Supporting Information

Critical Review on Bromate Formation during Ozonation and Control Options for its Minimization

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S.1: Alternative Designs for O_3 and O_3/H_2O_2 Application

The HiPOX system uses multiple ozone injection locations in a tubular reactor while the PRO$_3$MIX approach uses a single ozone gas injection with a series of inefficient static mixers to sequentially transfer ozone.[1,2] The MEMBRO$_3$X concept uses an ozone-resistant hollow fiber membrane for ozone mass transfer to the water phase containing H_2O_2.[3] Overall, these approaches are geared towards low local ozone residual concentrations by distributed ozone addition and fast transformation of O_3 to $^{\cdot}OH$. This minimizes the formation of HOBr and can thus mitigate bromate formation.

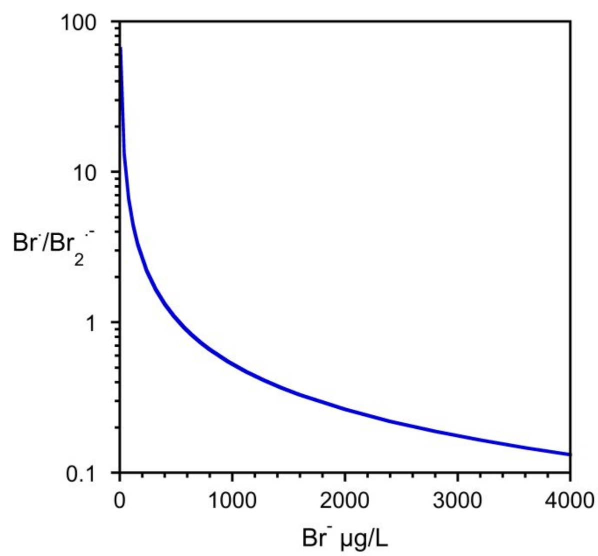

Figure S1. Ratio of the concentrations of $Br^{\cdot}/Br_2^{\cdot -}$ as a function of the bromide concentration according to the rate constants for equation 12.

Table S1 Summary of bromate formation models based on multiple linear regressions and water matrix.

Water Matrix	Predictive Equation	Units	Boundary Conditions	Ref.
SW	1.$[BrO_3^-] = 1.55x10^{-6} [Br^-]^{-0.73}[DOC]^{-1.26}[pH]^{5.82}[O_3]^{1.57}t^{0.28}$ 2. $[BrO_3^-] = 1.63x10^{-6} [Br^-]^{-0.73}[DOC]^{-1.3}[pH]^{5.79}[O_3]^{1.59}t^{0.27}[NH_3\text{-}N]^{-0.033}$	BrO_3^- (µg/L), Br^- (µg/L), DOC (mg/L), O_3 (mg/L), NH_3-N (mg/L), pH, t (min), Temp (20 °C)	70 < Br^- < 440 1.1 < DOC < 8.4 6.5 < pH < 8.5 1.1 < O_3 < 10.0 1 < t < 120	4
SW, GW	$[BrO_3^-] = 1.5x10^{-3}[DOC]^{-0.74}[pH]^{2.26}[O_3]^{0.64} [Br^-]^{0.61}[temp]^{2.03}$	BrO_3^- (µg/L), Br^- (µg/L), DOC (mg/L), O_3 (mg/L), pH, Temp (°C)	250 < Br^- < 1500 3.0 < DOC < 7.0 6.5 < pH < 8.5 1.5< O_3 < 17.5 20 < T < 30	5
SW	$[BrO_3^-] = 7.76x10^{-7}[Br^-]^{0.88}[DOC]^{-1.18}[NH_3\text{-}N]^{-0.18}[O_3]^{1.42}pH^{5.11}[IC]^{0.18}t^{0.27}$	BrO_3^- (µg/L), Br^- (µg/L), DOC (mg/L), O_3 (mg/L), NH_3-N (mg/L), pH, IC (mg/Las $CaCO_3$), t (min), Temp (20 °C)	100 < Br- < 1000 1.5 < DOC < 6.0 1.0 < IC < 216 6.5 < pH < 8.5 0.005 < NH_3-N < 0.7 1.5< O_3 < 6.0 1 < t < 30	6
SW	1. $[BrO_3^-] = 4.36x10^{-4}[Br^-]^{-1.136}[DOC]^{-1.267}[pH]^{1.774}[O_3]^{1.575}[time]^{1.014}$ 2. $[BrO_3^-] = 2.75x10^{-4}[Br^-]^{-1.137}[DOC]^{-1.186}[pH]^{0.253}[O_3]^{1.598}[time]^{1.014}[NH_3\text{-}N]^{-0.086}$	BrO_3^- (µg/L), Br^- (µg/L), DOC (mg/L), O_3 (mg/L), NH_3-N (mg/L), pH, IC (mg/Las $CaCO_3$), t (min)	75 < Br- < 145 6.5 < pH < 8.5 T = 20 °C 1.1 < O_3 < 10.0 1.1 < DOC < 8.4 1 < t < 120 0 < NH_3-N < 1.5	7
DW	$[BrO_3^-] = 5.41x10^{-5} [Br^-]^{-0.040}[DOC]^{-1.080}[pH]^{4.7}[O_3]^{1.120} [time]^{0.304} [temp]^{0.580}$ $[BrO_3^-]_{@temp} = [BrO_3^-]_{@20°C}(1.035)^{Temp-20}$	BrO_3^- (µg/L), Br^- (µg/L), DOC (mg/L), O_3 (mg/L), NH_3-N (mg/L), pH, IC (mg/Las $CaCO_3$), t (min), Temp (°C)	70 < Br^- < 440 1.1 < DOC < 8.4 6.5 < pH < 8.5 1.1 < O_3 < 10.0 1 < t < 120	8
DW	1. $[BrO_3^-] = 1.19x10^{-7} [Br^-]^{-0.96} [UV_{254}]^{-0.623}[pH]^{5.68}[O_3]^{1.307} [time]^{0.336} [Alk]^{-0.201}$	BrO_3^- (µg/L), Br^- (µg/L), O_3 (mg/L), UV_{254} (cm^{-1}), pH, Alk	70 < Br^- < 440 0.010 < UV_{254} < 0.280	9

	2. $[BrO_3^-] = 8.71x10^{-8} [Br^-]^{-0.944} [UV_{254}]^{-0.593}[pH]^{5.81}[O_3]^{1.279} [time]^{0.337} [Alk]^{-0.167}[NH_3\text{-}N]^{-0.051}$	(mg/Las $CaCO_3$), t (min), Temp (°C)	1.1 < DOC < 8.4 6.5 < pH < 8.5 1.1 < O_3 < 10.0 1 < t < 120 13 < Alk <216 0.02 < NH_3-N < 3	
DW	$[BrO_3^-] = 1.5xO_3$ CT + 0.5 + 1.4xO_3 CT + 0.2	BrO_3^- (μg/L), O_3 CT (mg-O_3-min/L)	0 < O_3 CT < 2.0 T = 12, 20 °	10
DW	$[BrO_3^-] = [NH_3\text{-}N]^{-0.15} [DOC]^{-0.26}[Alk]^{0.45}pH^{-0.44}[Cl^-]^{-0.14} [O_3]^{0.63}$ time$^{0.54}$ $[BrO_3^-] = [NH_3\text{-}N]^{-0.14} [DOC]^{-0.22}[Alk]^{0.42}pH^{-0.3}[O_3]^{0.63}$ time$^{0.54}$ $[BrO_3^-] = [Br^-]^{-1.74} [Turbidity]^{-0.31}[EC]^{2.11}$ $[BrO_3^-] = [Br^-]^{0.78} [Cl^-]^{0.75}[EC]^{-1.19}$ $[BrO_3^-] = [Br^-]^{0.47} [O_3]^{0.62}$ time$^{0.51}$ $[BrO_3^-] = [EC]^{0.46} [O_3]^{0.62}$ time$^{0.50}$	BrO_3^- (μg/L), Br^- (μg/L), DOC (mg/L), O_3 (mg/L), NH_3-N (mg/L), Cl (mg/L), pH, Alk (mg/Las $CaCO_3$), t (min), EC (μS/cm), Turbidity (NTU)	161 < Br^- < 4084 115 < Alk <246 0.50 < DOC < 1.4 16 < Cl < 1170 334 < EC < 3940 0.06 < NTU < 0.60 7.10 < pH < 8.07 0.0 < NH_3-N < 0.019 0.5< O_3 < 3.5 0 < t < 60 T = 20-23 °C	11
RO	$[BrO_3^-] = e^{-19.40}[Br^-]^{0.8}dose^{1.26}t^{0.89}pH^{7.28}$	BrO_3^- (mg/L), Br^- (mg/L), pH, O_3 (mg/L), t (min)	1. < Br^- < 4.0 6.0 < pH < 9.0 25 < O_3 < 58.3 15 < t < 35	12
RW	$[BrO_3^-] = 3.855x10^{-8}[Br^-]^{1.43}(O_3 \text{ mg/min})^{0.93}pH^{3.01}T^{1.20}t\text{^}^{0.83}$	BrO_3^- (μg/L), Br^- (μg/L), DOC (mg/L), O_3 (mg/min), NH_3-N (mg/L), pH, IC (mg/Las $CaCO_3$), t (min), Temp (°C)	50 < Br^- < 1000 3.0 < pH < 8.0 0.5 < O_3 < 2.25 0 < t < 180 15 < T < 35	13
RW	1. $[BrO_3^-] = 0.603x10^{-1} [Br^-]^{0.35}[O_3]^{1.31}$ 2. $d[BrO_3^-]/dt = k' x [O_3]^{1.4}$	1. BrO_3^- (μg/L), Br^- (μg/L), O_3 (mg/L), pH = 7.5 2. $[BrO_3^-]$ (M), $[O_3]$ (M), k' ($M^{-(ab-1)}$ s^{-1})	50 < Br^- < 300 0.7 < O_3 < 3.8 a = 0.5, b= 1.4 k' = 0.069 at pH 6.5 k' = 0.45 at pH 7.5 k' = 2.1 at pH 8.5	14
SW, WW	$[BrO_3^-] = 7.64x10^{-9}*e^{(0.237*HS(\%))}$	BrO_3^- (μg/L), Br^- (μg/L), DOC (mg/L),	0 < HS % <100 100 < Br^- < 500	15

		UV_{254} (cm^{-1}), EC (µS/cm), HS (%) = % reduction in emission at 415 - 490 nm	5.82 < DOC < 14.87 0.130 < UV_{254} < 0.727 6.92 < pH < 7.48 314 < EC < 652	
WW	$[Br^{-}: BrO_3^{-}] = 0.08[O_3:TOC]^{2.26}$	$Br^{-}: BrO_3^{-}$ (mg Br^{-}: mg BrO_3^{-}), O_3:TOC (mg O_3: mg TOC)	0.2 < O_3:TOC < 1.95 42 < Br^{-} < 820	[16]
WW	$[Br^{-}: BrO_3^{-}] = 0.07[O_3:TOC]^{2.13}$	$Br^{-}: BrO_3^{-}$ (mg Br^{-}: mg BrO_3^{-}), O_3:TOC (mg O_3: mg TOC)	0.2 < O_3:TOC < 1.55 100 < Br^{-} < 870 86 < Alk <206 6.26 < DOC < 11.0 7.0 < pH < 8.0 T = 20-28 °C	[17]

SW = surface water; GW = ground water; RO = reverse osmosis permeate; RW = reagent water; WW = waste water.

Table S2 Studies on ammonium addition as a bromate control strategy during ozonation. SW = Surface Water, *DOC (mg/L)

Scale	Water Type	pH	TOC (mg/L)	Alkalinity (mg/L as $CaCO_3$)	Ozone exposure (Ct) (mg.min/L)	NH_3 Dose (ug NH_3-N/L)	Bromate Minimization (%)	Reference
Bench	GW	8.2	4.0	132	~0.37	300	67	[18]
Bench	GW	8.2	4.0	132	~0.93	600	83	[18]
Bench	SW	8	1.3*	2.4 mM	8-9	164	50	[19]
Pilot	SW	8	2.59	137	4.1	100	42-62	[20]
Pilot	SW	8	2.59	137	4.09	300	65-70	[20]
Pilot	SW	8	2.59	137	3.93	500	70-73	[20]
Pilot	SW	8.3	3.7	73	~6.8	200	40-67	[21]
Pilot	SW	8.3	3.7	73	~6.8	900	60	[21]

Table S3 Performance of Cl_2-NH_3 as a bromate control strategy during ozone treatment. *DOC (mg/L)

Scale	Water Type	pH	TOC (mg/L)	Alkalinity (mg/L as $CaCO_3$)	Ozone Exposure (mg.min/L)	Cl_2 dose (mg/L)	NH_3 dose (ug NH_3-N/L)	Bromate Minimization (%)	Reference
Bench	SW	7.5	1.7*	2.6 mM	6	0.7	82	61	[22]
Bench	SW	7.5	1.7*	2.6 mM	6	0.7	164	81	[22]
Bench	SW	7.5	1.7*	2.6 mM	6	0.7	247	83	[22]
Bench	SW	7.5	1.7*	2.6 mM	6	0.7	329	83	[22]
Bench	GW	8.2	4	132	0.35	2	0.6	92	[18]
Pilot	SW	8	2.59	137	4.50	0.25	100	44-69	[20]
Pilot	SW	8	2.59	137	4.19	0.5	100	66-72	[20]
Pilot	SW	8	2.59	137	3.98	0.25	300	78-82	[20]
Pilot	SW	8	2.59	137	3.90	0.5	300	75-81	[20]
Pilot	SW	8	2.59	137	4.41	0.5	500	93-94	[20]

Table S4 Performance of preformed monochloramine for bromate control during ozone treatment

Scale	**Water Type**	**pH**	**TOC (mg/L)**	**Alkalinity (mg/L as $CaCO_3$)**	**Specific Ozone Dose***	**Dose (mg NH_2Cl as Cl_2 /L)**	**Bromate Minimization (%)**	**Reference**
Pilot	WW	7.1	6.6	178	Up to 1.2 mg O_3:TOC	1	68	[23]
Pilot	WW	7.1	6.6	178	Up to 1.2 mg O_3:TOC	3	84	[23]
Pilot	WW	7.1	6.6	178	Up to 1.2 mg O_3:TOC	5	87	[23]

Table S5 Performance of hydrogen peroxide for bromate control during ozone treatment, ND=not determined, *DOC (mg/L)

Scale	Water Type	pH	TOC (mg/L)	Alkalinity (mg/L as $CaCO_3$)	Specific Ozone Dose (mg O_3: mg DOC)	H_2O_2 Dose (mol H_2O_2:mol O_3)	Bromate Minimization (%)	Reference
Bench	SW	8.1	1.6	96.4	1.61	0.14	21	[24]
Bench	SW	8.1	1.6	96.4	1.61	0.28	26	[24]
Bench	SW	8.1	1.6	96.4	1.61	0.71	45	[24]
Bench	SW	8.1	1.6	96.4	1.61	1.4	60	[24]
Bench	SW	7.9	2.4	163.3	1.05	0.14	-29	[24]
Bench	SW	7.9	2.4	163.3	1.05	0.28	-21	[24]
Bench	SW	7.9	2.4	163.3	1.05	0.71	-7	[24]
Bench	SW	7.9	2.4	163.3	1.05	1.4	14	[24]
Bench	SW	8.0	6.4	106.9	0.39	0.14	-60	[24]
Bench	SW	8.0	6.4	106.9	0.39	0.28	-114	[24]
Bench	SW	8.0	6.4	106.9	0.39	0.71	-120	[24]
Bench	SW	8.0	6.4	106.9	0.39	1.4	-129	[24]
Bench	WW	7.3	8.6	ND	1.2	0.5	15	[25]
Bench	WW	7.3	8.6	ND	1.2	1	35	[25]
Bench	WW	7.0	4.7	145	1	0.5	32	[26]
Bench	WW	7.0	4.7	145	1	1	46	[26]
Bench	WW	7.2	4.7	220	1	0.5	19	[26]
Bench	WW	7.2	4.7	220	1	1	32	[26]
Bench	WW	7.1	7.0	105	1	0.5	27	[26]
Bench	WW	7.1	7.0	105	1	1	25	[26]
Bench	WW	6.9	7.1	123	1	0.5	14	[26]
Bench	WW	6.9	7.1	123	1	1	17	[26]
Bench	WW	7.6	5.7	134	1	0.5	-50	[26]

Bench	WW	7.6	5.7	134	1	1	0	[26]
Bench	WW	7.3	15.0	332	1	0.5	37	[26]
Bench	WW	7.3	15.0	332	1	1	48	[26]
Bench	WW	7.3	7.0	205	1	0.5	14	[26]
Bench	WW	7.3	7.0	205	1	1	14	[26]
Bench	WW	7.3	6.3	169	1	0.5	13	[26]
Bench	WW	7.3	6.3	169	1	1	8	[26]
Bench	WW	7.0	4.7	145	1.5	0.5	32	[26]
Bench	WW	7.0	4.7	145	1.5	1	45	[26]
Bench	WW	7.2	4.7	220	1.5	0.5	10	[26]
Bench	WW	7.2	4.7	220	1.5	1	36	[26]
Bench	WW	7.1	7.0	105	1.5	0.5	13	[26]
Bench	WW	7.1	7.0	105	1.5	1	34	[26]
Bench	WW	6.9	7.1	123	1.5	0.5	23	[26]
Bench	WW	6.9	7.1	123	1.5	1	41	[26]
Bench	WW	7.6	5.7	134	1.5	0.5	11	[26]
Bench	WW	7.6	5.7	134	1.5	1	22	[26]
Bench	WW	7.3	15.0	332	1.5	0.5	0	[26]
Bench	WW	7.3	15.0	332	1.5	1	-5	[26]
Bench	WW	7.3	7.0	205	1.5	0.5	55	[26]
Bench	WW	7.3	7.0	205	1.5	1	57	[26]
Bench	WW	7.3	6.3	169	1.5	0.5	-7	[26]
Bench	WW	7.3	6.3	169	1.5	1	14	[26]
Bench	WW	7.8	7.8*	ND	1.5	0.6-1.5	36-67	[16]

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