

Supporting Information for
Superior Removal of Disinfection Byproduct Precursors and Pharmaceuticals from
Wastewater in a Staged Anaerobic Fluidized Membrane Bioreactor Compared to
Activated Sludge

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Table S1: Basic water quality data and hydraulic residence times.

Analyte Sample	Unit	January			March			April		
		Primary Effluent	Aerobic Effluent	SAF-MBR Effluent	Primary Effluent	Aerobic Effluent	SAF-MBR Effluent	Primary Effluent	Aerobic Effluent	SAF-MBR Effluent
DOC	mg/L	6.2	4.5	3.2	8.4	5.5	2.9	9.8	4.9	3.4
UV ₂₅₄	cm ⁻¹	0.145	0.102	0.048	0.169	0.120	0.045	0.264	0.114	0.057
SUVA ₂₅₄	L/mg•m	2.3	2.3	1.5	2.0	2.2	1.5	2.7	2.3	1.7
Bromide	µg/L	229	128	109	121	146	107	106	112	102
Ammonia	mg/L as N	25.5	<0.2	27.9	29.3	<0.2	32.3	19.6	<0.2	25.9
Nitrite	mg/L as N	0.19	0.08	0.03	<0.02	0.25	<0.02	<0.02	0.02	<0.02
Nitrate	mg/L as N	0.2	7.2	<0.1	<0.1	7.2	<0.1	<0.1	4.4	<0.1
Temperature	°C	11.0	NM	11.0	17	15.0	17	18	15	18
HRT	hrs	NA	11.3	6.8	NA	11.4	6.8	NA	9.9	6.8
Alkalinity	mg/L as CaCO ₃	NM	NM	NM	210	65.0	280	200	90	250
TCOD	mg/L	237	NM	22	266	74.6	53.5	232	17.7	20.9
TBOD ₅	mg/L	102	NM	9	195	15.1	15.5	102	0	9.5
TSS	mg/L	82	NM	0	72	30.0	0	62	2.5	0
Total Phosphorus	mg/L as P	NM	NM	NM	3.3	1.8	3.7	2.3	0.4	2.1
Total Nitrogen	mg/L as N	NM	NM	NM	40	10.0	40	35	4	27
pH	pH Units	6.1	6.9	7.6	7.5	7.2	NM	7.5	7.3	7.9

NM = not measured

Analytical details. A 1 mL aliquot was reserved for analysis by direct injection in the event that concentrations measured in the SPE extracts exceeded the range of the standard curve. Internal standards (typically 5 ng) were added to the samples prior to solid phase extraction or direct injection. For SPE analysis, samples were extracted onto pre-cleaned (12 mL HPLC-grade methanol) Waters Oasis HLB cartridges. Cartridges were then washed with 6 mL deionized water and eluted with 10 mL of HPLC-grade methanol. Extracts were blown to dryness with N₂ gas. Samples were heated to 40 °C during the drying procedure and reconstituted with deionized water (2 × 0.5 mL); control studies indicated that recoveries ranged from 90-120%.¹ Pharmaceutical compounds were analyzed via liquid chromatography/tandem mass spectrometry (Agilent 6460 triple quadrupole system) using methods modified from Jasper and Sedlak.²

Chromatographic separation was accomplished using a 150 mm x 3.00 mm Phenomenex Synergi 4 µm Hydro-RP column. Compounds were eluted with 0.6 mL min⁻¹ methanol and 0.1% acetic acid in water with a gradient starting at 0% methanol and peaking at 95% methanol for 1 minute starting at 11 minutes (total run time was 17 minutes). Compounds were detected using electrospray ionization (ESI) in positive mode with a 7 ms dwell time and a gas temperature of 350° C, a gas flow rate of 12 L/min at 60 psi, a sheath gas temperature of 400° C at a flow rate of 11 L/min, and a capillary voltage of 3600 V (Table S2).

Preformed monochloramine stocks were formed by titrating sodium hypochlorite into ammonium chloride to achieve a 1:1.2 Cl:N molar ratio, and standardized.³ After a 3 d reaction time, total chlorine residual was measured by the *N,N*-diethyl-*p*-phenylene-diamine (DPD) colorimetric method,⁴ final pH was measured, and residual chlorine was quenched with 33 mg/L ascorbic acid. A 40 mL subsample was acidified to pH 3.5 with 0.5 M H₂SO₄ and analyzed for halogenated DBPs, including regulated and iodinated trihalomethanes (THMs) and haloacetonitriles (HANs), by solid phase extraction (Varian Bond Elut-PPL cartridges, 200 mg) after spiking with 1,2-dibromopropane as an internal standard.⁵ The remaining 450 mL was spiked with deuterated internal standards (20 ng/L *d*₆-*N*-nitrosodimethylamine and *d*₈-*N*-nitrosomorpholine), extracted and analyzed for *N*-nitrosamines via gas chromatography/tandem mass spectrometry using a modified version of EPA method 521.^{6,7}

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Table S2. Compound-Specific Mass Spectroscopy Parameters

Compound	Precursor Ion (M+H)⁺ (m/z)	Fragmentor Voltage (V)	Product Ions (m/z)	Collision Energy (V)	Cell Accelerator Voltage (V)
Abacavir	287	90	191 150	15 35	2
Abacavir-d4	291	100	195	15	2
Acyclovir	226	75	152 135	10 45	2
Acyclovir-d4	230	70	152	10	2
Atenolol	267	130	190 145	16 24	7
Atenolol-d7	274	130	145	24	7
Carbamazepine	237	120	194 179	15 35	7
Carbamazepine-d10	247	120	204	20	7
Emtricitabine	248	60	130 113	10 45	2
Emtricitabine- ¹³ C, ¹⁵ N ₂	251	55	133	10	2
Lamivudine	230	65	112 95	10 45	2
Lamivudine- ¹³ C, ¹⁵ N ₂	233	75	115	10	5
Metoprolol	268	130	116 159	14 17	7
Metoprolol-d7	275	130	123	14	7
Metoprolol Acid	268.1	130	190.9 144.9	17 25	7
Metoprolol Acid-d5	273.1	130	196	17	7
Propranolol	260	98	183 116	12 13	7
Propranolol-d7	267	98	116	13	7
Sulfamethoxazole	254	110	156 92	10 25	7
Sulfamethoxazole-d4	258	110	96	25	7
Trimethoprim	291	140	261 123	17 20	7
Trimethoprim-d3	294	140	123	20	7

Table S3: Pharmaceutical and related compound concentrations in wastewater samples prior to chloramination.

Compound	Class	Month	Primary Effluent	Aerobic Secondary Effluent		SAF-MBR Effluent		Average % reduction p-value
			ng/L	ng/L	% removal	ng/L	% removal	
Abacavir	anti-viral	January	18	<1	100%	<1	100%	0.4226
		March	26	<1	100%	1	96%	
		April	37	14	62%	14	62%	
Acyclovir	anti-viral	January	705	154	78%	25	96%	0.0012
		March	701	194	72%	40	94%	
		April	418	215	49%	23	94%	
Atenolol	beta-blocker	January	643	440	32%	9	99%	< 0.001
		March	469	432	8%	<25	100%	
		April	370	299	19%	6	98%	
Carbamazepine	anti-convulsant	January	184	153	17%	5	97%	< 0.001
		March	108	152	-41%	<25	100%	
		April	123	133	-8%	5	96%	
Emtricitabine	anti-viral	January	8	<5	100%	13	-63%	0.6505
		March	<5	21	NA	<5	NA	
		April	30	16	47%	5	83%	
Lamivudine	anti-viral	January	86	12	86%	1	99%	0.0105
		March	95	26	73%	<1	100%	
		April	96	32	67%	10	90%	
Metoprolol	beta-blocker	January	NQ	6	NA	<1	NA	0.0047
		March	NQ	4	NA	1	NA	
		April	NQ	2	NA	<1	NA	
Metoprolol Acid	transformation product	January	NQ	558	NA	27	NA	< 0.001
		March	214	305	-43%	<12	100%	
		April	113	211	-87%	<12	100%	
Propranolol	beta-blocker	January	NQ	42	NA	<0.3	NA	0.0016
		March	38	50	-32%	<12	100%	
		April	NQ	57	NA	0.3	NA	
Sulfamethoxazole	antibiotic	January	276	117	58%	33	88%	0.0021
		March	272	39	86%	<15	100%	
		April	207	117	43%	19	91%	
Trimethoprim	antibiotic	January	NQ	101	NA	<0.4	NA	0.0123
		March	3	31	-933%	<19	NA	
		April	NQ	36	NA	0.4	NA	

NQ = not quantifiable due to matrix interference

NA = not applicable due to non-quantifiable primary effluent sample

Table S4: Nitrosamine concentrations in wastewater samples prior to chloramination. Average recoveries of the two deuterated internal standards (d₆-NDMA and d₈-NMOR) were 77% and 76%, respectively. Average nitrosamine recovery from wastewater matrix spikes (20 ng/L) was 94% (range 67-131%).

Sampling Date	Effluent Type	NDMA	NMEA	DMNA	NDEA	NDPA	NPIP	NPYR	NMOR	NDBA
January	Primary	3.5	<2	13.6	NQ	2.7	3.7	<2	35.7	<2
	Aerobic	8.9	2.3	16.6	NQ	<2	2.3	<2	30.2	<2
	SAF-MBR	<2	4.7	6.5	NQ	4.4	<2	<2	3.5	3.7
March	Primary	18.6	12.0	15.2	NQ	18.7	13.7	<2	33.9	6.1
	Aerobic	19.5	8.8	17.4	NQ	15.4	11.7	<2	24.9	11.9
	SAF-MBR	4.3	13.0	2.5	NQ	25.1	17.0	<2	4.0	5.5
April	Primary	12.1	10.1	24.2	NQ	10.3	5.1	<2	19.0	13.2
	Aerobic	11.3	3.9	33.7	NQ	3.5	<2	<2	21.3	<2
	SAF-MBR	3.4	5.4	29.3	NQ	9.0	<2	<2	3.3	2.3

NM = not measured

NQ = not quantified due to matrix interference

Table S5: Halogenated DBP concentrations in wastewater samples prior to chloramination. Average recovery of halogenated DBPs from wastewater matrix spikes (40 µg/L) was 83% (range 69-106%).

Sampling Date	Effluent Type	Chloroform	BDCM	DBCM	Bromoform	1,1-DCP	1,1,1-TCP	TCNM	DCAN	BCAN	DBAN	DCIM	BCIM	DBIM	TIM
January	Primary	5.5	<1	<1	2.0	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
	Aerobic	3.7	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
	SAF-MBR	2.7	<1	<1	3.1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
March	Primary	NM	<1	<1	4.6	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
	Aerobic	15.7	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
	SAF-MBR	16.7	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
April	Primary	32.2	<1	<1	1.4	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
	Aerobic	10.7	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
	SAF-MBR	16.6	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

NM = Not measured

N.B.: All other analytes were not detected in all samples

Table S6: Mean nitrosamine, nitramine, and THM4 concentrations after chloramination. Standard deviations of experimental replicate values presented when available (n = 2 - 3).

Compound	Class	Month	Mean Concentrations (ng/L)									% reduction
			Primary Effluent		Aerobic Secondary Effluent			SAF-MBR Effluent			% reduction	vs aerobic
			Mean	Std. Dev.	Mean	Std. Dev.	% removal	ng/L	Std. Dev.	% removal	vs aerobic	p-value
NDMA	Nitrosamine	January	13.2		5.8		56%	3.7		72%	36%	0.0137
		March	20.5		31.8	4.6	-55%	14.3	0.6	30%	55%	
		April	15.7	0.1	23.7	2.1	-51%	12.4	1.6	21%	48%	
NMOR	Nitrosamine	January	14.2		14.9		-5%	3.7		74%	75%	0.0011
		March	31.2	1.9	26.9	5.9	14%	5.2	0.1	83%	81%	
		April	22.3	3.0	23.8	7.1	-7%	3.7	0.5	83%	84%	
DMNA	Nitramine	January	12.2		3.7		70%	4.5		63%	-22%	0.9037
		March	15.2	0.4	17.1	1.1	-13%	9.9	0.3	100%	42%	
		April	27.6	0.2	32.2	0.1	-17%	41.8	4.2	-51%	-30%	
THM4	Trihalomethane	January	28.7		32.1		-12%	9		69%	72%	0.5211
		March	101.3	34	54.7	3.2	46%	76.8	16	24%	-40%	
		April	59.5	14	89.7	2.3	-51%	47.2	21	21%	47%	

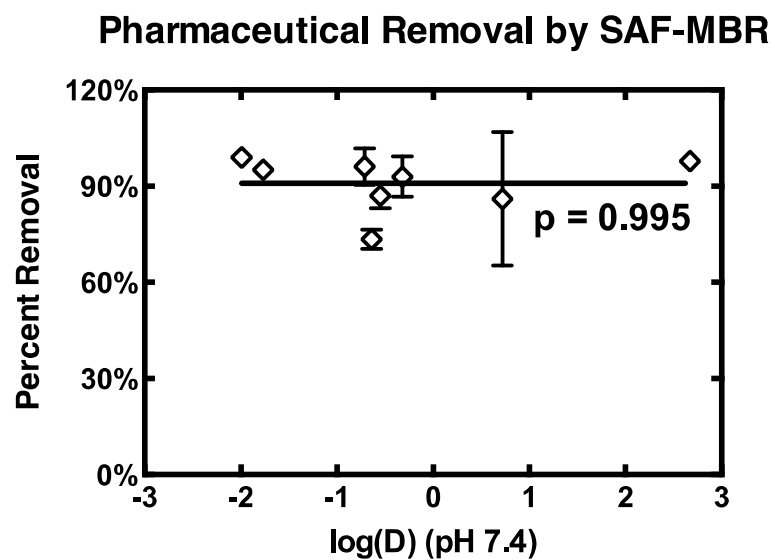


Figure S1: Correlation of percent removal of pharmaceuticals between primary effluent and SAF-MBR effluent with pH-corrected logD values. LogD values, representing the $\log K_{ow}$ (octanol-water partition constant) values corrected to pH 7.4, were calculated using ACD/Labs Percepta software.