Freezing Induced Bromate Reduction by Dissolved Organic Matter and the Formation of Organobromine Compounds

Supporting Information

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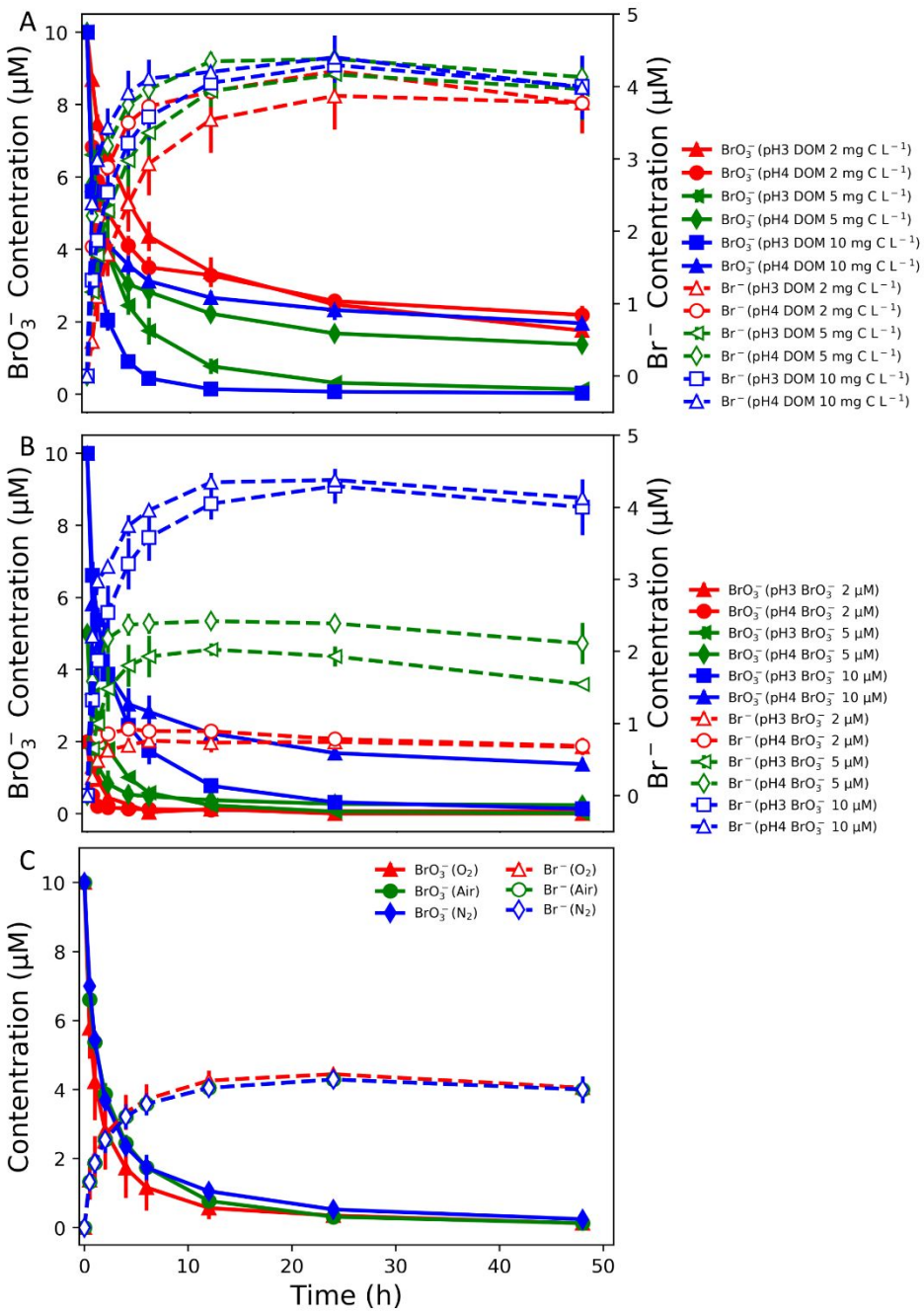

Figure S1. The concentration variation of bromate (BrO_3^-) and bromide (Br^-) in bromate frozen reduction. A: in the presence of different concentrations of DOM with 10 μM bromate, B: in the presence of different initial concentrations of bromate with 5 mg C L^{-1} DOM. C. in different saturated gas (N_2, air, O_2) with 5 mg C L^{-1} DOM and 10 μM bromate at pH 3.

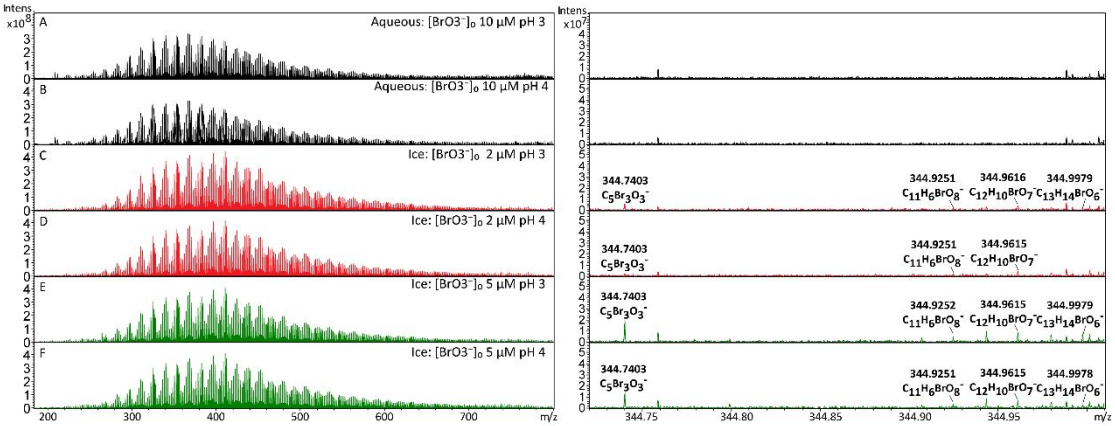

Figure S2. Negative-ion ESI-FT-ICR mass spectra of the bromate reduced samples (left) and the newly-occurred bromine-containing peaks at a nominal mass *m/z* 345 (right) in control aqueous solutions and frozen solutions with different initial bromate contents.

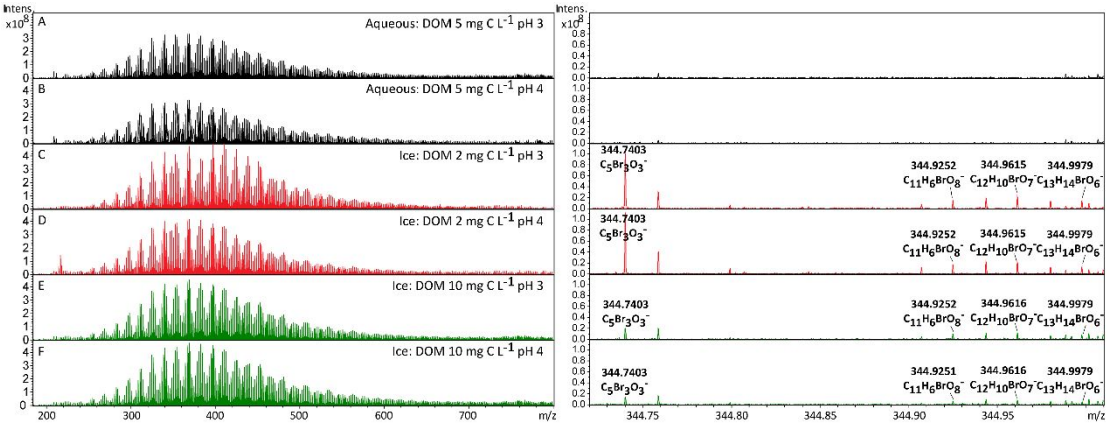

Figure S3. Negative-ion ESI-FT-ICR mass spectra of the bromate reduced samples (left) and the newly-occurred bromine-containing peaks at a nominal mass *m/z* 345 (right) in control aqueous solutions and frozen solutions with different initial DOM contents.

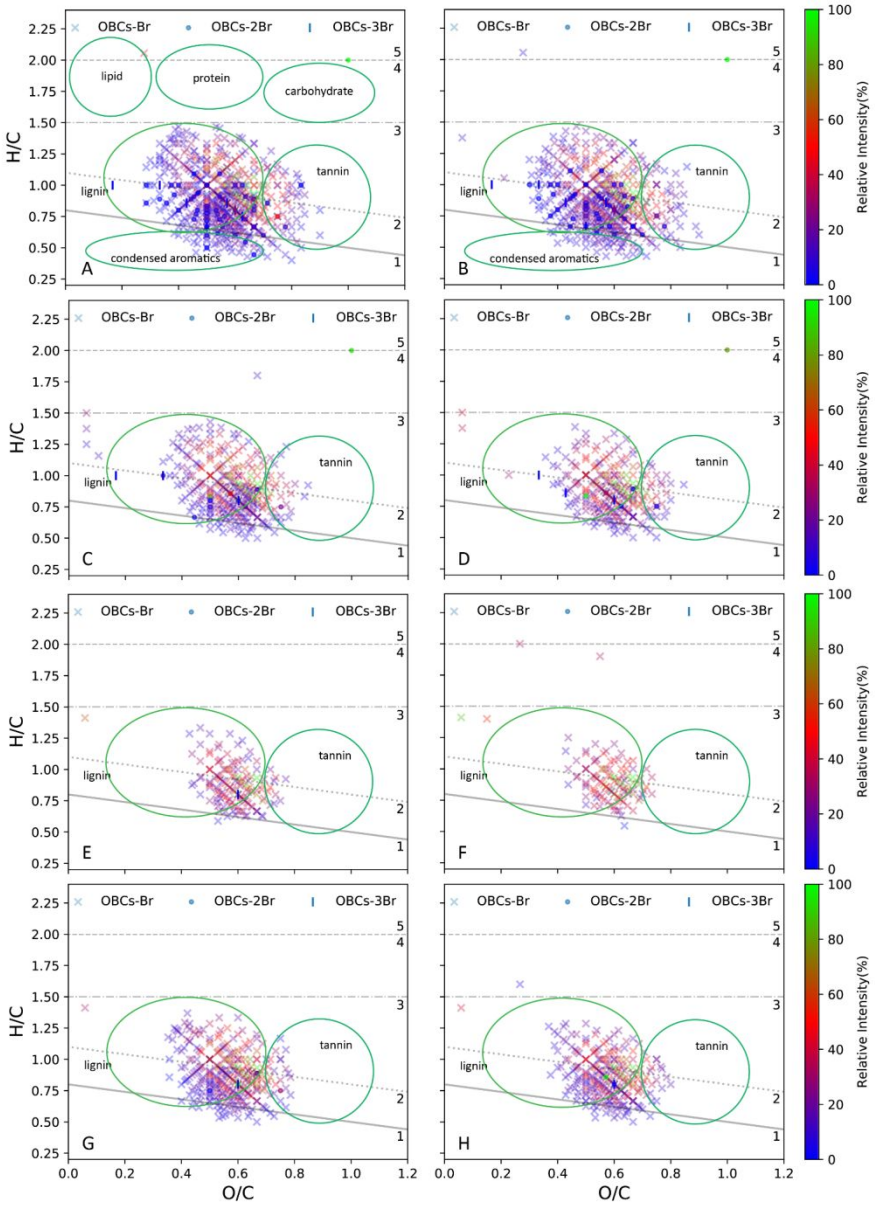

Figure S4. Molecular compositions and distributions of the OBCs generated in bromate frozen reduction solutions at pH 3 (left) and pH 4 (right). The initial content of BrO_3^- and DOM were 10 μM and 2 mg C L^{-1} (A and B), 10 μM and 10 mg C L^{-1} (C and D), 2 μM and 5 mg C L^{-1} (E and F), 5 μM and 5 mg C L^{-1} (G and H). Implemented elemental ratio criteria for compounds: [1] lipid (H/C=1.5–2.2, O/C=0–0.3), protein (H/C=1.5–2.2, O/C=0.3–0.67), carbohydrates (H/C=1.5–2.4, O/C=0.67–1.0), lignin (H/C=0.7–1.5, O/C=0.1–0.67), tannins (H/C=0.5–1.5, O/C=0.67–1.0), and condensed aromatic structures (H/C=0.2–0.7, O/C=0.1–0.67).

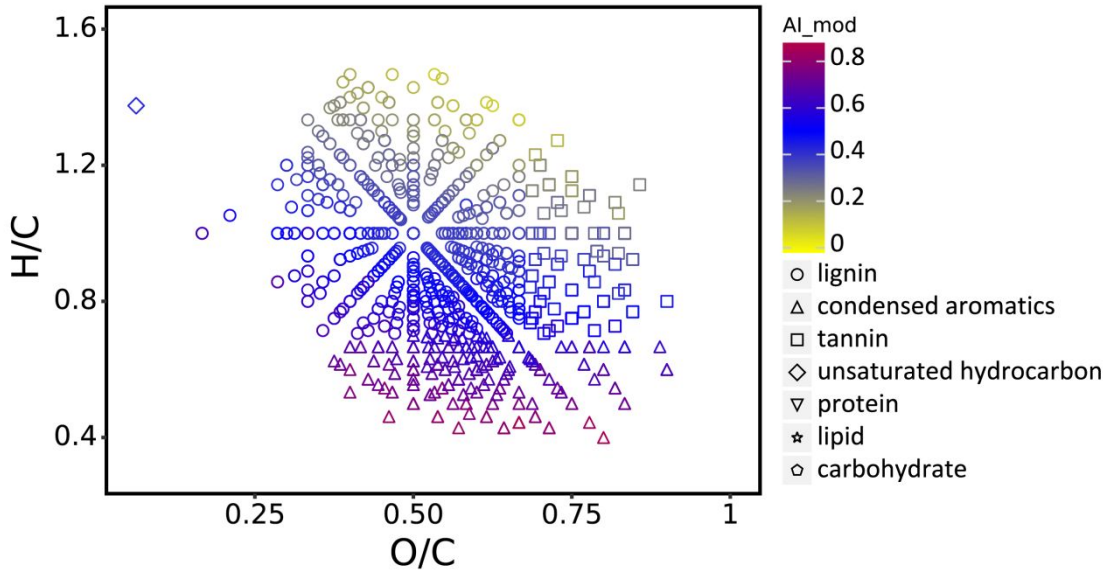

Figure S5. The joint distributions of OBCs generated in bromate frozen reduction solutions at pH 3 and pH 4.

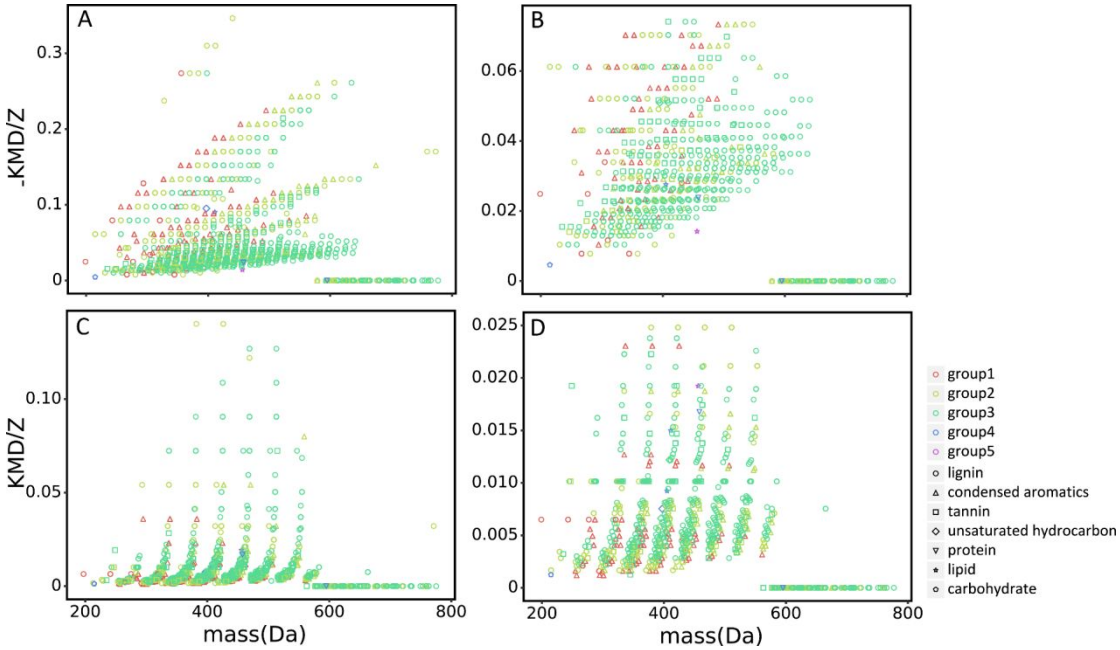

Figure S6. Modified Kendrick diagrams of the OBCs based on $-CH_2$ (A and B) and −COOH (C and D).

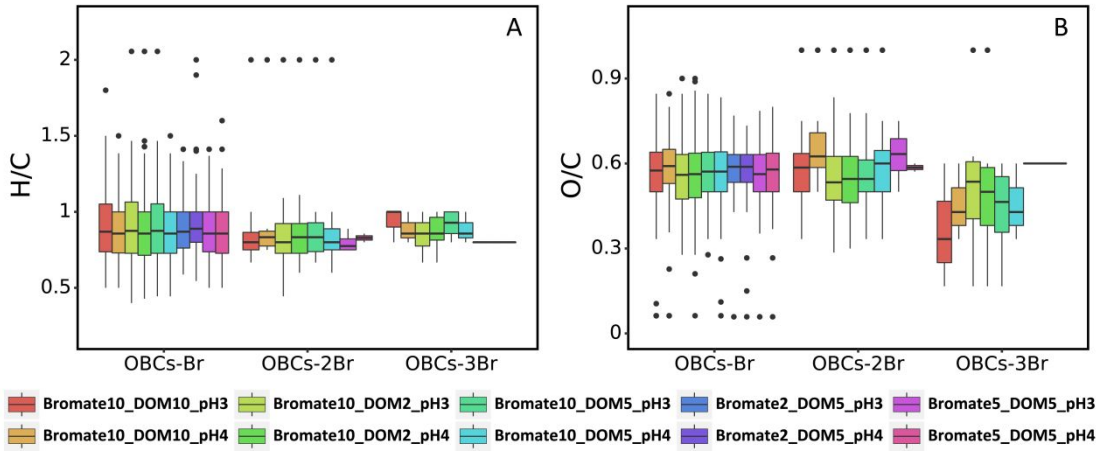

Figure S7. Boxplots of H/C and O/C for OBCs generated at different conditions. The number after bromate, DOM and pH represents the concentration of bromate (μM) and DOM (mg C L^{-1}), and pH value.

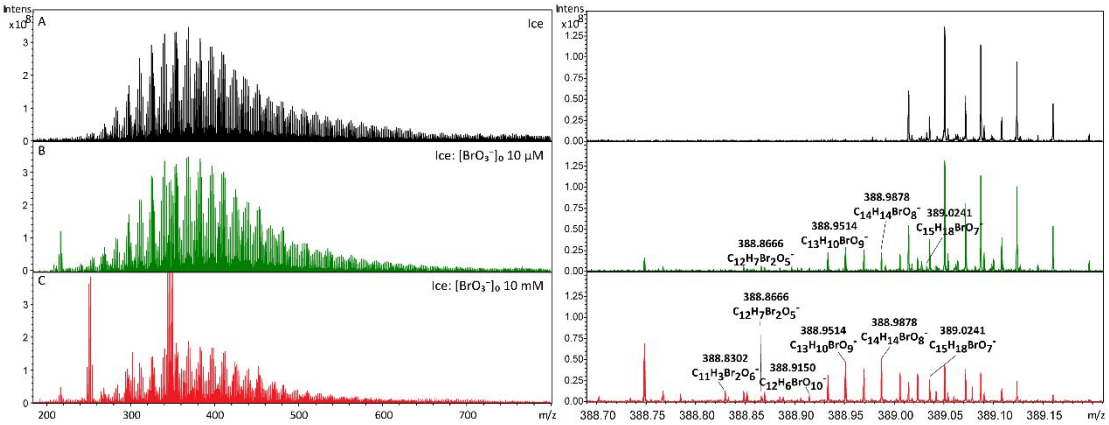

Figure S8. Negative-ion ESI-FT-ICR mass spectra of the bromate reduced samples (left) and the newly-occurred bromine-containing peaks at a nominal mass *m/z* 389 (right) in frozen solutions without bromate (A), 10 μM bromate (B) and 10 mM bromate (C). The pH and DOM content were 3 and 2 mg C L^{-1}.

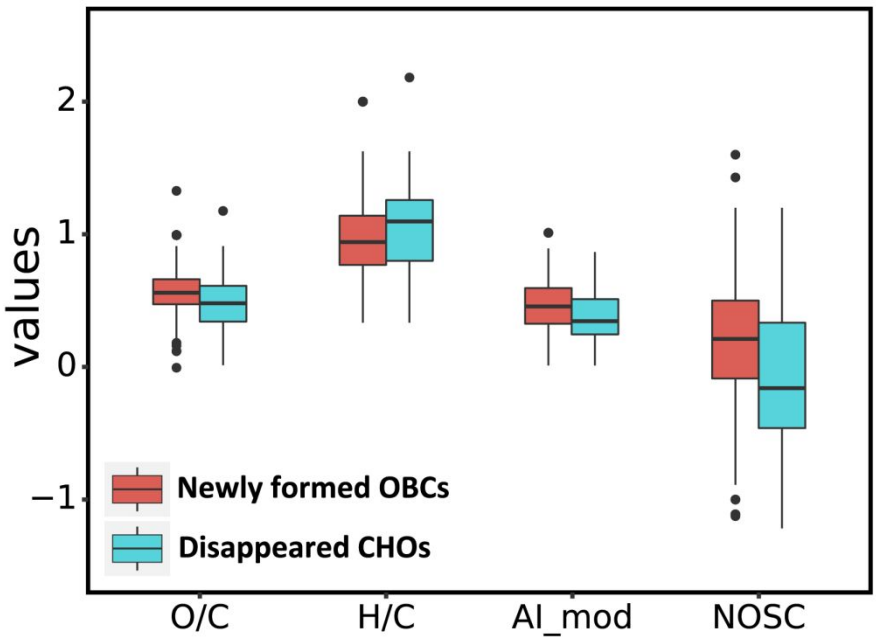

Figure S9. Boxplot of O/C, H/C, AI_mod and NOSC for the disappeared CHOs and newly formed OBCs in the presence of 10 mM bromate and 2 mg C L^{-1} DOM.

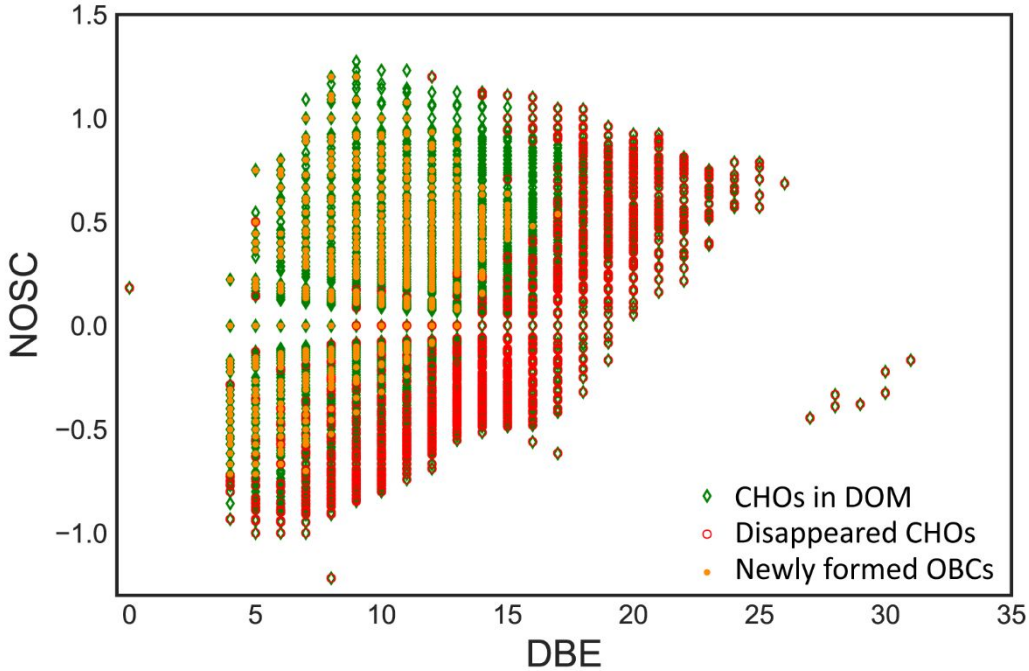

Figure S10. Plot of NOSC vs. DBE for the unbrominated CHOs, the disappeared CHOs and newly formed OBCs in the presence of 10 mM bromate and 2 mg C L^{-1} DOM.

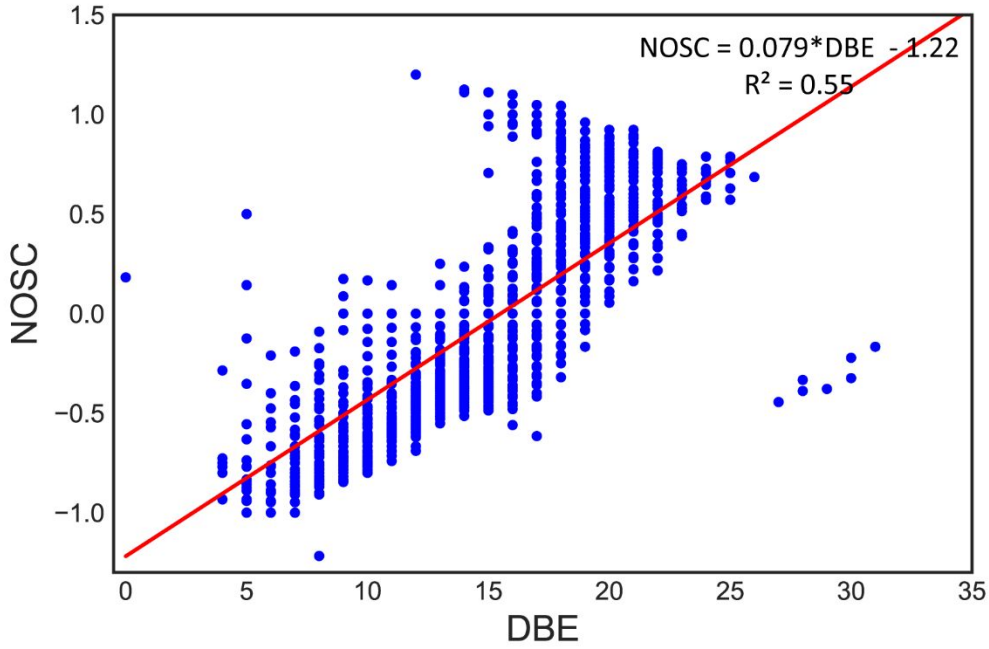

Figure S11. The correlation analysis between NOSC and DBE for the disappeared CHOs in DOM after 48 h of bromate frozen reduction.

Table S1. The statistics of OBCs formed in bromate frozen reduction

Experimental conditions	$[BrO_3^-]_0$ 10 μM DOM 2 mg C L^{-1}		$[BrO_3^-]_0$ 10 μM DOM 5 mg C L^{-1}		$[BrO_3^-]_0$10 μM DOM 10 mg C L^{-1}		$[BrO_3^-]_0$ 2 μM DOM 5 mg C L^{-1}		$[BrO_3^-]_0$ 5 μM DOM 5 mg C L^{-1}	
	pH 3	pH 4	pH 3	pH 4	pH 3	pH 4	pH 3	pH 4	pH 3	pH 4
Total number	603	539	440	348	325	256	142	110	300	252
OBCs-Br	534	483	403	326	310	246	141	110	295	249
OBCs-2Br	61	49	31	19	12	7	0	0	4	2
OBCs-3Br	8	7	6	3	3	3	1	0	1	1
CHOBr	580	527	435	343	319	252	141	106	299	250
CHONBr	20	9	4	2	3	2	0	0	0	0
CHOSBr	1	0	0	0	0	0	0	1	0	0
CHONSBr	2	3	1	3	3	2	1	3	1	2
SAR	545	482	401	318	303	241	140	106	292	246
SAOR	58	57	39	30	22	15	2	4	8	6
group1	85	74	51	43	26	19	2	1	23	17
group2	191	189	144	119	109	92	50	31	102	92
group3	324	273	243	184	187	143	90	76	175	142
group4	1	1	1	2	3	2	0	2	0	1
group5	2	2	1	0	0	0	0	0	0	0
lignin	412	355	297	234	230	174	107	89	218	177
condensed aromatics	130	126	89	71	58	46	19	8	53	48
tannin	58	54	52	41	32	33	15	10	28	25

Table S2. The statistics of element ratios for OBCs formed in bromate frozen reduction

Experimental conditions		$[BrO_3^-]_0$ 10 μM DOM 2 mg C L^{-1}		$[BrO_3^-]_0$ 10 μM DOM 5 mg C L^{-1}		$[BrO_3^-]_0$10 μM DOM 10 mg C L^{-1}		$[BrO_3^-]_0$ 2 μM DOM 5 mg C L^{-1}		$[BrO_3^-]_0$ 5 μM DOM 5 mg C L^{-1}	
		pH 3	pH 4	pH 3	pH 4	pH 3	pH 4	pH 3	pH 4	pH 3	pH 4
Total number		603	539	440	348	325	256	142	110	300	252
O/C	mean	0.56	0.56	0.57	0.57	0.57	0.59	0.58	0.58	0.56	0.57
	std	0.12	0.12	0.11	0.11	0.12	0.11	0.08	0.1	0.1	0.1
	min	0.17	0.06	0.17	0.06	0.06	0.06	0.06	0.06	0.06	0.06
	25%	0.47	0.48	0.5	0.5	0.5	0.53	0.53	0.53	0.5	0.52
	50%	0.56	0.56	0.57	0.57	0.57	0.59	0.59	0.59	0.56	0.58
	75%	0.63	0.64	0.64	0.64	0.64	0.65	0.63	0.63	0.63	0.64
	max	1	1	1	1	1	1	0.77	0.73	0.79	0.8
H/C	mean	0.9	0.88	0.89	0.87	0.9	0.88	0.88	0.92	0.88	0.86
	std	0.25	0.24	0.23	0.21	0.22	0.2	0.17	0.21	0.19	0.18
	min	0.4	0.43	0.44	0.44	0.5	0.5	0.59	0.55	0.5	0.5
	25%	0.73	0.71	0.73	0.73	0.75	0.74	0.76	0.8	0.74	0.73
	50%	0.87	0.86	0.87	0.86	0.87	0.86	0.86	0.89	0.86	0.85
	75%	1.02	1	1	1	1	1	1	1	1	1
	max	3	3	2.06	2	2	2	1.41	2	1.41	1.6

1. Lee, M.-H.; Lee, Y. K.; Derrien, M.; Choi, K.; Shin, K. H.; Jang, K.-S.; Hur, J. Evaluating the contributions of different organic matter sources to urban river water during a storm event via optical indices and molecular composition. Water Res. 2019, 115006.