Electronic Supplementary Information

Surface water treatment utilizing UV/H_2O_2 with subsequent soil aquifer treatment for drinking water purposes: Impact on Micropollutants, Dissolved Organic Matter and Biological Activity

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Table S1. Device list of online sensors and probes.

Parameter	Locations	Device	Manufacturer
UVA	Rhine river sand filtrate, after AOP	ColorPlus	SIGRIST-Photometer, Switzerland
pH, T	Rhine river sand filtrate, after AOP	CPS11D-7AS21*	Endress+Hauser, Switzerland
Turbidity	Rhine river sand filtrate	Monitor AMI Turbiwell 7027	SWAN Analytical Instruments, Switzerland
EC	Rhine river sand filtrate, after AOP		Endress+Hauser, Switzerland
H_2O_2	After AOP	AquaDMS	SIGRIST-Photometer, Switzerland
DO	Rhine river sand filtrate, after AOP	COS22D-AA1A2B22	Endress+Hauser, Switzerland
Redox	Rhine river sand filtrate, after AOP	CPS72D-7PT21**	Endress+Hauser, Switzerland
Flow	Rhine river sand filtrate, after AOP	3021 25D 72014BT41 C1	GEMÜ Gebr. Müller Apparatebau, Germany
Flow	Soil column effluents	MIK-5NA15AE34R	KOBOLD Messring, Germany

Table S2. Operational parameters of the soil columns in the test phase (November 2017 – August 2018).

Parameter	Unit	Reference column	Test column
Feed	-	Rhine river sand filtrate	AOP effluent
Flow			
Median	L/h	7.3	6.4
Standard deviation	L/h	2.6	3.2
Operating hours (flow > 0.6 L/h)			
Operating (share of 7253 h)	h	7121 (98%)	7019 (97%)
Stopped (share of 7253 h)	h	132 (2%)	234 (3%)
Number of shut downs	-	10	16
Mean duration of shut downs	h	13.2	14.6

Table S3. Operational parameters of the UV/H_2O_2 process during the test phase (November 2017 – August 2018).

Parameter	Unit	Median	Standard deviation
Flow	L/h	566	51
UV intensity	W/m^2	36.2	3.9
Residual H_2O_2	mg/L	3.6	0.7

Table S4. Selected properties of the investigated micropollutants.

Substance	CAS No.	Type	Molecular weight (Da)	k_{OH} / 10^9 [$M^{-1}s^{-1}$]	ε_{254} [$M^{-1}cm^{-1}$]	Φ_{254} [mol/einstein]	logD [-][a]	Measurement range (ng/L)	Measurement uncertainty (%)	Theoretical limit of quantification (ng/L)
Ethylendiamine Tetraacetate (EDTA)	60-00-4	Complexing agent	292.2	2.00[b,1] 0.52[c,1]	7890[d,2]	0.56[e,2]	-6.40[f]	500 – 5000	20	40
Acesulfame (ACE)	33665-90-6	Artificial sweetener	201.2	3.80±0.27[3]	~31600[g,4]	0.26[4]	-2.77	10 – 1600	11	2.2
Iopamidol (IPA)	62883-00-5	X-ray contrast media	777.1	3.42±0.28[5]	22700[6]	0.03318[6]	-2.31	10 – 500	27	5.0
Iomeprol (IME)	78649-41-9	X-ray contrast media	777.1	2.03±0.13[5]	~24000[g,7]	n.a.	-2.61	10 – 500	24	5.3
Metformin (MET)	657-24-9	Type 2 diabetes drug	129.2	1.4±0.16[8]	940±93[9]	0.014±0.0064[9]	-3.36	10 – 800	39	3.4
1H-Benzotriazole (BTZ)	95-14-7	Anti-corrosive agent	119.1	8.34±0.37[10]	5592[10]	0.012[10]	1.50	10 – 320	34	7.7
Iopromide (IPR)	73334-07-3	X-ray contrast media	791.1	3.34±0.14[5]	21040±210[11]	0.039±0.004[11]	-2.12	10 – 500	12	5.0

[a] Values for logD obtained at pH 7.4, predicted by ACD/Labs at chemspider.com. [b] For $[Fe(EDTA)]^{2-}$. [c] For $[Fe(EDTA)]^{-}$. [d] Average for all [Fe(EDTA)] species at pH 6. [e] pH 6, with 0.1 mM H_2O_2. [f] For EDTA only. [g] Value visually obtained from a plot.

Table S5. Overview on performance parameters of the applied analytical methods.

Analytical Method	Limit of quantification	Standard deviation	Measuring range
Dissolved organic carbon by LC-OCD	0.1 mg C/L	10%	0.1 – 5.0 mg C/L
H_2O_2 by titanium oxalate (photometric)	0.3 mg H_2O_2/L	5%	0.3 – 10 mg H_2O_2/L
Intact cell counts by flow cytometry	200 cells/mL	10%	10^3 – 10^6 cells/mL
ATP by luminescence	0.0004 nmol/L	30%	0.001 – 0.1 nmol/L

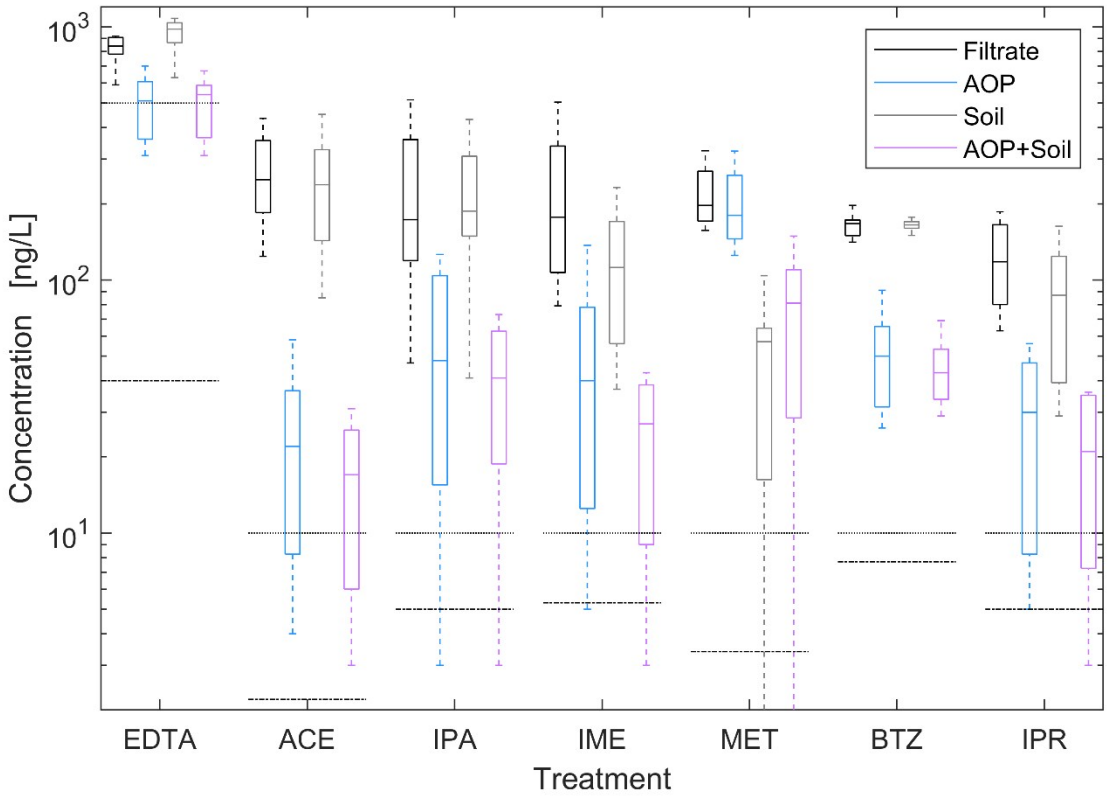

Figure S1. Concentrations of micropollutants along the treatment trains. *n* = 7 for all. Central mark of boxes: median; lower and upper edges of boxes: 25th and 75th percentiles, respectively; whiskers: minimum and maximum values. Dotted line: lowest point of calibration. Dot-stroked line: theoretical limit of quantification.

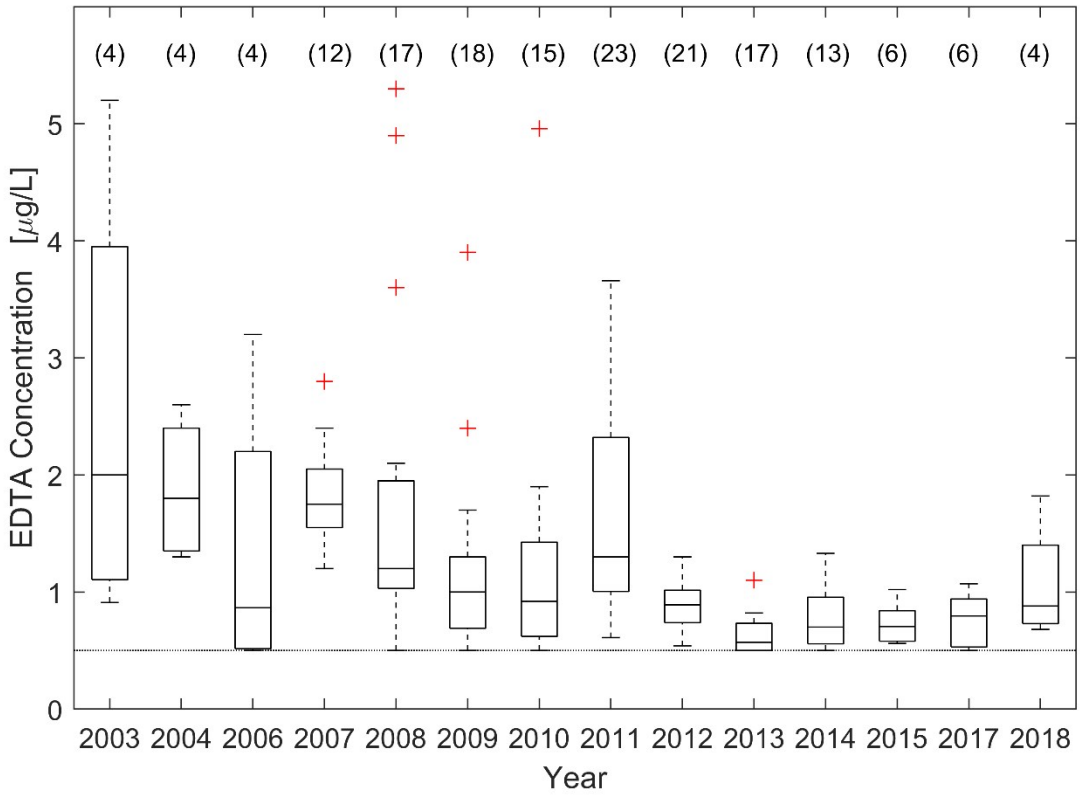

Figure S2. Concentrations of EDTA in the raw Rhine river water between 2003 and 2018. Values below the lowest point of calibration (i.e., 0.5 µg/L) are reported as 0.5 µg/L. *n* indicated in brackets for the respective year. Central mark of boxes: median; left and right edges of boxes: 25th and 75th percentiles, respectively; whiskers: minimum and maximum values. Outliers, i.e., values outside ±2.7 standard deviations from median (99.3% coverage of normally distributed data), marked as a red cross. Dotted line: lowest point of calibration. Data from monitoring measurements by iwb.

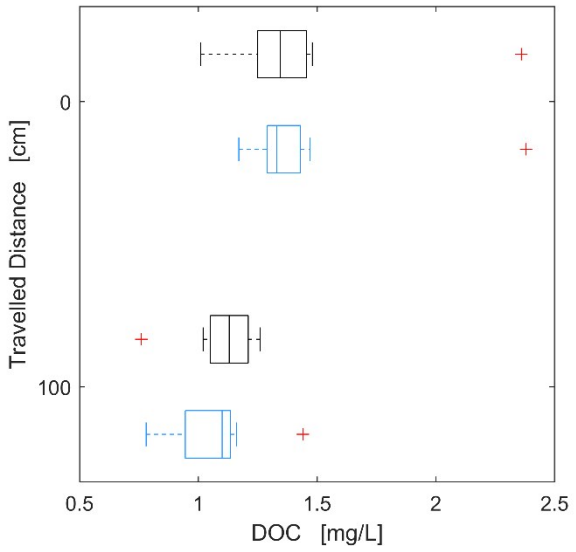

Figure S3. DOC concentrations along the soil columns, receiving Rhine river sand filtrate (black) and UV/H_2O_2 treated water (blue). *n* = 8 for all. Central mark of boxes: median; left and right edges of boxes: 25th and 75th percentiles, respectively; whiskers: minimum and maximum values. Outliers, i.e., values outside ±2.7 standard deviations from median (99.3% coverage of normally distributed data), marked as a red cross. No statistically significant differences were detected between the groups at the influents (0 cm) and effluents (100 cm) of the columns.

Table S6. Overview on the evaluation by categories of the dissolved organic matter (*n* = 8, November 2017 – August 2018), median values ± sample standard deviations.

Treatment	DOC [mg/L]	Chrom. DOC [mg/L]	Biopolymers [mg/L]	Humic Substances [mg/L]	HS Peak Maximum [min]	Building Blocks [mg/L]	LMW A+N [mg/L]
Filtrate	1.3±0.4	1.2±0.4	0.1±0.0	0.8±0.1	43.9±0.5	0.2±0.0	0.1±0.1
AOP	1.3±0.4	1.2±0.4	0.1±0.0	0.9±0.1	44.5±0.5	0.2±0.1	0.2±0.1
Soil	1.1±0.2	1.1±0.2	0.0±0.0	0.7±0.1	43.8±0.5	0.2±0.0	0.1±0.0
AOP + Soil	1.1±0.2	1.1±0.2	0.0±0.0	0.8±0.1	44.2±0.5	0.2±0.0	0.1±0.0

Chrom. DOC: chromatographic DOC. HS: Humic Substances. LMW A+N: low molecular weight acids and neutrals. Differences between results from chromatographic DOC and the distinct fractions are caused by rounding inaccuracies.

Table S7. p values of paired t-tests of the day-wise evaluation by categories of the dissolved organic matter (*n* = 8, November 2017 – August 2018).

DOC	Filtrate	AOP	Soil	AOP + Soil
Filtrate	-	0.6851	0.0195	0.0302
AOP	0.6851	-	0.0236	0.0344
Soil	0.0195	0.0236	-	0.6636
AOP + Soil	0.0302	0.0344	0.6636	-
Chrom. DOC				
Filtrate	-	0.4036	0.0240	0.0597
AOP	0.4036	-	0.0237	0.0508
Soil	0.0240	0.0237	-	0.8611
AOP + Soil	0.0597	0.0508	0.8611	-
Biopolymers				
Filtrate	-	0.1991	0.0014	0.0024
AOP	0.1991	-	0.0001	0.0002
Soil	0.0014	0.0001	-	0.1803
AOP + Soil	0.0024	0.0002	0.1803	-
Humic Substances				
Filtrate	-	0.3847	0.0002	0.0068
AOP	0.3847	-	0.0215	0.0129
Soil	0.0002	0.0215	-	0.3135
AOP + Soil	0.0068	0.0129	0.3135	-
HS peak maximum				
Filtrate	-	0.3516	0.0013	0.0454
AOP	0.3516	-	0.0015	0.0303
Soil	0.0013	0.0015	-	0.1575
AOP + Soil	0.0454	0.0303	0.1575	-
Building Blocks				
Filtrate	-	0.4234	0.0108	0.0272
AOP	0.4234	-	0.3653	0.3710
Soil	0.0108	0.3653	-	0.7110
AOP + Soil	0.0272	0.3710	0.7110	-

Table S7 (continued). p values of paired t-tests of the day-wise evaluation by categories of the dissolved organic matter.

LMW A+N				
Filtrate	-	0.2454	0.1910	0.2381
AOP	0.2454	-	0.0654	0.0851
Soil	0.1910	0.0654	-	0.7799
AOP + Soil	0.2381	0.0851	0.7799	-

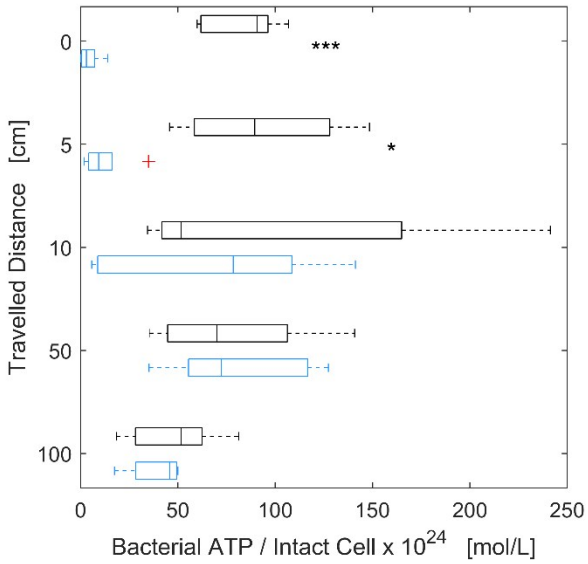

Figure S4. Bacterial ATP per intact cell in the water phase along the soil columns, receiving Rhine river sand filtrate (black) and UV/H_2O_2 treated water (blue). *n* = 5 for all, except *n* = 4 for Rhine river sand filtrate after 5 cm travelled distance. Central mark of boxes: median; left and right edges of boxes: 25th and 75th percentiles, respectively; whiskers: minimum and maximum values. Outliers, i.e., values outside ±2.7 standard deviations from median (99.3% coverage of normally distributed data), marked as a red cross. Significant differences between groups in paired two-sided t-tests are marked with "⌦" and "⌦⌦⌦" for $p < 0.05$ and $p < 0.001$, respectively.

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