Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.

Supplementary information

Step-by-step analysis of drinking water treatment trains using size-exclusion chromatography to fingerprint and track protein-like and humic/fulvic-like fractions of dissolved organic matter

Alexey Ignatev, Tuula Tuhkanen

Department of Biological and Environmental Science, University of Jyväskylä

PO Box 35, FI-40014, Jyväskylä, Finland

alexey.n.ignatev@jyu.fi, alexignat@gmail.com (A. Ignatev)

tuula.a.tuhkanen@jyu.fi (T. Tuhkanen)

Table of contents

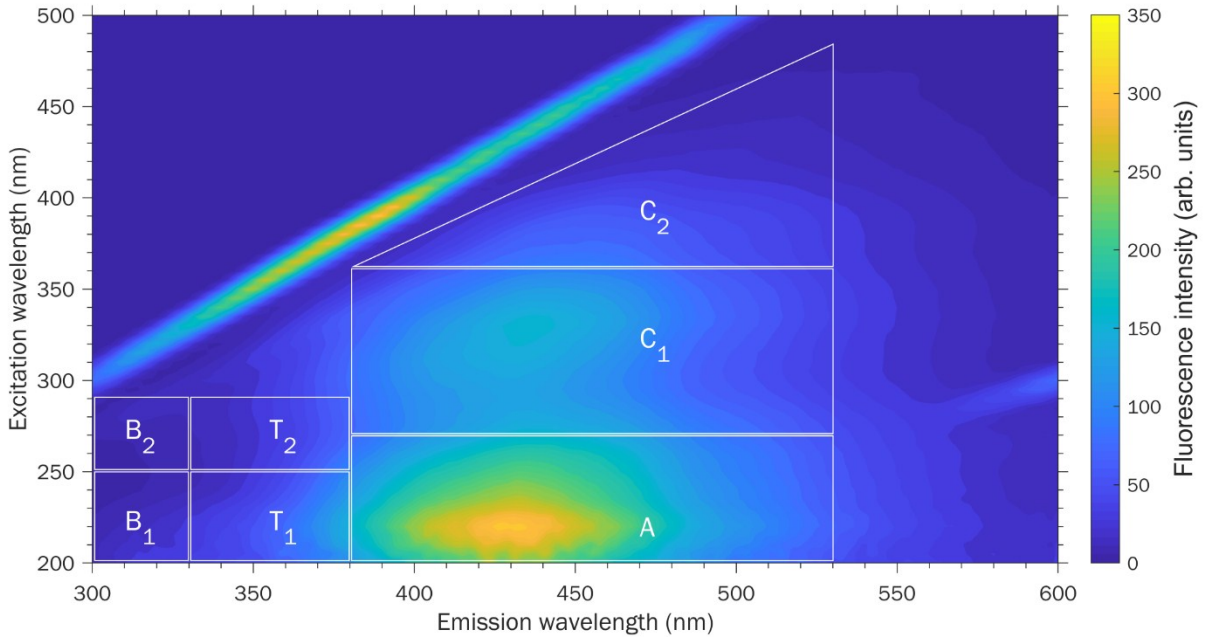

Fig. S1. Typical EEM fluorescence spectrum of a raw water (sampled from lake Päijänne, Finland, on 10.07.2018). Regions corresponding to tyrosine-like (B_1, B_2), tryptophan-like (T_1, T_2) and humic/fulvic-like (A, C_1, C_2) fluorescence are indicated with white triangles.

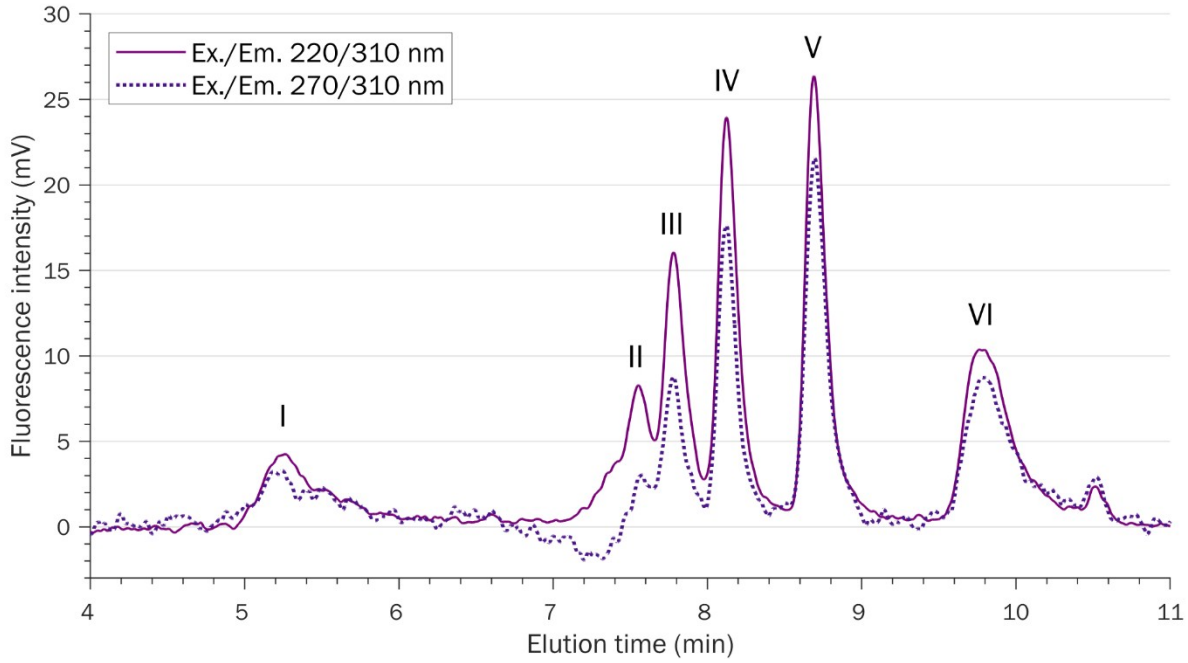

Fig. S2. Comparison of HPSEC chromatograms demonstrating influence of excitation wavelength on intensity of tyrosine-like fluorescence (emission at 310 nm) of a raw water (sampled from lake Konnevesi, Finland, on 14.03.2017). Overlapping with Raman scatter peak of water led to higher noise of fluorescence signal at 270/310 nm compared to 220/310 nm (note degraded peak II).

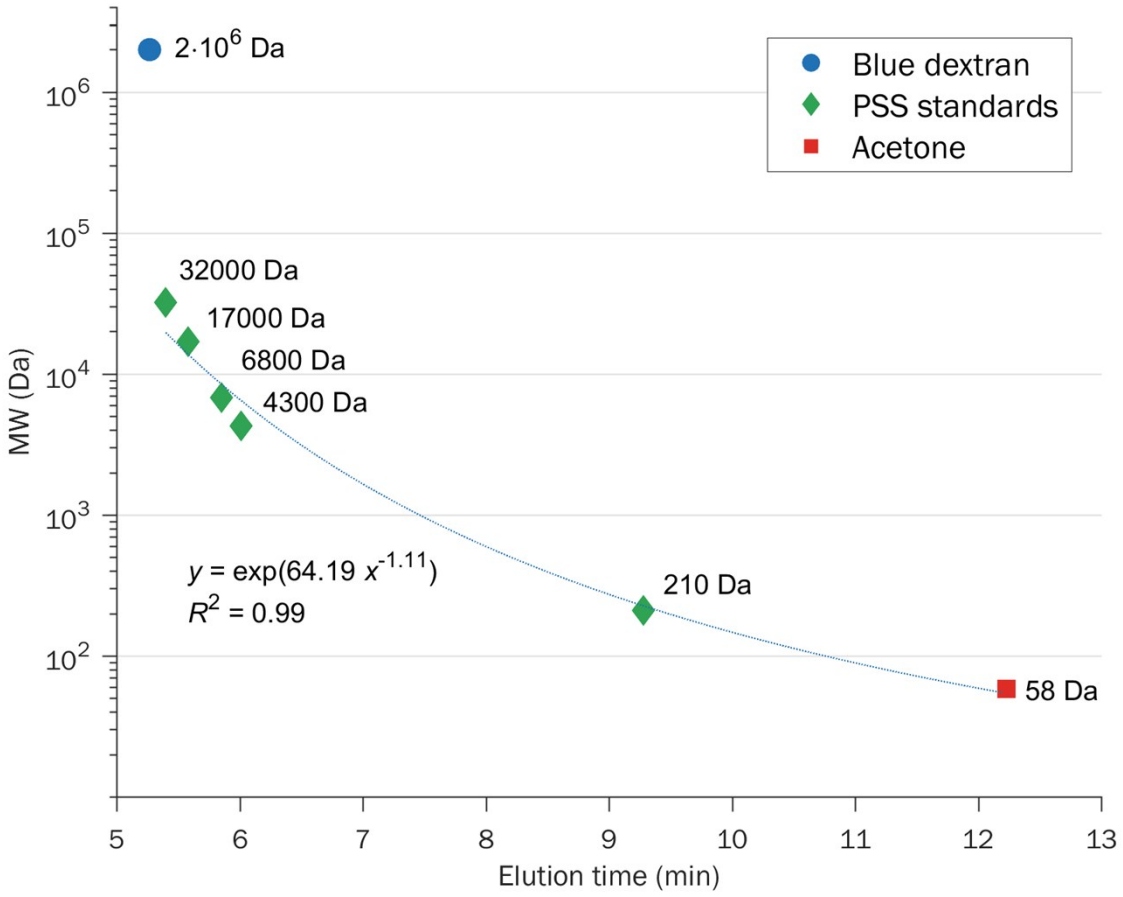

Fig. S3. Calibration of the size-exclusion column using acetone, polystyrene sulphonate (PSS) standards, and blue dextran. The fitting equation was used to calculate apparent MW of DOM fractions and estimate M_W and M_N.

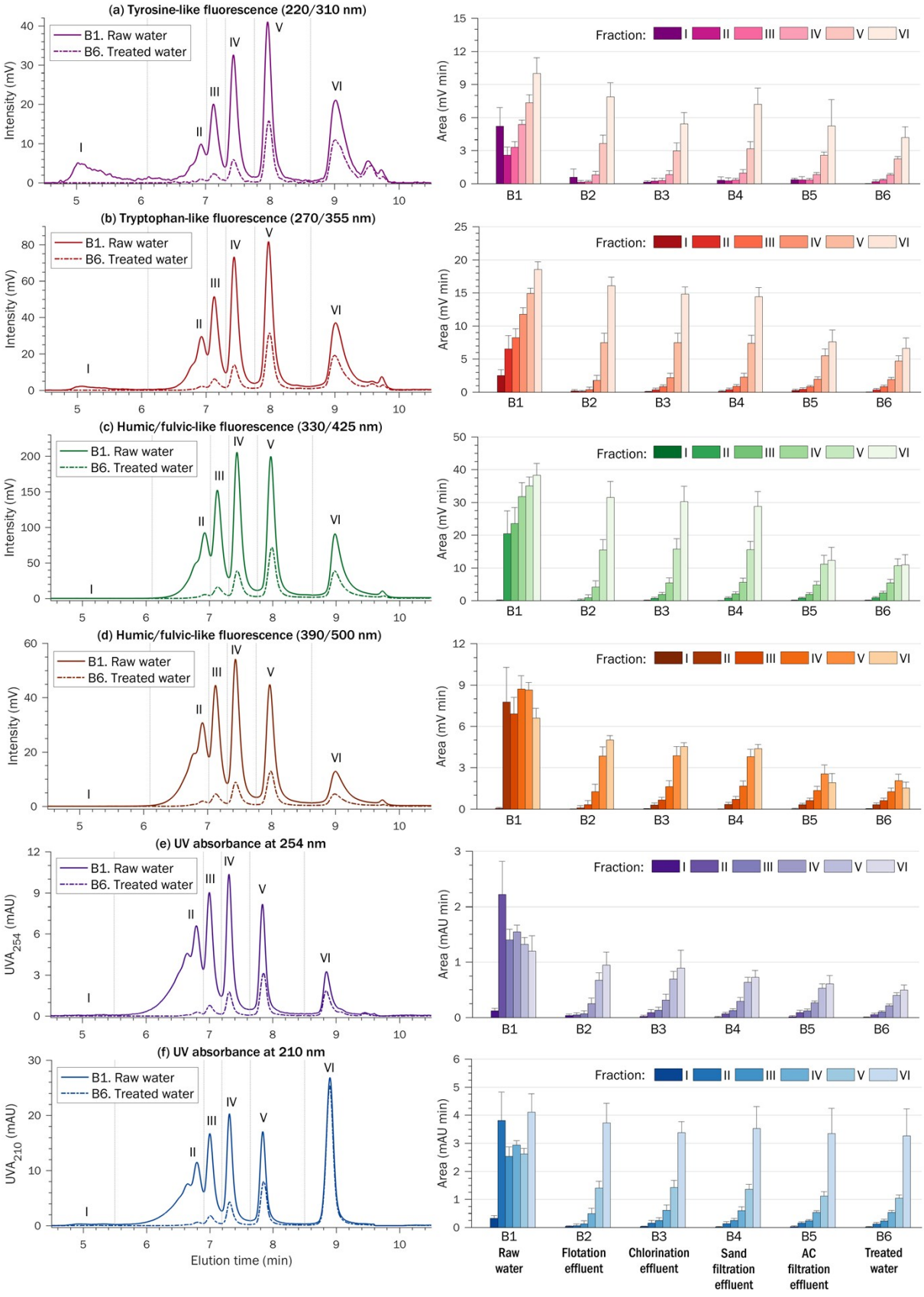

Fig. S4. Characterization of DOM at DWTP B. Left column: superimposed HPSEC chromatograms of raw water and treated water with (a)-(d) fluorescence and (e)-(f) UV detection. Right column: evolution of DOM fractions I-VI along the water treatment train (mean area ± SD, n = 4).

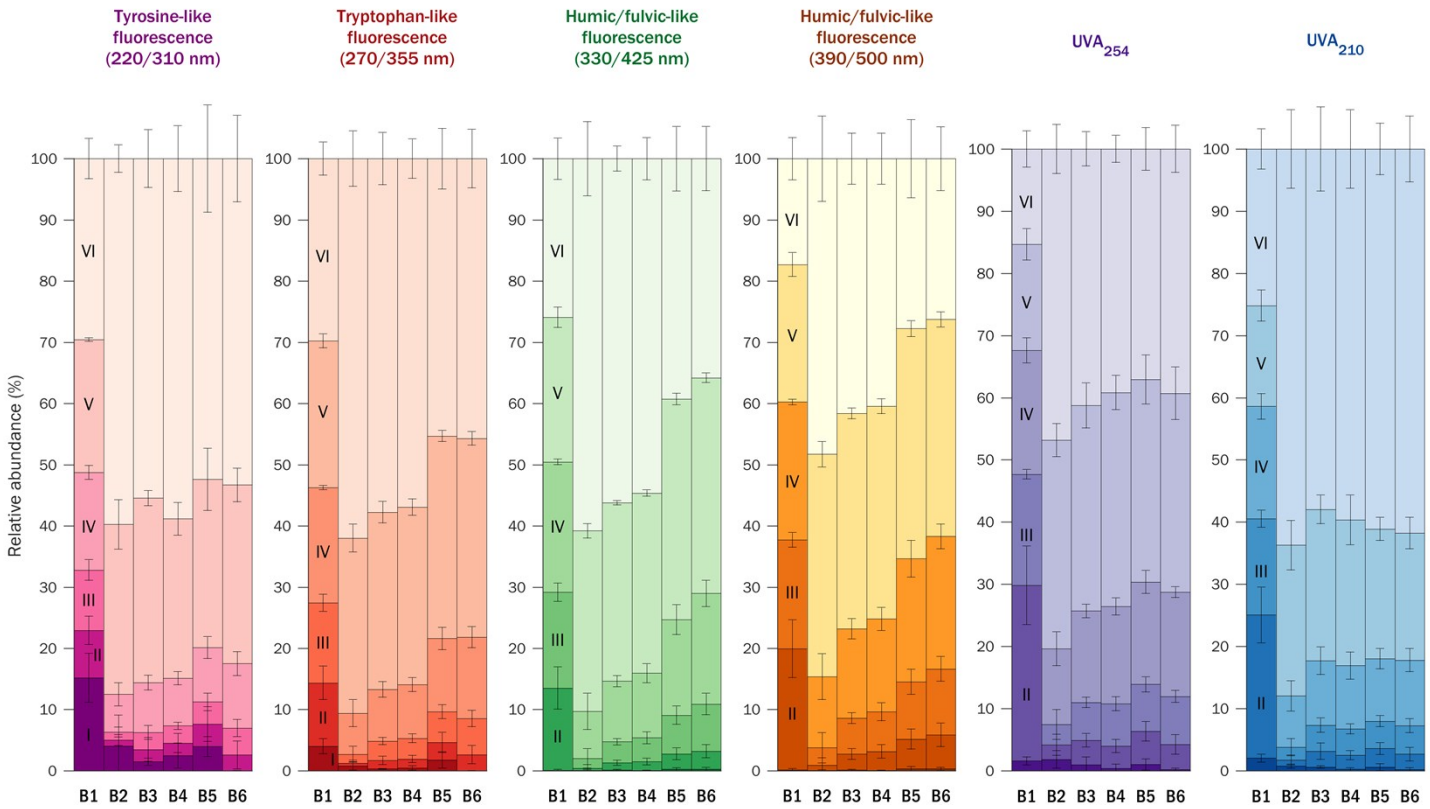

Fig. S5. Relative abundance of fluorescing and UV absorbing DOM fractions I-VI in raw water (B1), process water (B2-B5), and treated water (B6) at DWTP B (mean ± SD, n = 4). Locations of sampling points B1-B6 are shown in Fig.1.

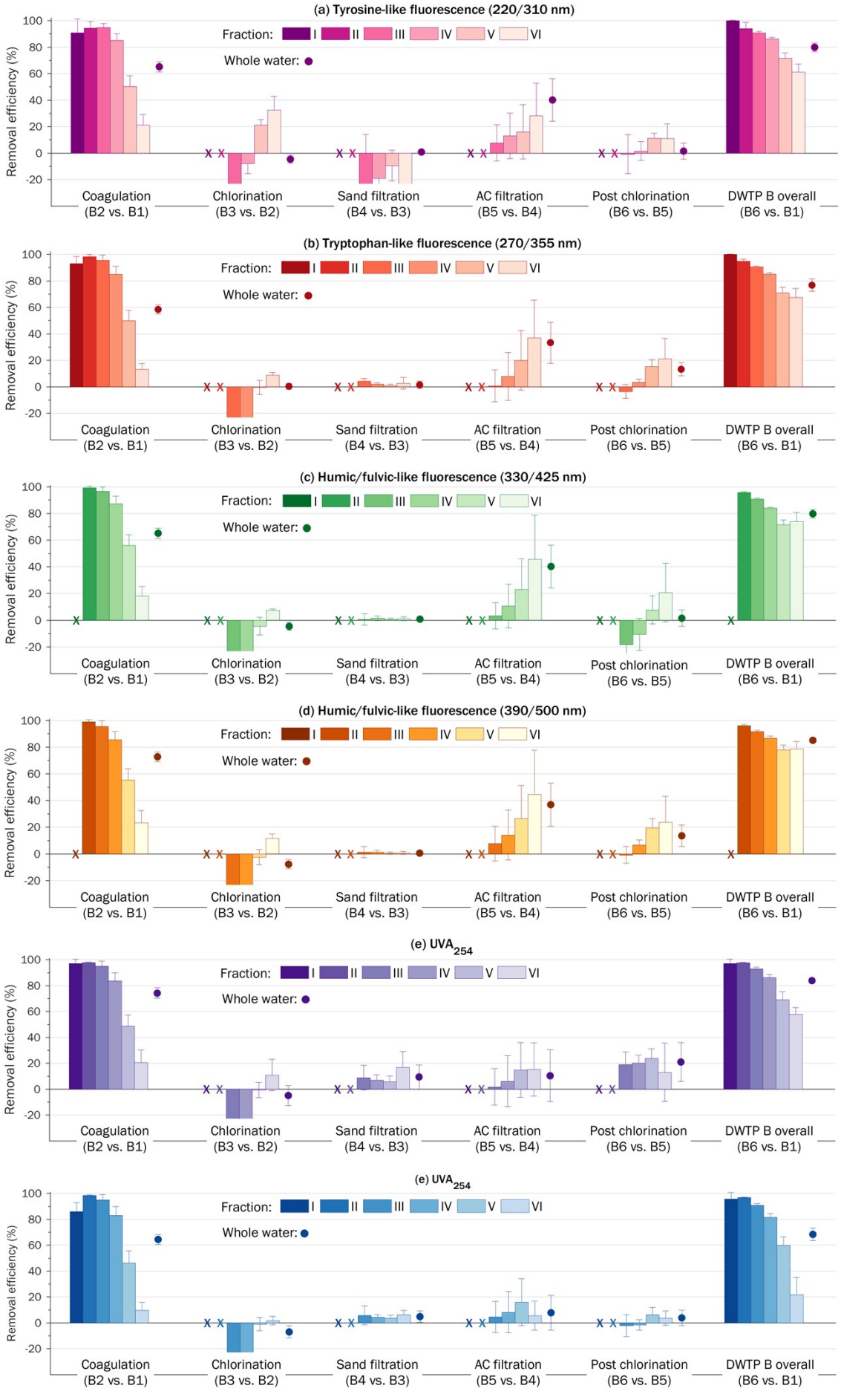
(a) Tyrosine-like fluorescence (220/310 nm)
(b) Tryptophan-like fluorescence (270/355 nm)
(c) Humic/fulvic-like fluorescence (330/425 nm)
(d) Humic/fulvic-like fluorescence (390/500 nm)
(e) UVA254
(e) UVA254
Fraction: I II III IV V VI
Whole water:
Removal efficiency (%)
100
80
60
40
20
0
-20
Coagulation (B2 vs. B1)
Chlorination (B3 vs. B2)
Sand filtration (B4 vs. B3)
AC filtration (B5 vs. B4)
Post chlorination (B6 vs. B5)
DWTP B overall (B6 vs. B1)

Fig. S6. Step-by-step, fraction-by-fraction, and overall efficiency of DWTP B (mean ± SD, $n = 4$). Absent or removed fractions are denoted with 'X'. Negative removal efficiencies indicate formation of DOM (during chlorination)

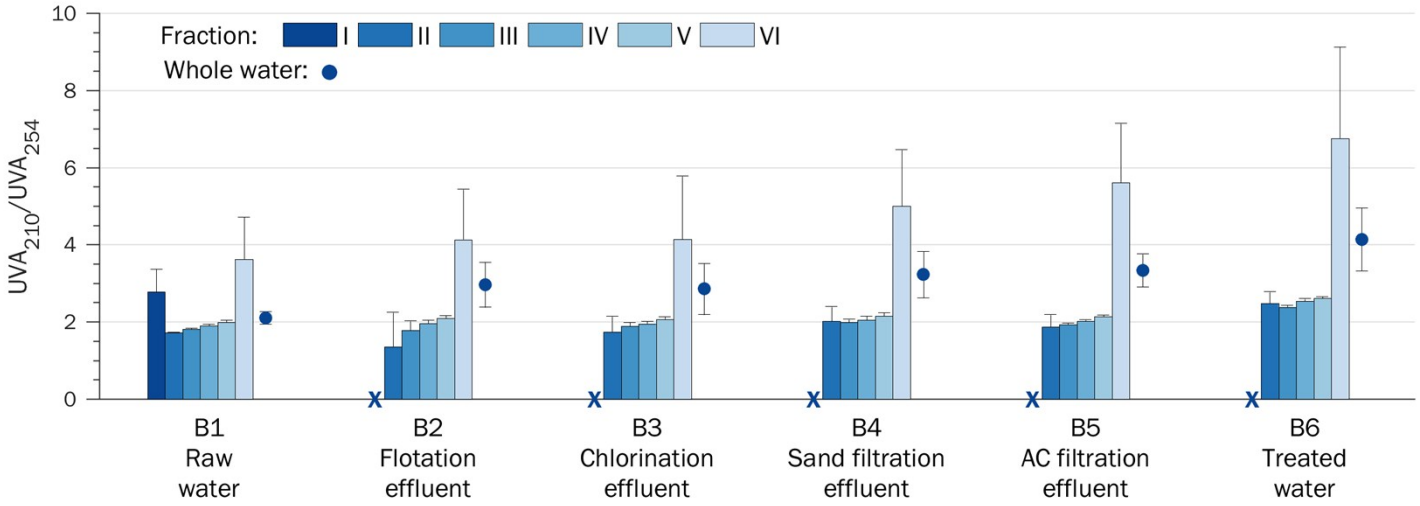

Fig. S7. Ratio UVA_{210}/UVA_{254} of DOM fractions and whole water samples from DWTP B (mean ± SD, $n = 4$). Lower values indicate higher aromatic character. Removed in the coagulation/flocculation high MW fraction I is denoted with "X".

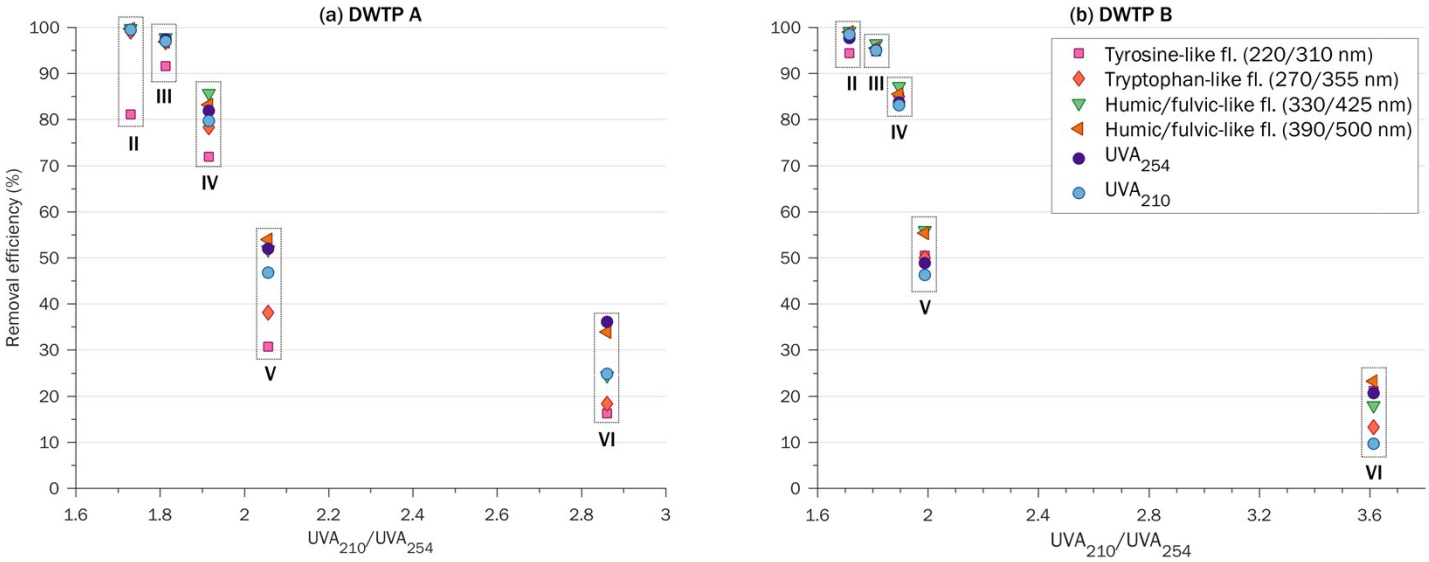

Fig. S8. Correlation between removal efficiencies by coagulation and ratio UVA_{210}/UVA_{254} of DOM fractions II-VI for (a) DWTP A and (b) DWTP B.

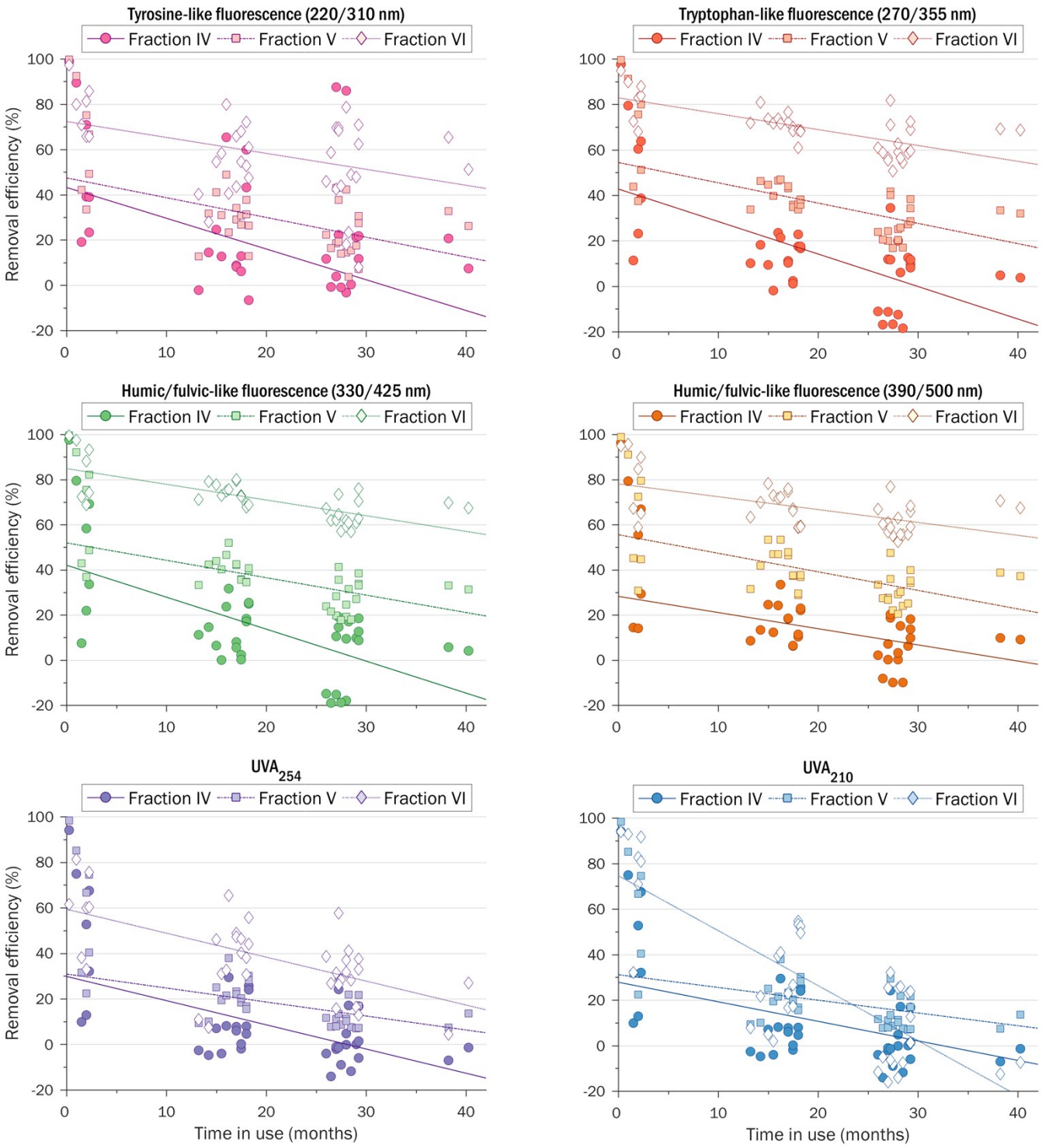

Fig. S9. Decline of AC filtration efficiency at DWTP A over time in regards to removal of fluorescing and UV absorbing DOM fractions IV-VI. Each point represents a single sample of AC filtration effluent collected from one of the eight parallel AC tanks. The linear trend lines were calculated using robust regression (MATLAB *robustfit*, bisquare weight function), ρ is Pearson correlation coefficient (n = 38).

Table S1. Main parameters of the HPSEC-UV-fluorescence method.

Eluent flow rate	1 mL min^{-1}
Injection volume	50 µL
Autosampler temperature	4 °C
Column oven temperature	25 °C
Elution time	30 min
PDA detector	
Wavelength range	200-400 nm
Cell temperature	40 °C
Slit width	1.2 nm
Data acquisition rate	4.17 Hz
Fluorescence detector	
$\lambda_{ex}/\lambda_{em}$	220/310 nm (tyrosine-like) 270/355 nm (tryptophan-like) 330/425 nm (humic/fulvic-like) 390/500 nm (humic/fulvic-like)
Cell temperature	25 °C
Sensitivity	High
Gain	1×
Data acquisition rate	5.00 Hz

Table S2. Water quality parameters at DWTP A in 2017 (*n* is the total number of analyses of raw and treated waters).*

	Raw water (A1)			Treated water (A7)			*n*
	Mean	Min	Max	**Mean**	Min	Max	(raw/treated)
Temperature (°C)	**10.3**	2.2	18.3	**10.2**	3.6	15.0	51/24
pH	**7.3**	7.8	7.0	**8.4**	8.1	9.0	51/111
Alkalinity (mmol L^{-1})	**0.46**	0.41	0.49	**0.63**	0.56	0.72	12/12
Hardness (mmol L^{-1})	**0.22**	0.22	0.22	**0.40**	0.39	0.42	12/12
Turbidity (FNU)	**2.2**	1.4	3.8	**0.09**	0.05	0.11	51/84
Conductivity (mS/m)	**7.1**	6.3	10.9	**12.1**	11.7	14.3	51/75
TOC (mg L^{-1})	**6.8**	6.3	7.7	**1.8**	1.6	2.5	12/12
NH_4-N (µg L^{-1})	***n.d.***	*n.d.*	*n.d.*	**0.11**	0.08	0.14	0/12
Cl_2 (mg L^{-1})	***n.d.***	*n.d.*	*n.d.*	**0.34**	0.19	0.41	0/120
Al (mg L^{-1})	**0.00**	0.00	0.00	**0.02**	0.00	0.06	3/48
Fe (mg L^{-1})†	**0.197**	0.197	0.197	**0.005**	0.000	0.023	3/24
Mn (mg L^{-1})‡	**0.085**	0.085	0.085	**0.003**	0.000	0.009	3/24

* The data were provided by DWTP A.
† In 2018, the concentration of Fe was 0.158 mg L^{-1}.
‡ In 2018, the concentration of Mn was 0.176 mg L^{-1}.

Table S3. Water quality parameters measured at DWTP B in 2017 (*n* is the total number of analyses of raw and treated waters).*

	Raw water (B1)			Treated water (B6)			*n*
	Mean	Min	Max	**Mean**	Min	Max	(raw/treated)
Temperature (°C)	**7.8**	0.5	18.7	**8.0**	0.8	19.0	249/249
pH	**7.2**	6.9	7.7	**8.2**	7.9	8.5	248/249
Alkalinity (mmol L^{-1})	**0.28**	0.26	0.29	**0.69**	0.61	0.76	54/249
Hardness (°dH)	**1.1**	1.0	1.2	**3.4**	3.2	3.6	52/52
Hardness (mmol L^{-1})	**0.20**	0.18	0.21	**0.61**	0.57	0.64	52/52
Turbidity (NTU)	**2.1**	0.27	11	**0.05**	0.03	0.09	249/249
Conductivity (mS/m)	**6.3**	6.1	6.5	**15.1**	14.7	15.5	51/51
UVA_{254} (AU)	**0.139**	0.128	0.159	**0.024**	0.013	0.30	22/20
TOC (mg L^{-1})	**6.1**	5.8	6.3	**2.2**	1.6	2.7	51/248
Total N (µg L^{-1})	**350**	310	380	**170**	110	220	6/6
NH_4-N (µg L^{-1})	**7**	2	15	**2**	2	3	7/7
NO_3-N (mg L^{-1})	**< 0.10**	< 0.10	< 0.10	**< 0.10**	< 0.10	< 0.10	7/7
NO_2-N (mg L^{-1})	**< 1**	< 1	1	**< 1**	< 1	< 1	7/7
Total P (µg L^{-1})	**14**	10	18	**< 3**	< 2	6	8/8
Cl_2 (mg L^{-1})	***n.d.***	*n.d.*	*n.d.*	**0.44**	0.38	0.50	0/249
Al (mg L^{-1})	**< 0.03**	< 0.02	0.07	**< 0.02**	< 0.02	0.03	7/8
Fe (mg L^{-1})	**< 0.10**	< 0.02	0.25	**< 0.02**	< 0.02	< 0.02	52/248
Mn (mg L^{-1})	**< 0.03**	< 0.01	0.05	**< 0.01**	< 0.01	< 0.01	7/48

* The data are published online at https://www.tampere.fi/material/attachments/vesi/vesi/bOKLI2SYl/Ruskon_kayttotarkkailu_2017.pdf.

Table S4. Characteristics of whole water at different steps of DWTP B (mean ± SD, n = 4).

	B1 Raw water	B2 Flotation effluent	B3 Chlorination effluent	B4 Sand filtration effluent	B5 AC filtration effluent	B6 Treated water
DOC (mg L^{-1})	6.3 ± 0.5	2.7 ± 0.2	2.7 ± 0.1	2.7 ± 0.2	2.3 ± 0.3	2.3 ± 0.2
SUVA (L mg^{-1} m^{-1})	2.5 ± 0.3	1.5 ± 0.4	1.6 ± 0.5	1.4 ± 0.2	1.4 ± 0.3	1.1 ± 0.2
UVA_{210}/UVA_{254}	2.1 ± 0.2	2.9 ± 0.6	2.8 ± 0.5	2.9 ± 0.5	3.5 ± 0.5	4.1 ± 0.6
Total UV absorbance (mAU min)						
254 nm	7.8 ± 0.8	2.0 ± 0.5	2.1 ± 0.7	1.9 ± 0.3	1.6 ± 0.3	1.3 ± 0.2
210 nm	16.3 ± 1.4	5.9 ± 1.0	5.9 ± 0.7	5.9 ± 0.9	5.4 ± 1.1	5.2 ± 1.1
Total fluorescence (mV min)						
Tyrosine-like (220/310 nm)	33.8 ± 3.1	13.2 ± 2.5	9.9 ± 2.6	12.3 ± 2.6	9.7 ± 2.9	7.8 ± 1.0
Tryptophan-like (270/355 nm)	62.5 ± 5.4	26.1 ± 3.3	25.8 ± 3.5	25.5 ± 3.5	16.7 ± 2.7	14.5 ± 2.5
Humic/fulvic-like (330/425 nm)	149.3 ± 19.1	52.2 ± 8.9	54.0 ± 10.1	52.8 ± 8.3	31.1 ± 7.6	30.3 ± 6.1
Humic/fulvic-like (390/500 nm)	38.7 ± 4.4	10.6 ± 1.5	11.0 ± 1.7	10.9 ± 1.3	6.8 ± 1.6	5.8 ± 1.2

Table S5a. Number average MW DWTP A (mean ± SD, $n = 3$).

	A1 Raw water	A2 Ozonation effluent	A3 Flotation effluent	A4 Sand filtration effluent	A5 Chlorination effluent	A6 AC filtration effluent	A7 Treated water
UV detection							
254 nm	803 ± 99	788 ± 49	460 ± 60	395 ± 71	411 ± 64	428 ± 37	467 ± 42
210 nm	789 ± 60	735 ± 46	411 ± 31	386 ± 25	386 ± 18	380 ± 13	371 ± 13
Fluorescence detection							
Tyrosine-like (220/310 nm)	433 ± 32	442 ± 42	327 ± 36	318 ± 34	316 ± 38	349 ± 45	342 ± 39
Tryptophan-like (270/355 nm)	474 ± 46	497 ± 46	329 ± 36	317 ± 35	317 ± 38	381 ± 42	373 ± 42
Humic/fulvic-like (330/425 nm)	513 ± 58	576 ± 56	336 ± 39	326 ± 39	332 ± 40	412 ± 43	406 ± 44
Humic/fulvic-like (390/500 nm)	605 ± 58	657 ± 60	375 ± 45	359 ± 42	367 ± 44	442 ± 46	435 ± 50

Table S5b. Weight average MW DWTP A (mean ± SD, $n = 3$).

	A1 Raw water	A2 Ozonation effluent	A3 Flotation effluent	A4 Sand filtration effluent	A5 Chlorination effluent	A6 AC filtration effluent	A7 Treated water
UV detection							
254 nm	1398 ± 98	1486 ± 359	609 ± 88	567 ± 60	610 ± 42	705 ± 107	653 ± 29
210 nm	1378 ± 104	1377 ± 283	573 ± 44	528 ± 38	576 ± 29	573 ± 44	550 ± 38
Fluorescence detection							
Tyrosine-like (220/310 nm)	925 ± 143	912 ± 141	547 ± 79	500 ± 48	500 ± 25	605 ± 63	509 ± 43
Tryptophan-like (270/355 nm)	850 ± 37	896 ± 117	463 ± 53	435 ± 29	428 ± 41	520 ± 42	522 ± 37
Humic/fulvic-like (330/425 nm)	857 ± 45	965 ± 148	463 ± 51	438 ± 46	451 ± 45	556 ± 32	558 ± 33
Humic/fulvic-like (390/500 nm)	996 ± 46	1114 ± 190	525 ± 61	494 ± 46	507 ± 43	601 ± 38	603 ± 33

Table S5c. Dispersities DWTP A (mean ± SD, $n = 3$).

	A1 Raw water	A2 Ozonation effluent	A3 Flotation effluent	A4 Sand filtration effluent	A5 Chlorination effluent	A6 AC filtration effluent	A7 Treated water
UV detection							
254 nm	1.76 ± 0.27	1.88 ± 0.42	1.32 ± 0.03	1.45 ± 0.20	1.50 ± 0.22	1.67 ± 0.41	1.41 ± 0.14
210 nm	1.76 ± 0.22	1.87 ± 0.29	1.39 ± 0.06	1.37 ± 0.08	1.50 ± 0.14	1.51 ± 0.16	1.48 ± 0.14
Fluorescence detection							
Tyrosine-like (220/310 nm)	2.16 ± 0.44	2.08 ± 0.38	1.68 ± 0.22	1.58 ± 0.22	1.59 ± 0.13	1.76 ± 0.33	1.49 ± 0.06
Tryptophan-like (270/355 nm)	1.81 ± 0.20	1.81 ± 0.24	1.41 ± 0.10	1.38 ± 0.06	1.35 ± 0.03	1.37 ± 0.04	1.40 ± 0.06
Humic/fulvic-like (330/425 nm)	1.68 ± 0.14	1.68 ± 0.21	1.38 ± 0.07	1.34 ± 0.05	1.36 ± 0.03	1.36 ± 0.06	1.38 ± 0.07
Humic/fulvic-like (390/500 nm)	1.66 ± 0.15	1.70 ± 0.25	1.40 ± 0.07	1.38 ± 0.07	1.38 ± 0.04	1.36 ± 0.05	1.39 ± 0.09

Table S6a. Number average MW DWTP B (mean ± SD, $n = 4$).

	B1 Raw water	B2 Flotation effluent	B3 Chlorination effluent	B4 Sand filtration effluent	B5 AC filtration effluent	B6 Treated water
UV detection						
254 nm	766 ± 88	384 ± 34	413 ± 34	415 ± 34	444 ± 37	440 ± 27
210 nm	593 ± 44	321 ± 15	339 ± 20	339 ± 20	333 ± 21	334 ± 20
Fluorescence detection						
Tyrosine-like (220/310 nm)	442 ± 10	295 ± 15	314 ± 16	303 ± 31	339 ± 36	332 ± 22
Tryptophan-like (270/355 nm)	460 ± 5	293 ± 14	311 ± 12	311 ± 9	355 ± 32	357 ± 27
Humic/fulvic-like (330/425 nm)	506 ± 20	302 ± 20	320 ± 10	326 ± 13	379 ± 27	398 ± 26
Humic/fulvic-like (390/500 nm)	586 ± 23	331 ± 27	361 ± 13	368 ± 16	436 ± 37	449 ± 31

Table S6b. Weight average MW DWTP B (mean ± SD, $n = 4$).

	B1 Raw water	B2 Flotation effluent	B3 Chlorination effluent	B4 Sand filtration effluent	B5 AC filtration effluent	B6 Treated water
UV detection						
254 nm	1348 ± 82	598 ± 95	655 ± 71	662 ± 36	692 ± 64	679 ± 37
210 nm	1160 ± 92	437 ± 46	497 ± 57	501 ± 33	500 ± 84	484 ± 44
Fluorescence detection						
Tyrosine-like (220/310 nm)	859 ± 164	413 ± 51	455 ± 36	445 ± 59	526 ± 79	501 ± 55
Tryptophan-like (270/355 nm)	790 ± 60	392 ± 33	444 ± 20	446 ± 16	519 ± 50	520 ± 45
Humic/fulvic-like (330/425 nm)	818 ± 46	397 ± 43	448 ± 22	459 ± 26	536 ± 40	571 ± 41
Humic/fulvic-like (390/500 nm)	944 ± 60	451 ± 55	529 ± 27	540 ± 30	630 ± 51	656 ± 44

Table S6c. Dispersities DWTP B (mean ± SD, $n = 4$).

	B1 Raw water	B2 Flotation effluent	B3 Chlorination effluent	B4 Sand filtration effluent	B5 AC filtration effluent	B6 Treated water
UV detection						
254 nm	1.78 ± 0.25	1.58 ± 0.36	1.59 ± 0.24	1.60 ± 0.14	1.57 ± 0.23	1.54 ± 0.05
210 nm	1.96 ± 0.15	1.36 ± 0.12	1.46 ± 0.11	1.48 ± 0.06	1.50 ± 0.17	1.45 ± 0.05
Fluorescence detection						
Tyrosine-like (220/310 nm)	1.94 ± 0.34	1.39 ± 0.11	1.45 ± 0.05	1.46 ± 0.05	1.55 ± 0.21	1.51 ± 0.11
Tryptophan-like (270/355 nm)	1.72 ± 0.14	1.34 ± 0.05	1.43 ± 0.02	1.43 ± 0.02	1.46 ± 0.04	1.46 ± 0.04
Humic/fulvic-like (330/425 nm)	1.62 ± 0.09	1.31 ± 0.05	1.40 ± 0.03	1.41 ± 0.03	1.41 ± 0.04	1.44 ± 0.04
Humic/fulvic-like (390/500 nm)	1.61 ± 0.11	1.36 ± 0.06	1.47 ± 0.05	1.47 ± 0.03	1.45 ± 0.07	1.46 ± 0.04