

Supporting Information for:

Formation of Disinfection By-products during Ballast Water Treatment with Ozone, Chlorine, and Peracetic Acid: Influence of Water Quality Parameters

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1 Scheme

Table S1. Water quality characteristics for the nine selected water sources from The Netherlands, Norway, and Germany.

Parameter	Netherlands (NE)			Norway (NOR)			Germany (DE)		
	F	B	S	F	B	S	B1	B2	S
GPS (deg, min, sec)	52°54'52.0"N 5°06'07.3"E (Lake IJssel)	52°57'26.9"N 5°00'03.9"E (Wadden Sea, North Holland)	52°59'14.1"N 4°49'08.8"E (Wadden Sea, North Holland)	59°36'56.49"N 10°39'7.49"E (surface) (Solbergstrand, Oslo Fjord)	59°36'56.49"N 10°39'7.49"E (1 m depth) (Solbergstrand, Oslo Fjord)	59°36'56.49"N 10°39'7.49"E (60 m depth) (Solbergstrand, Oslo Fjord)	54°31'10.0" N 9°40'30.0"E (Schlei, Baltic Sea)	54°50'10.0"N 9°49'60.0"E (Flensburg Firth, Baltic Sea)	54°07'00.0"N 8°51'30.0"E (outside Büsum harbour, North Sea)
DOC (mg/L-C)	4.5	3.6	1.9	8.8	2.3	1.2	6.1	3.0	2.5
SUVA (L/(mg×m))	3.41	2.68	2.11	3.73	2.0	1.0	3.1	1.38	2.18
pH	8.4	7.9	8.0	8.1	8.04	7.91	8.2	8.0	8.0
Alkalinity (mM)	2.01	2.31	2.52	1.28	2.1	2.38	3.26	2.16	2.15
Ammonia (µg-N/L) ^a	100.4	-	-	7.2	-	-	173.6	-	-
Bromide (mg/L (µM))	0.3 (3.75)	38.4 (480)	62.6 (782)	0.044 (0.09)	54.5 (681)	68.5 (856)	12 (150)	42 (525)	54 (675)
Chloride (M)	3.46×10^{-3}	0.2911	0.466	5.72×10^{-4}	0.431	0.510	0.092	0.343	0.436

^a cannot be measured in high salinity waters due to analytical interferences

Table S2. List of kinetic experiments and parameters tested for the NE and NOR waters for treatment with ozone, free chlorine, and PAA at a dose of 5.0 mg/L (104 μ M), 7.4 mg/L-Cl₂ (104 μ M), and 150 mg/L (2.0 mM), respectively.

Water	Oxidant	Temp (C)	Tested Parameters						
			Bromate	Primary Oxidant Residual	Secondary Oxidant (HOBr)	THMs	HAAs	Primary Oxidant Residual	Secondary Oxidant (HOBr)
Reaction time			15 min	15 min	15 min	5 days	5 days	5 days	5 days
NE-F	Ozone	22	×	×	×	×			×
NE-F	Ozone	4	×	×	×	×			×
NE-B	Ozone	22	×	×	×	×			×
NE-B	Ozone	4	×	×	×				
NE-S	Ozone	22	×	×	×	×			×
NE-S	Ozone	4	×	×	×	×			×
NE-F	Free chlorine	22				×		×	×
NE-F	Free chlorine	4				×		×	×
NE-B	Free chlorine	22				×		×	×
NE-B	Free chlorine	4				×		×	×
NE-S	Free chlorine	22				×		×	×
NE-S	Free chlorine	4				×		×	×
NE-F	PAA	22				×		×	×
NE-F	PAA	4				×		×	×
NE-B	PAA	22				×		×	×
NE-B	PAA	4				×		×	×
NE-S	PAA	22				×		×	×
NE-S	PAA	4				×		×	×
NOR-F	Ozone	22	×	×	×		×	×	×
NOR-F	Ozone	4	×	×	×		×	×	×
NOR-B	Ozone	22	×	×	×		×	×	×

NOR-B	Ozone	4	×	×	×		×	×	×
NOR-S	Ozone	22	×	×	×		×	×	×
NOR-S	Ozone	4	×	×	×		×	×	×
NOR-F	Free chlorine	22					×	×	×
NOR-F	Free chlorine	4					×	×	×
NOR-B	Free chlorine	22					×	×	×
NOR-B	Free chlorine	4					×	×	×
NOR-S	Free chlorine	22					×	×	×
NOR-S	Free chlorine	4					×	×	×
NOR-F	PAA	22					×	×	×
NOR-F	PAA	4					×	×	×
NOR-B	PAA	22					×	×	×
NOR-B	PAA	4					×	×	×
NOR-S	PAA	22					×	×	×
NOR-S	PAA	4					×	×	×

Table S3. List of dosage experiments and parameters tested for the NOR and DE waters in which NOR and DE waters were exposed to various dosages of ozone, free chlorine, and PAA from 0.5-5.0 mg/L (10-104 μ M), 1-9 mg/L-Cl₂ (14-126 μ M), and 7.5-150 mg/L (0.1-2 mM), respectively, at 22 \pm 2°C for one reaction time between 18 to 26 h.

Water	Oxidant	Temp (C)	Reaction time (Bromate/HAA/Primary Oxidant Residual/HOBr)	Reaction time (THMs)	Tested Parameters				
					Bromate	THMs	HAA	Primary Oxidant Residual	Secondary Oxidant (HOBr)
NOR-F	Ozone	22	24 h	24 h	×	×	×		×
NOR-B	Ozone	22	24 h	24 h	×	×	×		×
NOR-S	Ozone	22	24 h	24 h	×	×	×		×
NOR-F	Free chlorine	22	24 h	24 h	×	×	×	×	×
NOR-B	Free chlorine	22	24 h	24 h	×	×	×	×	×
NOR-S	Free chlorine	22	24 h	24 h	×	×	×	×	×
NOR-F	PAA	22	18.3 h	24 h	×	×	×		
NOR-B	PAA	22	18.3 h	24 h	×	×	×		
NOR-S	PAA	22	18.3 h	24 h	×	×	×		
DE-B1	Ozone	22	24 h	24 h	×	×	×		×
DE-B1	Ozone	22	24 h	24 h	×	×	×		×
DE-B1	Ozone	22	24 h	24 h	×	×	×		×
DE-B2	Free chlorine	22	26 h	24 h	×	×	×	×	×
DE-B2	Free chlorine	22	26 h	24 h	×	×	×	×	×
DE-B2	Free chlorine	22	26 h	24 h	×	×	×	×	×
DE-S	PAA	22	22 h	24 h	×	×	×		
DE-S	PAA	22	22 h	24 h	×	×	×		
DE-S	PAA	22	22 h	24 h	×	×	×		

Table S4. Parent and product masses, collision energies, and S-lens RF amplitude values for, bromate, HAAs, internal, and surrogate standards measured in this study.

HAA	Parent mass (<i>m/z</i>)	Product mass (<i>m/z</i>)	Collision Energy (V)	S-lens RF amplitude (V)
Bromate	126.9	110.9	25	85
Bromate	128.6	112.9	25	85
MCAA	93.00	35.0	12	40
MBAA	136.920	79	13	36
MBAA-C ¹³	139.930	81.0	13	36
DCAA	126.94	82.94	12	42
DCAA-C ¹³	127.94	83.9	12	42
BCAA	172.9	128.9	12	50
DBAA	216.85	172.9	13	47
TCAA	160.9	116.9	9	30
TBAA	252.82	81.0	25	75
BDCAA	162.9	81.0	15	50
DBCAA	206.85	79.0	17	50
2-BrBu	165.00	79.0	16	30

Table S5. A kinetic model was established using Kintecus®¹ in order to predict bromate formation in bromide-containing synthetic waters. The equations used to perform this model are listed below:

k (M ⁻¹ s ⁻¹)	Equation	Description
1.66e+9	HOBr ==> OBr ^{-a}	Forward reaction for hypobromous acid equilibrium (k _f); μ = 0 M; 20 C; Eigen et al. 1962 ²
8.34e+9	OBr ⁻ ==> HOBr ^a	Backward reaction for hypobromous acid equilibrium (k _b); μ = 0 M; 20 C; Eigen et al. 1962 ²
160/258	O ₃ + Br ⁻ ==> OBr ⁻ + O ₂	Haag and Hoigné 1983 ³ , Liu et al. 2001 ⁴
1.00E+02	O ₃ + OBr ⁻ ==> BrO ₂ ⁻ + O ₂	von Sonntag and von Gunten 2012 ⁵
3.30E+02	O ₃ + OBr ⁻ ==> Br ⁻ + 2O ₂	von Sonntag and von Gunten 2012 ⁵
1.00E+6	O ₃ + BrO ₂ ⁻ ==> BrO ₃ ⁻ + O ₂ ^b	von Sonntag and von Gunten 2012 ⁵

^a These reaction rate constants were estimated by first assuming that k_f/k_b is equal to [OBr⁻]/[HOBr] which is equal to 1.66×10⁹/8.34×10⁹ given that this is the ratio between the two acid-base species at pH 8.0. For other pH values different ratios of k_f/k_b were selected. The values were set to be at 10⁹ since it is a rapid acid-base equilibrium reaction.

^b The reaction rate is stated to be > 1×10⁵ M⁻¹s⁻¹ (see reaction 3 in main manuscript). Therefore, a value of 1×10⁶ M⁻¹s⁻¹ was selected but could be set up to 1×10¹⁰ M⁻¹s⁻¹ with no significant effect on the modeling results.





Figure S1. Map locations for the nine waters from (a) The Netherlands, (b) Norway, and (c) Germany.

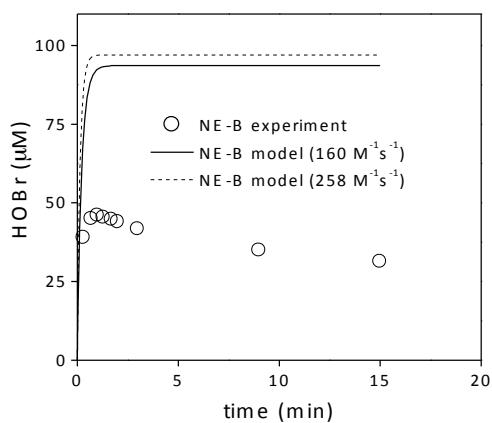


Figure S2. Comparison of the HOB_r formed when the NE-B water was ozonated to measure bromate formation. The experimental data are identical to those presented in Figure 1e, and the two model curves were simulated using Kintecus® in which the reaction rate for reaction 1 was either 160 or 258 M⁻¹s⁻¹ and the initial conditions are identical to the experimental data ([Br⁻]₀ = 38.4 mg/L (480 µM), [O₃]₀ = 5.0 mg/L (104 µM), pH 7.9).

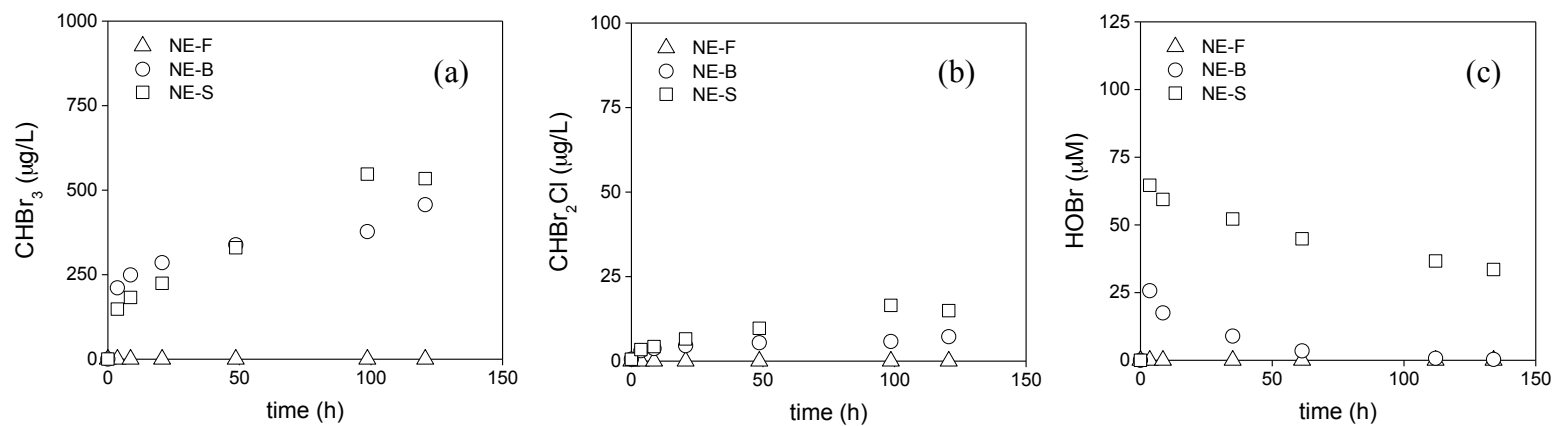


Figure S3. Formation of (a) CHBr₃ (b) CHBr₂Cl and (c) HOBr over 5 days (120 h) during ozonation (5.0 mg/L) of the NE-F, NE-B, and NE-S waters (pH 7.8-8.1 for all three waters).

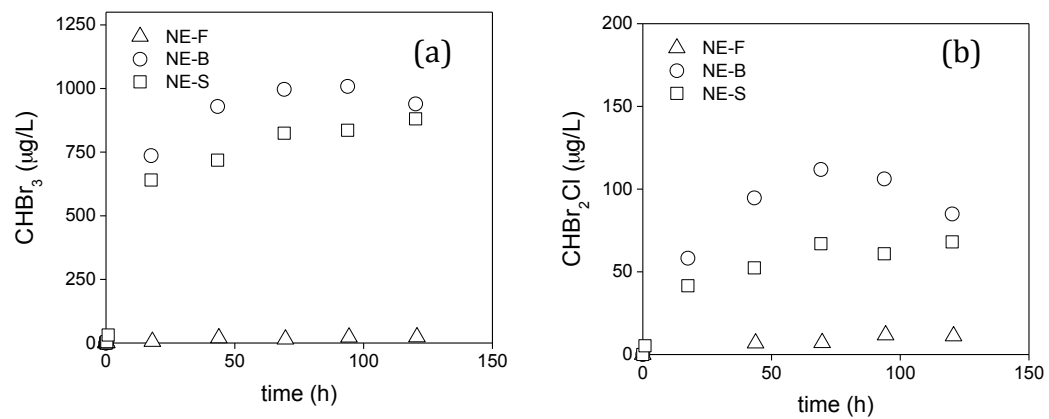


Figure S4. Formation of (a) CHBr_3 and (b) CHBr_2Cl over 5 days (120 h) during PAA treatment (150 mg/L) of the NE-F, NE-B, and NE-S waters (pH = 6.1-6.4 (NE-F); pH = 7.0-7.3 (NE-B); pH = 7.1-7.5 (NE-S))

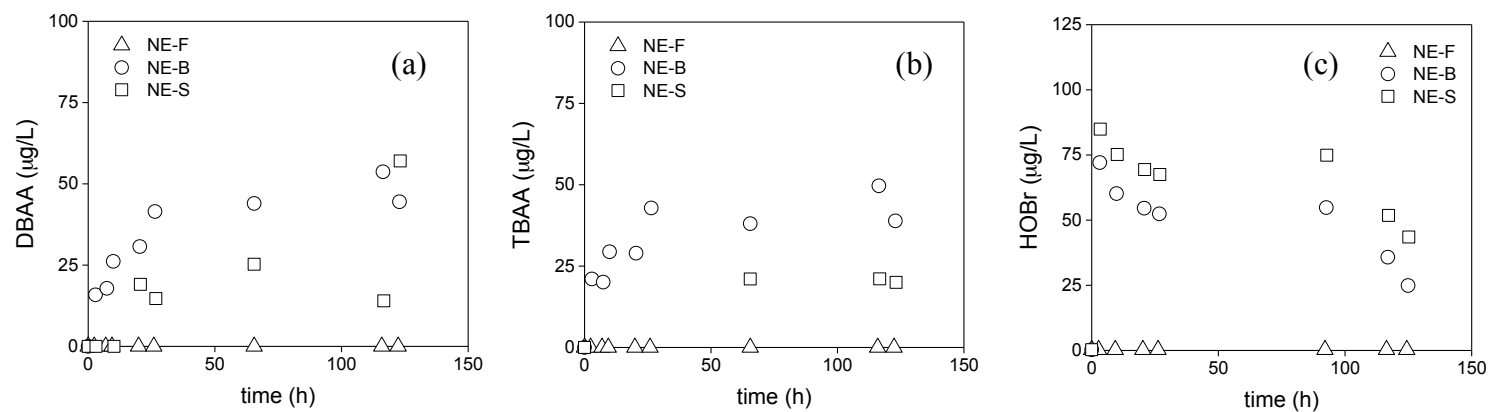


Figure S5. Formation of (a) DBAA (b) TBAA and (c) HOBr over 5 days (120 h) during ozonation (5.0 mg/L) of the NOR-F, NOR-B, and NOR-S waters (pH 7.6-8.0 for all three waters). The slight increase in the HOBr value at 90 min in Figure S5c is likely due to an experimental error.

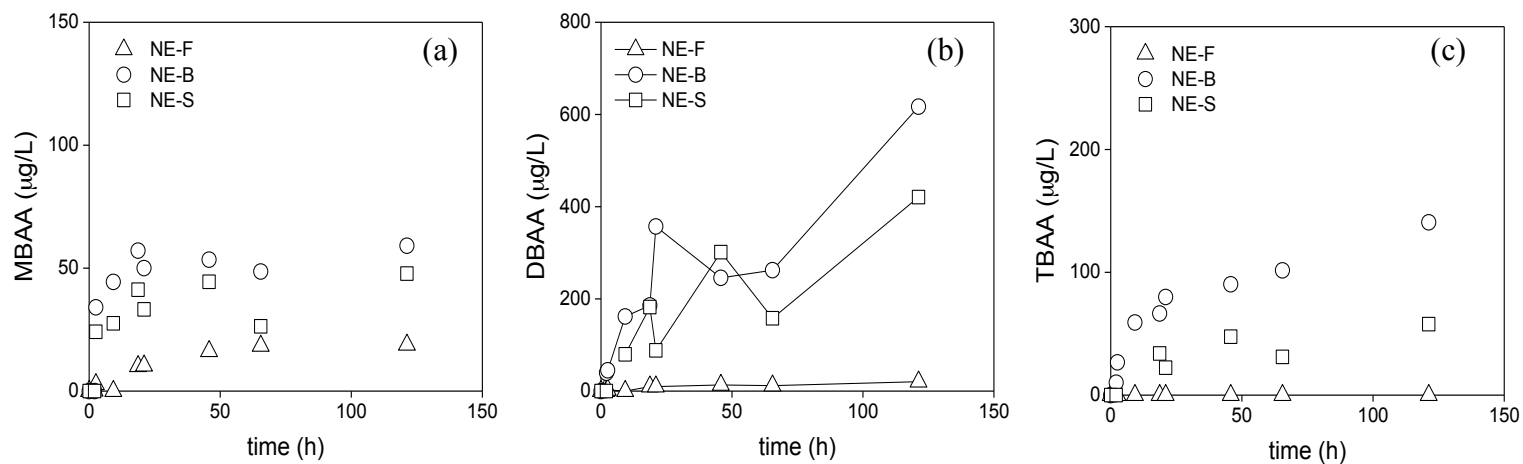


Figure S6. Formation of (a) MBAA, (b) DBAA, and (c) TBAA over 5 days (120 h) following PAA treatment (150 mg/L) of the NOR-F, NOR-B, and NOR-S waters (pH 6.8-7.2 for all three waters). The scatter in data presented in Figure S6b has been verified to not be due to analytical error but is most likely due to experimental error.

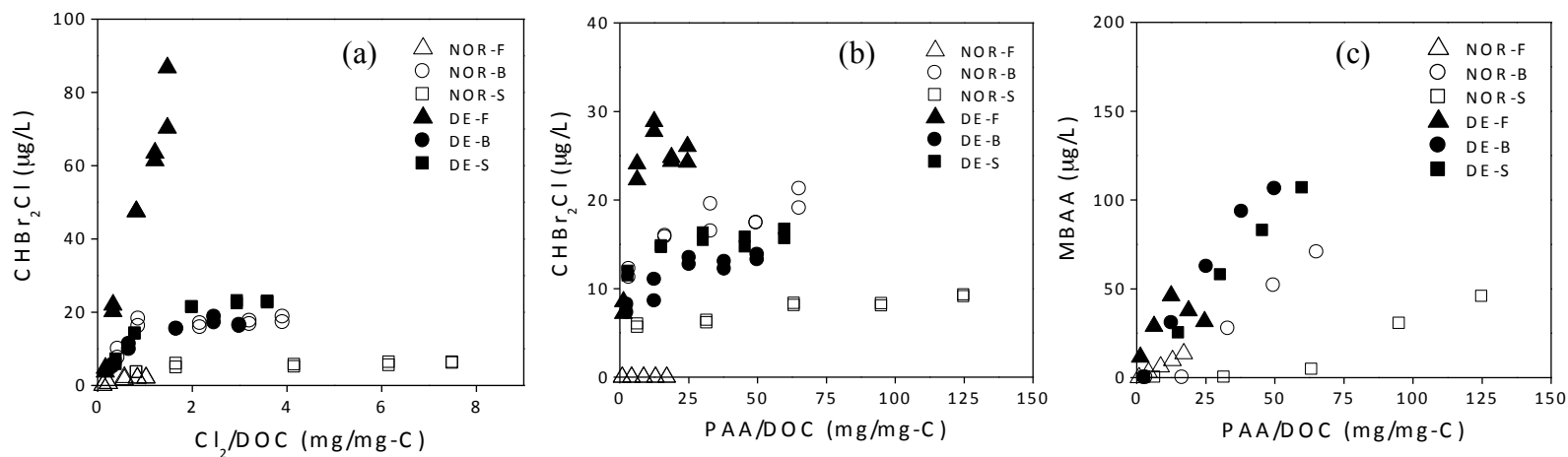


Figure S7. Formation of (a) CHBr₂Cl during chlorination (b) CHBr₂Cl during PAA treatment, and (c) MBAA during PAA treatment for the NOR and DE waters for various specific doses of each oxidant. The x-axis is plotted as the specific oxidant dose normalized to the DOC concentration (mg/mg C).

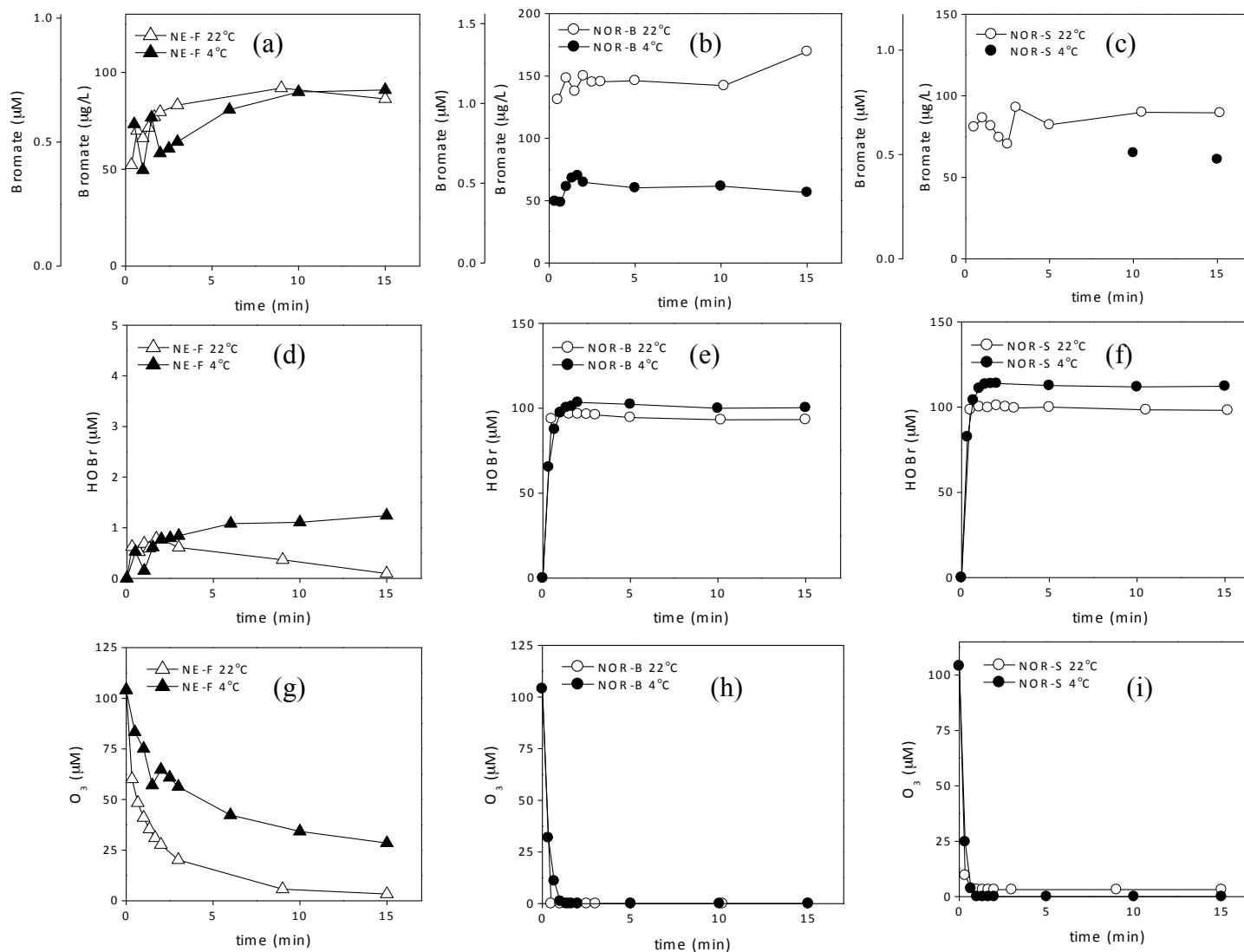


Figure S8. Effect of temperature, $22\pm 2^\circ\text{C}$ and $4\pm 2^\circ\text{C}$, on (a-c) bromate formation, (d-f) HOBr formation, and (g-i) the ozone residual concentration when the NE and NOR waters were ozonated ($[\text{O}_3]_0 = 5 \text{ mg/L}; 104 \mu\text{M}$) over 15 min. The temperature dependence for the NOR-F water was not evaluated.

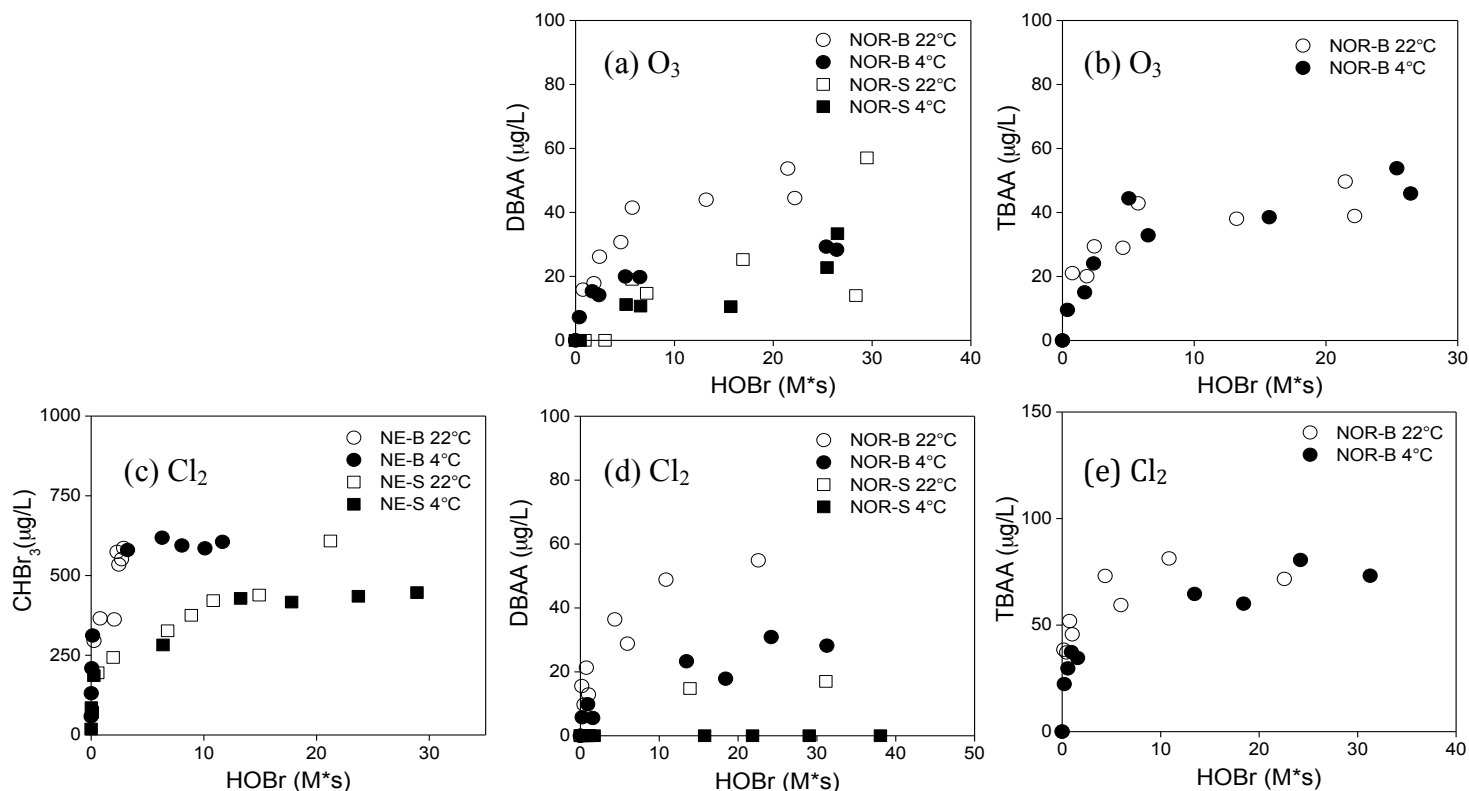


Figure S9. Effect of temperature, $22\pm 2^\circ\text{C}$ and $4\pm 2^\circ\text{C}$, on Br-DBP formation plotted against the HOBr exposure over 5 days (120 h) when the NE and NOR waters were (a-b) ozonated ($[\text{O}_3]_0 = 5 \text{ mg/L}; 104 \mu\text{M}$) and (c-e) chlorinated ($[\text{Cl}_2]_0 = 7.4 \text{ mg/L-Cl}_2; 104 \mu\text{M}$). Similar plots for such waters treated with PAA could not be established since the HOBr concentration was not measured for these experiments. Similar to Figure 7 (main manuscript), the temperature dependence for CHBr_3 formation was only evaluated in the NE waters and not evaluated during ozonation. The temperature dependence for DBAA and TBAA formation was only evaluated in the NOR waters.

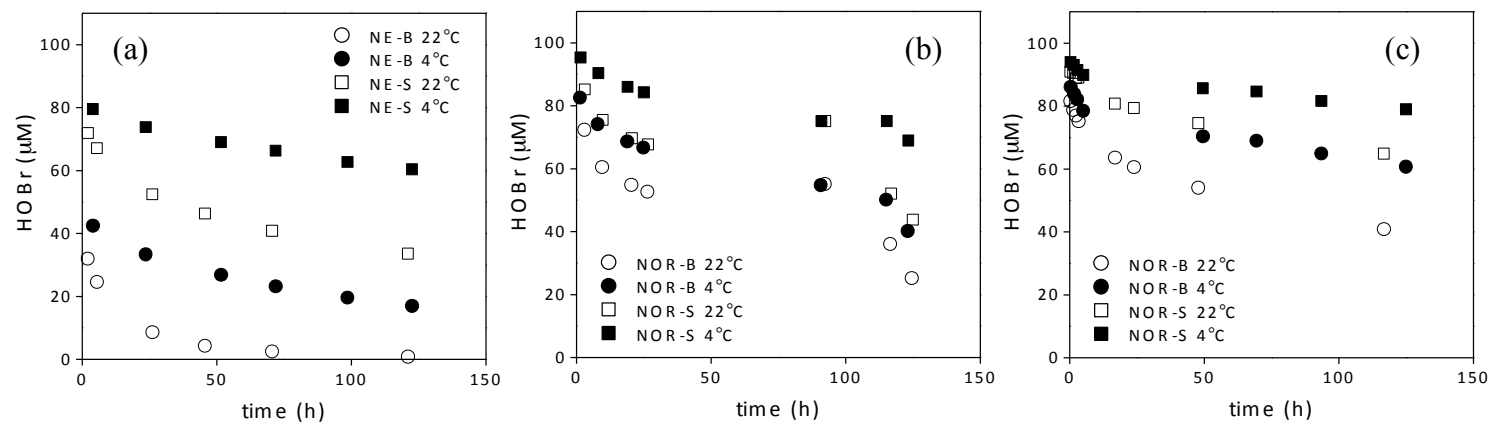
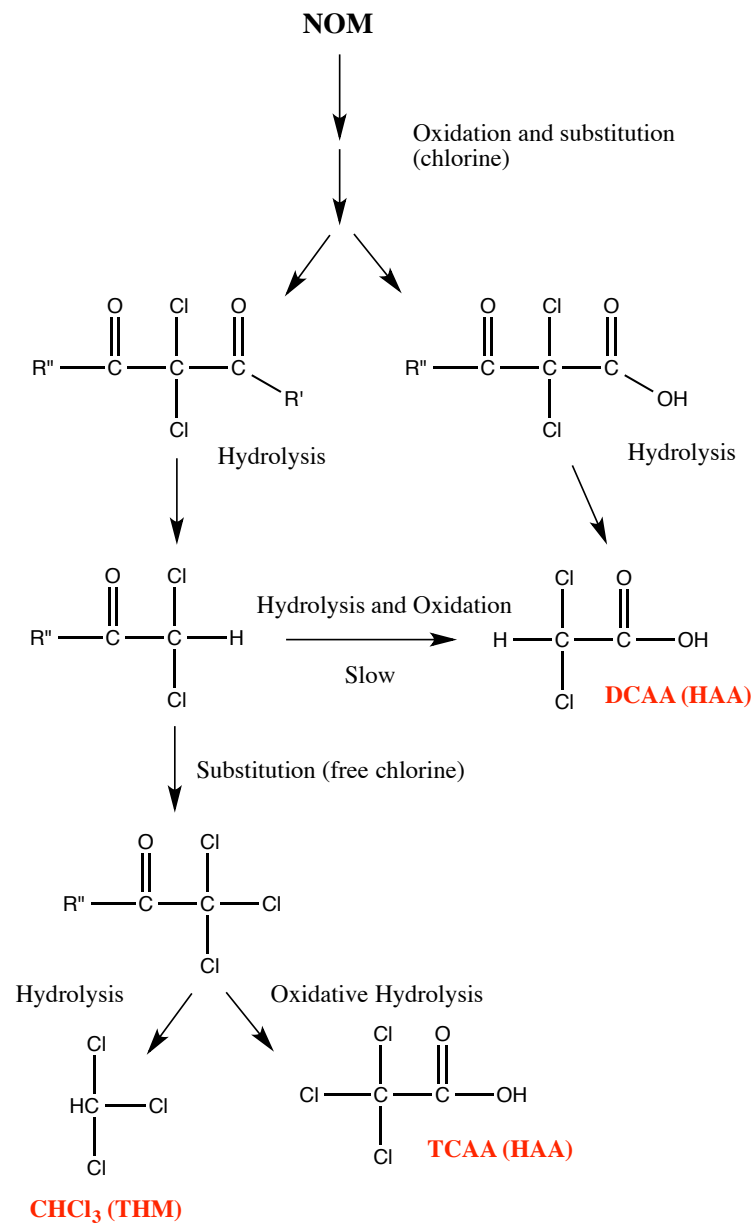


Figure S10. Effect of temperature, $22\pm 2^\circ\text{C}$ and $4\pm 2^\circ\text{C}$, on HOBr formation over 5 days (120 h) when (a) the NE-B and NE-S waters were chlorinated ($[\text{Cl}_2]_0 = 7.4 \text{ mg/L-Cl}_2; 104 \mu\text{M}$) and when the NOR-B and NOR-S water were either (b) ozonated ($[\text{O}_3]_0 = 5 \text{ mg/L}; 104 \mu\text{M}$) or (c) chlorinated ($[\text{Cl}_2]_0 = 7.4 \text{ mg/L-Cl}_2; 104 \mu\text{M}$).

Scheme S1. Simplified reaction scheme for THM and HAA (di- and tri-halogenated) formation following chlorination of natural organic matter (NOM). Adapted from Hua and Reckhow 2008.⁶



References

1. J. C. Ianni, in *Kintecus, Windows Version 5.2, 2014*, <http://www.kintecus.com>.
2. M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, 1962, **84**, 1355-1361.
3. W. R. Haag and J. Hoigné, *Environ. Sci. Technol.*, 1983, **17**, 261-267.
4. Q. Liu, L. M. Schurter, C. E. Muller, S. Aloisio, J. S. Francisco and D. W. Margerum, *Inorg. Chem.*, 2001, **40**, 4436-4442.
5. C. von Sonntag and U. von Gunten, *Chemistry of ozone in water and wastewater treatment: From basic principles to applications*, IWA Publishing, London, 2012.
6. G. H. Hua and D. A. Reckhow, *J. Am. Water Works Ass.*, 2008, **100**, 82-95.