Metolachlor-d6
Pharmaceuticals	Atenolol (ATN)	5	Atenolol-d7
	Sulfamethoxazole (SMX)	1 – 5	Sulfamethoxazole-d4
	Metoprolol (MET)	5 – 25	Metoprolol-d7
	Diclofenac (DCF)	1 – 50	Diclofenac-d4
	Carbamazepine (CBZ)	1	Carbamazepin-d8
Industrial compounds	Benzotriazole (BZT)	5 – 10	Benzotriazole-d4
	5-Methylbenzotriazole (MBZ)	1 – 5	5-Methylbenzotriazole-d6

66 [(1)] the sensitivity was improved during RSSCT and a range for LOQ is provided.

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Table S5. Characteristics of the 20 compounds detected in Hardwald groundwater (HGW) during pilot-plant experiments. log D_{OW} represents the partition coefficient of compounds at pH 8 while S and V are the Abraham solvation parameters. These parameters were used to determine the 10% breakthrough.

Categories	Compound	Concentration (ng L^{-1})	log D_{OW} (@ pH 8)[1]	MW (g mol^{-1})	S[1]	V[1]
X-ray contrast media	Iopamidol (IOA)[2]	104 ± 32	-2.21	777.09	4.72	3.68
	Diatrizoate (DTZ)[2]	26 ± 7	-0.77	613.91	3.25	2.50
Sweeteners	Sucralose (SUC)[2]	350 ± 42	-0.86	397.63	2.30	2.42
	Acesulfame (ACE)	150 ± 117	-0.51	201.24	2.00	0.98
Pesticides	Metolachlor ESA (MTE)	12 ± 7	-4.22	351.39	2.62	2.50
	Desphenylchloridazon (DCD)	17 ± 3	-4.14	145.44	1.41	0.92
	Hydroxyatrazine (HYA)	10 ± 2	-0.78	197.42	1.23	1,56
	Desethylatrazine (DEA)[2]	3.7 ± 0.4	1.48	187.63	1.42	1.34
	2,6-Dichlorobenzamide (DCB)[2]	2.4 ± 0.7	1.48	190.03	1.69	1.22
	Simazine (SIM)[2]	1.0 ± 0.1	2.20	201.66	1.20	1.48
	Atrazine (ATZ)[2]	3.3 ± 0.4	2.53	215.68	1.17	1.62
	Diuron (DIU)[2]	2.7 ± 0.4	2.70	233.09	1.66	1.60
Pharmaceuticals	Candesartan (CDS)	11 ± 3	-1.67	440.45	3.74	3.16
	Sulfamethoxazole (SMX)[2]	18 ± 6	-1.22	253.28	2.43	1.72
	Hydroxychlorothiazide (HCT)	7.1 ± 2.4	-0.22	297.74	2.77	1.73
	Lamotrigine (LMT)	18 ± 2	2.12	256.09	2.13	1.65
	Carbamazepine (CBZ)[2]	12 ± 2	2.23	236.27	2.06	1.81
	Dihydroxycarbamazepine (HCZ)	11 ± 2	2.37	270.29	1.96	1.85
Industrial compounds	Benzotriazole (BZT)[2]	26 ± 7	1.54	119.12	1.34	0.86
	5-Methylbenzotriazole (MBZ)[2]	36 ± 5	1.83	133.15	1.28	1.00

[1] calculated with Advanced Chemistry Development (https://ilab.acdlabs.com/iLab2/).

[2] compounds already presented in Table S1, SI (https://ilab.acdlabs.com/iLab2/).

75 Table S6. Limit of quantification and internal standard used for the 20 compounds detected in

76 Hardwald groundwater (HGW) during pilot-plant experiments.

Categories	Compound	LOQ (ng L^{-1})	Internal Standard
X-ray contrast media	Iopamidol (IOA)	2	Iopamidol-d3
	Diatrizoate (DTZ)	0.5	Diatrizoate-d6
Sweeteners	Sucralose (SUC)	7	Sucralose-d6
	Acesulfame (ACE)	3	Acesulfam-d4
Pesticides	Metolachlor ESA (MTE)	4	Metolachlor ESA-d11
	Desphenylchloridazon (DCD)	0.5	-
	Hydroxyatrazine (HYA)	3	Desethylatrazine-15N3
	Desethylatrazine (DEA)	1	Desethylatrazine-15N3
	2,6-Dichlorobenzamide (DCB)	0.5	2,6-Dichlorobenzamide-3,4,5 d3
	Simazine (SIM)	0.5	Simazine-d5
	Atrazine (ATZ)	0.5	Atrazine-d5
	Diuron (DIU)	0.5	Diuron-d6
Pharmaceuticals	Candesartan (CDS)	0.5	Candesartan-d5
	Sulfamethoxazole (SMX)	0.5	Sulfamethoxazole-d4
	Hydroxychlorothiazide (HCT)	3	Hydroxychlorothiazide-C13, d2
	Lamotrigine (LMT)	0.5	Lamotrigin-13C3, d3
	Carbamazepine (CBZ)	0.5	Carbamazepin-d8
	Dihydroxycarbamazepine (HCZ)	3	Carbamazepin-d8
Industrial compounds	Benzotriazole (BZT)	2	Benzotriazole-d4
	5-Methylbenzotriazole (MBZ)	0.5	5-Methylbenzotriazole-d6

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78 Table S7. Instrumental conditions for LC-HRMS/MS (QexactivePlus, Thermo Fisher

79 Scientific) analyses of Hardwald groundwater during pilot-plant experiments

Solvent	(A) Water and (B) Methanol acidified with 0.1% formic acid
Flow rate	300 µL min^{-1}
Gradient	0 - 1.5 min: constant at 95% A / 5% B 1.5 - 17.5 min: linear gradient up to 5% A / 95% B 25 - 25.1 min: switch to 95% A / 5% B 25.1 - 29 min: constant at 95% A / 5% B
MS conditions	Electrospray ionization (spray voltage: 5/-3.5 kV, sheath gas flow: 50, auxiliary gas flow: 10, capillary temperature 380°C, S-lens RF level: 100/50, probe heater temperature: 500/250°C) by separate measurements in positive and negative ionization mode
MS detection	Full scan (mass range: 100 – 1000 m/z, mass resolution R: 140000 at m/z 200) followed by five data-dependent MS/MS scans (R: 17500, normalized collision energy NCE: 50) were acquired using the exact masses of the protonated and deprotonated target molecules as trigger criteria for the data-dependent MS/MS in positive and negative ionization mode, respectively. The mass accuracy was determined to be < 5 ppm for all measurements.

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Text S1. Preparation of the feed solution for RSSCTs

Hardwald groundwater was collected at least once per month at the Hardwasser drinking water treatment plant located in the Hardwald forest near Basel. Water containers were stored at 4°C without any pre-filtration prior to use.

Some of the spiked 20 compounds are weakly soluble in water and therefore, micropollutant stock solutions were prepared in ethanol. However, ethanol leads to adsorption competition with the target compounds and microbial growth. Therefore, prior to the mixing with Hardwald groundwater, micropollutant stock solutions were placed in a 1 L amber glass bottle with a large opening at ambient temperature during 24 hours to evaporate the ethanol. Afterwards, approximately 1 L of Hardwald groundwater was added to the amber bottle and stirred for 30 minutes to dissolve the micropollutants, which were crystallized inside the bottle. The solution was weighed and added to a 25 L glass bottle, which was cleaned with nanopure water beforehand. The amber glass bottle was flushed several times with Hardwald groundwater and then poured in the 25 L glass bottle until the RSSCT feed solution reached 20 kg. The solution was stored at 4 °C and used within 10 days.

Text S2. Linear regression to calculate the specific throughput at 10% breakthrough for micropollutants in water

Kennedy et al. (2015) developed a linear regression to predict the specific throughput at 10% breakthrough ($BV_{10\%}$) for micropollutants based on experimental results obtained with different water matrices. This linear regression considers the parameters affecting the adsorption of micropollutant in water such as the initial dissolved organic carbon concentration (DOC_0), the pH-dependent octanol/water partition coefficient (log D_{OW}) and Abraham solvation parameters (S and V) and is describes as followed:

$$\ln BV10\% = (11.2 \pm 0.2) + (-0.242 \pm 0.052)DOC_0 + (0.138 \pm 0.041)\log K_{OW} + (-0.305 \pm 0.093)S + (0.157 \pm 0.069)V$$