

Supplementary information

Photo-transformation of Effluent Organic Matter by ZnO-based Sunlight Irradiation

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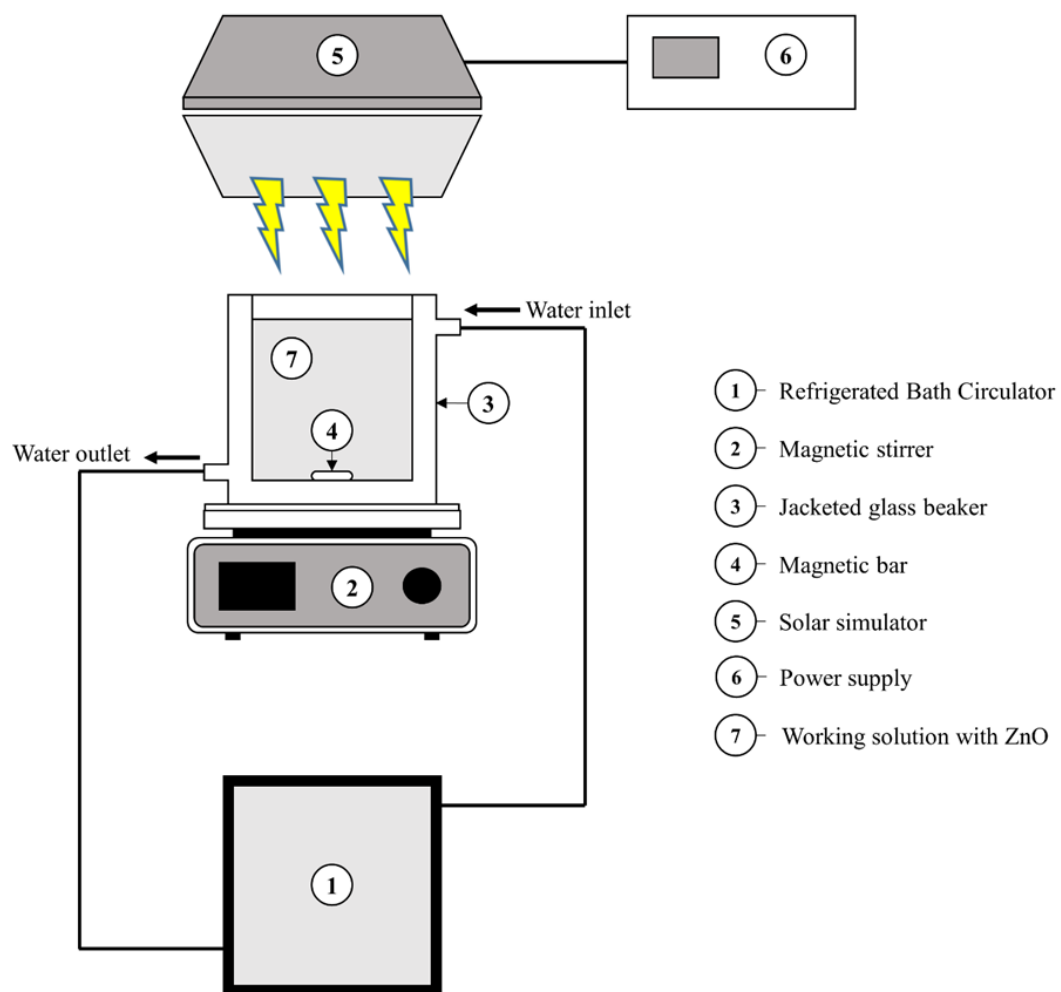
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Figure S1. Experimental setup for the sunlight-induced photocatalytic degradation of organic matter present in receiving waters using ZnO as a photocatalyst.

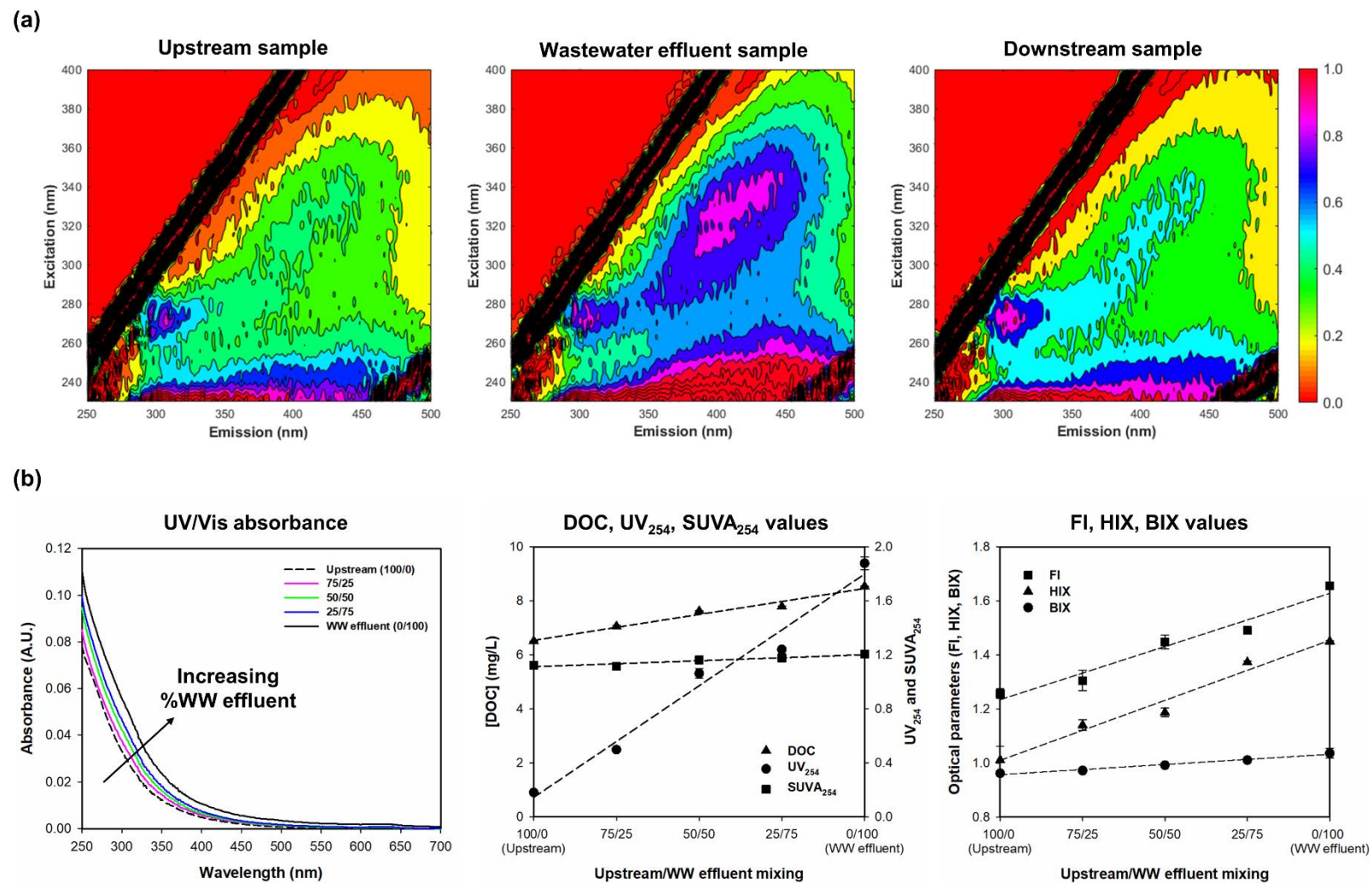


Figure S2. The UV/Vis absorption and EEM fluorescence spectrum for upstream, wastewater effluent, and downstream samples: (a) Fluorescence EEM spectra and (b) Changes in UV/Vis absorption spectra, DOC, UV_{254} , $SUVA_{254}$, FI, HIX, and BIX during the mixing between upstream and wastewater effluent (WW effluent).

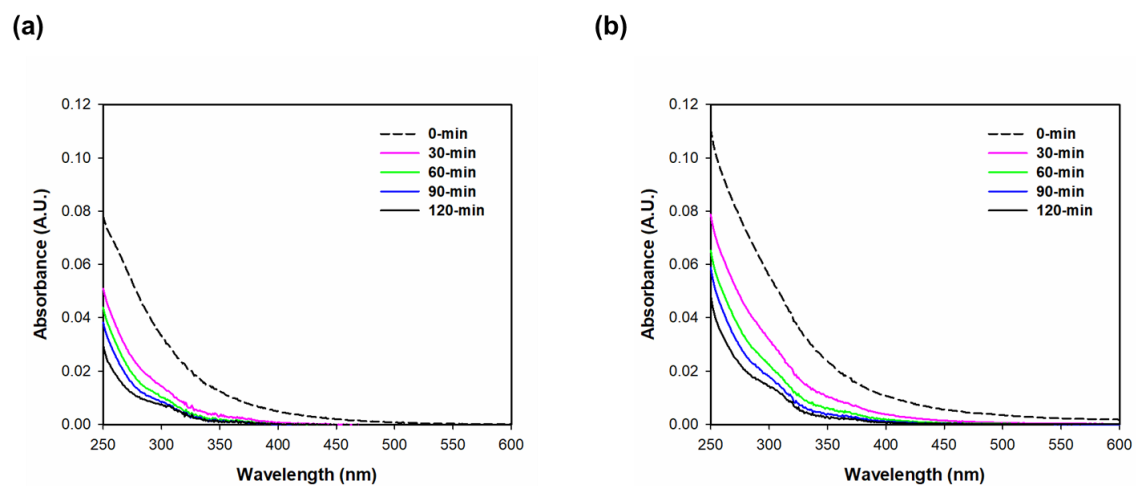


Figure S3. Changes of UV/Vis spectra during the photocatalytic degradation of organic matter with 0.2 g/L of ZnO dosage at pH 7: (a) DOM (upstream sample), and (b) EfOM (wastewater effluent).

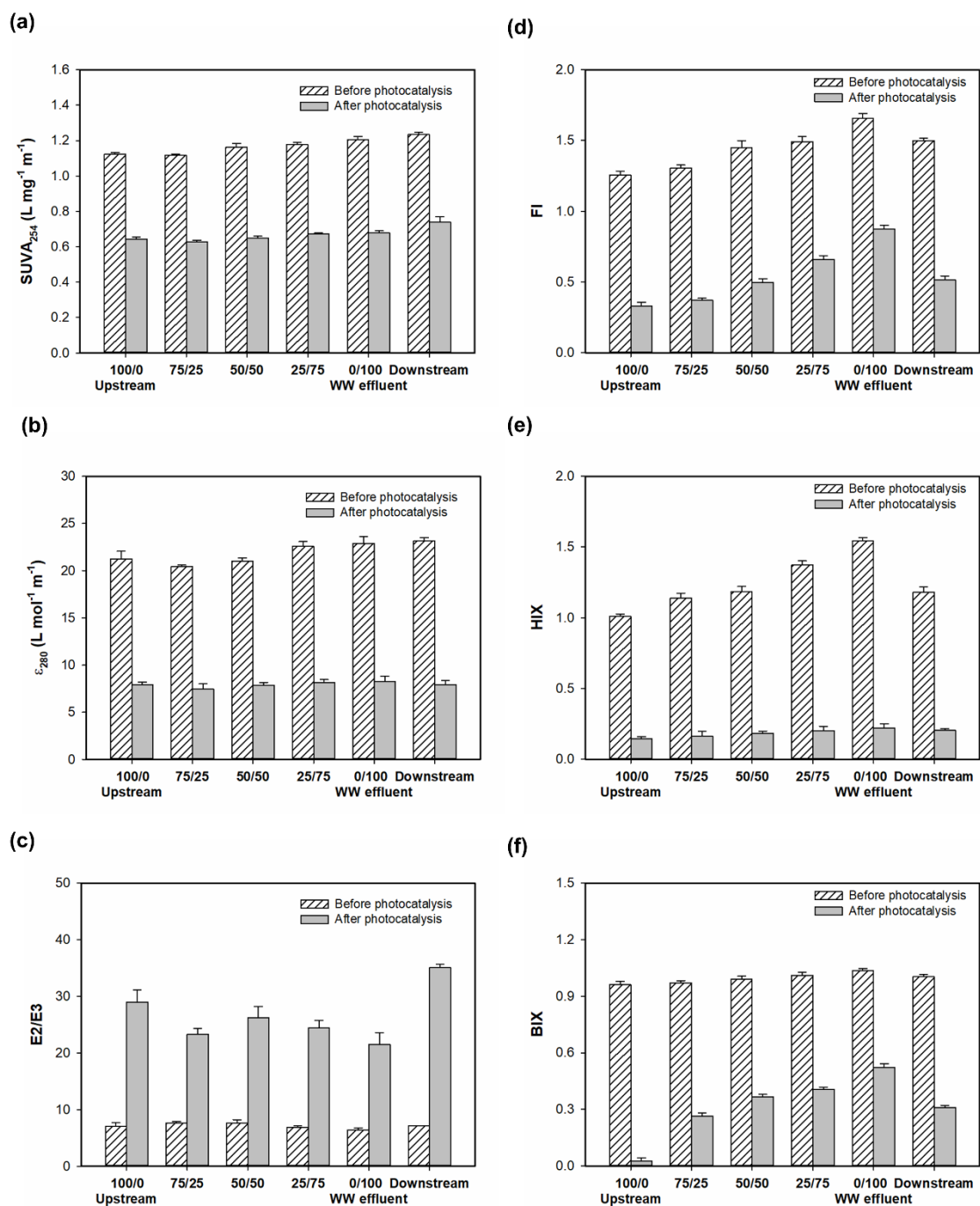


Figure S4. Changes of the optical parameters for upstream, wastewater effluent, and downstream samples by photocatalysis with 0.2 g/L of ZnO at pH 7: (a) $SUVA_{254}$, (b) ϵ_{280} , (c) E2/E3, (d) FI, (e) HIX, and (f) BIX.

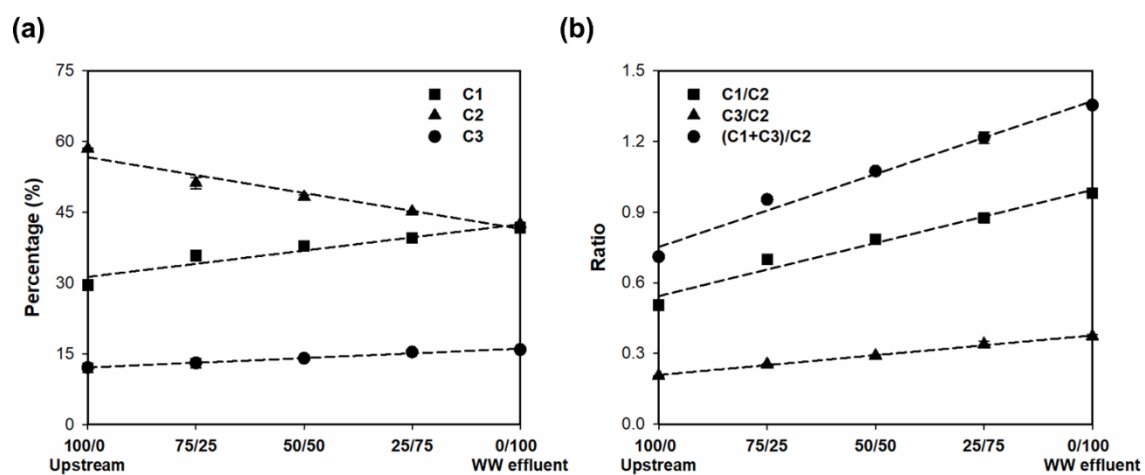


Figure S5. Changes in the relative distribution of PARAFAC components during the mixing between upstream and wastewater effluent: (a) Percentage contribution (%) and (b) PARAFAC component ratios.

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Table S1. Basic water properties of upstream, wastewater effluent, and downstream samples

Sample Type	DOC (mg/L)	UV ₂₅₄ (A.U.)	SUVA ₂₅₄ (L/mg-m)	FI	HIX	BIX	pH	Conductivity (µS/cm)	TN (mg/L)
Upstream of WWTP (DOM)	6.51	0.0729	1.119	1.28	1.01	0.93	6.83	394	9.85
	6.48	0.0734	1.133	1.24	1.01	1.00	6.80	391	9.94
	6.53	0.0732	1.121	1.25	1.00	0.96	6.89	392	9.94
	6.51	0.0732	1.124	1.26	1.01	0.96		392.3	9.91
Wastewater effluent (EfOM)	8.52	0.1022	1.199	1.65	1.55	1.03	6.68	567	14.55
	8.54	0.1019	1.193	1.63	1.42	1.04	6.64	565	14.77
	8.55	0.1045	1.223	1.69	1.38	1.04	6.67	571	14.80
	8.54	0.1029	1.205	1.66	1.45	1.04		567.7	14.70
Downstream of WWTP	8.10	0.0990	1.223	1.50	1.18	1.00	6.89	430	9.24
	7.98	0.0994	1.246	1.50	1.19	1.00	6.96	429	9.36
	8.05	0.0992	1.232	1.49	1.17	1.00	6.97	425	9.34
	8.04	0.0992	1.234	1.50	1.18	1.00		428.0	9.31

Table S2. Spectral characteristics of the three PARAFAC components identified by PARAFAC in this study and the comparison with those previously identified. The maxima wavelengths are presented in excitation/emission wavelengths.

Components	Ex _{max} /Em _{max}	Traditional peaks [1]	Comparison with other studies using PARAFAC	Description	Reference
C1	≤230(325)nm/406nm	"A" peak: 260/380–460 "M" peak: 312/380–420	C6:<250(300)/406: Marine and terrestrial humic substances	Humic-like component	[2]
			C3: An intermediate that is formed as a result of the photochemical degradation of terrestrial DOM		[3]
			C2: <240(340)/398: Humic-like fluorescence		[4]
			P1: (< 260)310/414: Marine and terrestrial humic materials		[5]
			C1: 240(310)/429.5: Humic-like component (peaks A + M)		[6]
			G2: <250,320/400: Microbial humic-like fluorescence		[7]
			C2: 305(<250)/400: Microbial humic-like		[8]
			C2: 250,310/400: Humic-like component		[9]
			C1: 230,330/420: Terrestrial humic-like		[10]
			C2: ≤240, 300/408 nm: Microbial humic-like substances		[11]
C2	≤230(276)nm/304nm	"B" peak: 275/310	Component 8: 275/304: Tyrosine-like fluorescence	Tyrosine-like component	[12]
			C4: 275/306: Tyrosine-like fluorescence		[13]
			C1/P5: Tyrosine-like fluorescence		[5]
			Tyrosine-like fluorescence		[13]
			C7: Tyrosine-like fluorescence		[14]
			G4: 250/304: Protein - tyrosine-like		[7]
C3	261nm/490nm	"A" peak: 260/380–460 "C" peak: 350/420–480	C2: 275(290)/306: Protein-like (tyrosine-like) components	Terrestrial-like humic substances	[15]
			C1:260(360)/480: Terrestrial humic substances		[2]
			P3:<260(380)/498: Terrestrial humic substances		[5]
			C3:260(370)/490: Terrestrial humic substances		[16]
			C4: 265(370)/490: Terrestrial-like humic substances		[17]
			C4: 270(390)/508: Terrestrial-like humic substances		[18]
			C4: 250(360)/500: Humic-like organic matter		[19]
			C5: 270(400)/490: Microbial humic-like		[20]

Table S3. Pearson's correlation coefficients between selected parameters for upstream, wastewater effluent, and downstream samples

	DOC	UV ₂₅₄	SUVA ₂₅₄	ε ₂₈₀	S ₂₇₅₋₂₉₅	S _R	E2/E3	FI	HIX	BIX	%C1	%C2	%C3
DOC	1												
UV ₂₅₄	0.984	1											
SUVA ₂₅₄	0.826	0.913	1										
ε ₂₈₀	0.651	0.707	0.748	1									
S ₂₇₅₋₂₉₅	0.634	0.661	0.626	0.767	1								
S _R	-0.642	-0.650	-0.576	-0.637	-0.903	1							
E2/E3	-0.323	-0.306	-0.222	-0.689	-0.610	0.317	1						
FI	0.963	0.938	0.764	0.604	0.606	-0.603	-0.340	1					
HIX	0.869	0.807	0.566	0.529	0.658	-0.668	-0.375	0.872	1				
BIX	0.861	0.849	0.719	0.659	0.724	-0.621	-0.511	0.833	0.863	1			
%C1	0.801	0.702	0.400	0.320	0.436	-0.504	-0.243	0.789	0.929	0.755	1		
%C2	-0.810	-0.716	-0.425	-0.350	-0.469	0.524	0.269	-0.809	-0.948	-0.781	-0.996	1	
%C3	0.802	0.730	0.480	0.423	0.543	-0.557	-0.335	0.831	0.964	0.822	0.944	-0.969	1

Table S4. Flow data at the points where we collected the upstream and downstream samples for three months in 2019. Unit: m³/s (Source: Han River Flood Control Office).

Date	Upstream	Downstream	Date	Upstream	Downstream	Date	Upstream	Downstream	Date	Upstream	Downstream
2019/05/01	265.44	400	2019/06/01	189.92	376.37	2019/07/01	153.95	409.17	2019/08/01	1600.38	2458.55
2019/05/02	239.42	437.73	2019/06/02	164.74	454.86	2019/07/02	158.28	570.49	2019/08/02	1045.48	2009.47
2019/05/03	269.58	547.2	2019/06/03	197.58	580.31	2019/07/03	171.46	743.95	2019/08/03	498.08	1557.76
2019/05/04	220.05	560.41	2019/06/04	252.77	679.79	2019/07/04	152.01	811.23	2019/08/04	564.1	1535.39
2019/05/05	181.11	661.72	2019/06/05	311.14	874.3	2019/07/05	147.93	871.3	2019/08/05	452.74	1317.23
2019/05/06	191.78	652.88	2019/06/06	235.87	786.99	2019/07/06	166.35	875.23	2019/08/06	205.36	918.48
2019/05/07	148.72	787.83	2019/06/07	463.09	934.88	2019/07/07	246.22	792.14	2019/08/07	508.21	1026.13
2019/05/08	259.6	777.32	2019/06/08	703.59	865.53	2019/07/08	182.86	623.9	2019/08/08	722.98	949.09
2019/05/09	278.05	551.87	2019/06/09	442.29	801.05	2019/07/09	166.77	471.63	2019/08/09	397.09	472.93
2019/05/10	259.76	536.71	2019/06/10	253.63	504.87	2019/07/10	157.91	383.96	2019/08/10	529.53	510.23
2019/05/11	170.51	436.2	2019/06/11	211.14	338.86	2019/07/11	204.04	346.48	2019/08/11	322.65	425.28
2019/05/12	211.18	332.66	2019/06/12	265.01	333.85	2019/07/12	204.17	290.87	2019/08/12	646.36	743.71
2019/05/13	212.7	298.34	2019/06/13	212.7	355.53	2019/07/13	183.16	305.65	2019/08/13	974.74	1119.03
2019/05/14	258.04	360.29	2019/06/14	215.85	391.86	2019/07/14	160.85	368.44	2019/08/14	631.13	1012.48
2019/05/15	185.41	344.94	2019/06/15	258.74	506.62	2019/07/15	256.4	438.3	2019/08/15	560.83	992.97
2019/05/16	166.81	421.57	2019/06/16	161.97	566.92	2019/07/16	246.59	540.98	2019/08/16	478.73	1133.8
2019/05/17	82.42	557.98	2019/06/17	224.98	649.74	2019/07/17	171.16	520.73	2019/08/17	419.26	1136.73
2019/05/18	184.71	715.05	2019/06/18	196.92	742.39	2019/07/18	156.67	558.94	2019/08/18	460.69	1081.74
2019/05/19	273.33	808.45	2019/06/19	184.62	763.94	2019/07/19	161.06	574.24	2019/08/19	378.66	941.05
2019/05/20	208.53	987.64	2019/06/20	281.53	694.42	2019/07/20	204.12	562.22	2019/08/20	320.47	776.26
2019/05/21	208.54	733.82	2019/06/21	305.29	638.9	2019/07/21	202.56	542.97	2019/08/21	295.51	601.85
2019/05/22	200.71	710.95	2019/06/22	227.96	510.89	2019/07/22	183.93	498.46	2019/08/22	260.11	553.49
2019/05/23	250.23	547.91	2019/06/23	200.76	404.53	2019/07/23	169.84	409.53	2019/08/23	246.91	432.98
2019/05/24	192.88	399.34	2019/06/24	198.27	332.04	2019/07/24	265.15	453.88	2019/08/24	231.91	378.99
2019/05/25	199.38	314.98	2019/06/25	209.71	276.17	2019/07/25	321.71	455.49	2019/08/25	190.07	285.22
2019/05/26	225.99	268.5	2019/06/26	289.67	252.47	2019/07/26	1144.39	962.29	2019/08/26	217.52	294.63
2019/05/27	308.7	315.73	2019/06/28	211.08	233.82	2019/07/27	1647.11	1314.61	2019/08/27	285.41	308.73
2019/05/28	279.54	284.44	2019/06/29	222.69	292.44	2019/07/28	1224.64	1065.41	2019/08/28	267.7	412.91
2019/05/29	215.83	246.48	2019/06/30	189.83	337.85	2019/07/29	577.13	690.3	2019/08/29	458.77	859.4
2019/05/30	215.91	252.47				2019/07/30			2019/08/30		
2019/05/31	211.64	280.11				2019/07/31					

Table S5. Discharge volume from the wastewater treatment plant into the Han river in 2019 (Source: Seoul Metropolitan Government).

Months	Municipal wastewater treatment plant flowrate (ton/day)		
	Process 1	Process 2	Summary
January	506,521	939,791	1,446,312
February	510,419	952,395	1,462,814
March	503,810	970,002	1,473,812
April	530,063	966,352	1,496,415
May	532,940	967,388	1,500,328
June	547,116	1,018,408	1,565,524
July	620,429	1,066,965	1,687,394
August	668,688	1,095,540	1,764,228
September	633,813	1,076,323	1,710,136
October	591,380	952,115	1,543,495
November	671,718	920,887	1,592,605
December	726,420	749,171	1,475,591

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