Supporting Information:

Disinfection byproducts in mixed chlorine dioxide and chlorine water treatment

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Text S1. Details of iodometric method to detect chlorite, chlorate and free chlorine

Potassium iodide (100 mg/L) and sodium thiosulfate (0.01 N) was used in iodometric method. Chlorine also reacts with iodide ion in both neutral and acidic solution to produce iodine.

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$
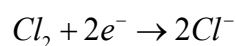
In the presence of high concentration of acid (pH 2 or less), the chlorite ion formed will react stoichiometrically to give chloride ion and 2 mol of iodine per mole of chlorite.

$$ClO_2^- + 4H^+ + 4I^- \rightarrow 2I_2 + Cl^- + 2H_2O$$
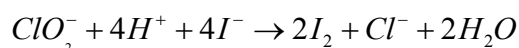
When pH was around 0.5, chlorate would also react with iodide ion.

$$ClO_3^- + 6H^+ + 6I^- \rightarrow 3I_2 + Cl^- + 3H_2O$$
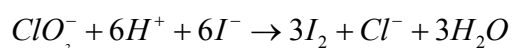
A 10 mL sample is put to a flask and buffered to pH 7 before addition of KI. After addition of KI, add 0.01 N $Na_2S_2O_3$ from a buret until the yellow color of the liberated iodine is almost discharged. Add 1 mL starch solution and titrate until blue color is completely discharged. The volume of $Na_2S_2O_3$ used was referred to A.

Then, a 5 mL 2.5 N hydrochloric acid is put to above solution and repeat the titration procedure, the volume of $Na_2S_2O_3$ used in this step was referred to B.

Another 10 mL sample is taken and is acidized to pH < 0.5. After 20-min reaction in the dark, a 10 mL KI solution is added to the sample and mixed. Then the solution is buffered to pH 7 and the titration procedure is repeated. The volume of $Na_2S_2O_3$ used in this step was referred to C.

Blank titration is also done to correct the influence of the possible impurities in oxidizing or reducing reagent. The volume of in blank titration was referred to D.

The concentrations of chlorate and chlorite can be calculated by the following equations:

Chlorate (mg/L) = [C-D-(A+B)]×13.908

Chlorite (mg/L) = B×16.863

Table S1. Water parameters for water samples

	SRNOM	HS	GM
pH	7.00	7.65	7.94
UV254 (m^{-1})	0.144	0.033	0.027
SUVA (L/mg·m)	3.6	1.2	2.5
Br^- (mg/L)	N.D.	N.D.	N.D.
SO_4^{2-} (mg/L)	2.4	5.9	23.6
NH_3-N (mg/L)	N.D.	0.02	0.03
NO_2-N (mg/L)	N.D.	N.D.	N.D.
NO_3-N (mg/L)	N.D.	6.9	7.1
PO_4^{3-} (mg/L)	N.D.	N.D.	0.23

N.D.: analyzed but below detection limits (0.02 mg/L).

Table S2. Percentages of each EEM region of water samples before/after pre-oxidation with ClO_2 or mixed oxidant (ClO_2/Cl_2).

sample	Region Ⅰ (%)	Region Ⅱ (%)	RegionⅢ (%)	Region Ⅳ (%)	Region Ⅴ (%)
SRNOM	0.5	1.9	14.1	6.3	77.2
ClO_2 alone	0.1	1.4	14.7	4.6	79.2
ClO_2/Cl_2 (1:0.5)	0.2	1.5	14.7	4.8	78.9
HS	1.4	11.5	23.5	13.6	50.0
ClO_2 alone	3.8	11.5	23.8	12.9	48.0
ClO_2/Cl_2 1:0.2	3.0	12.2	22.8	13.4	48.7
ClO_2/Cl_2 1:0.5	3.5	12.9	22.9	13.5	47.2
ClO_2/Cl_2 1:0.8	3.7	12.0	22.5	13.7	48.2
ClO_2/Cl_2 1:1	3.0	12.8	21.9	14.6	47.7
GM	5.6	13.6	22.7	14.5	43.6
ClO_2 alone	4.8	15.8	20.5	16.0	42.9
ClO_2/Cl_2 (1:0.5)	7.1	15.5	20.4	15.8	41.3

Table S3. Total THM concentration of HS sample after different treatment with presence of bromide (0-2 mg/L).

Bromide (mg/L)	Total THM concentration (µg/mg DOC)		
	No pre-oxidation	ClO_2	ClO_2/Cl_2 (1:0.5)
0	16.7	14.6	12.1
0.1	23.8	21.6	14.0
0.2	25.1	21.3	18.5
0.5	27.4	20.2	22.8
1	28.7	23.4	26.3
2	34.2	26.0	30.5

Table S4. The BIF of THMs and HANs generated in HS waters during pre-oxidation (Cl_2, ClO_2 and ClO_2/Cl_2) at 1 mg/L Br^-.

Reaction time	THMs			HANs		
	Cl_2	ClO_2	ClO_2/Cl_2 (1:0.5)	Cl_2	ClO_2	ClO_2/Cl_2 (1:0.5)
After 45min	1.20	0.00	2.37	0.88	0.00	1.78

Table S5. Residual chlorine after 24-hour chlorination (40 mg/L) with/without pre-oxidation.

Treatment	Residual Chlorine (mg/L)		
	SRNOM	HS	GM
ClO_2+Cl_2	21.5±1.0	23.9±0.4	24.9±0.3
Cl_2	18.5±0.3	21.3±1.0	24.6±0.7
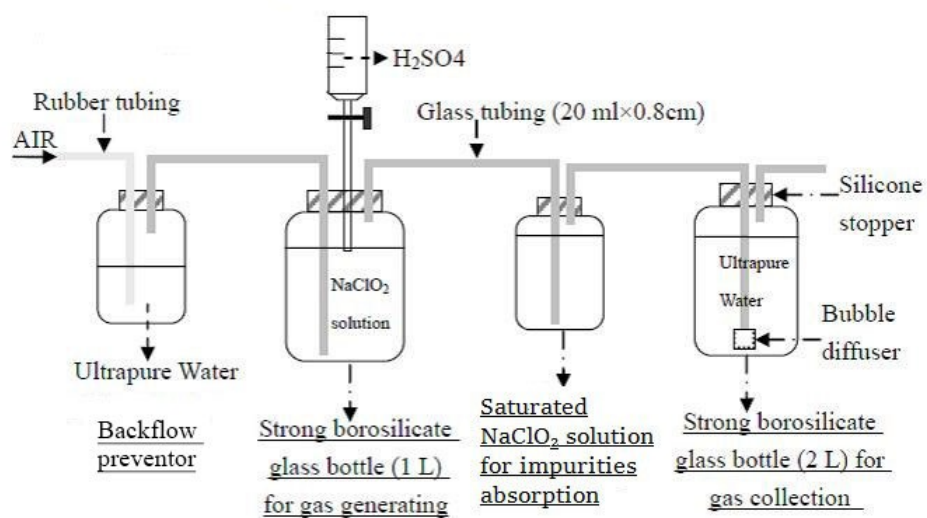
Fig. S1. The diagram to illustrate the generation of chlorine dioxide in high purity.

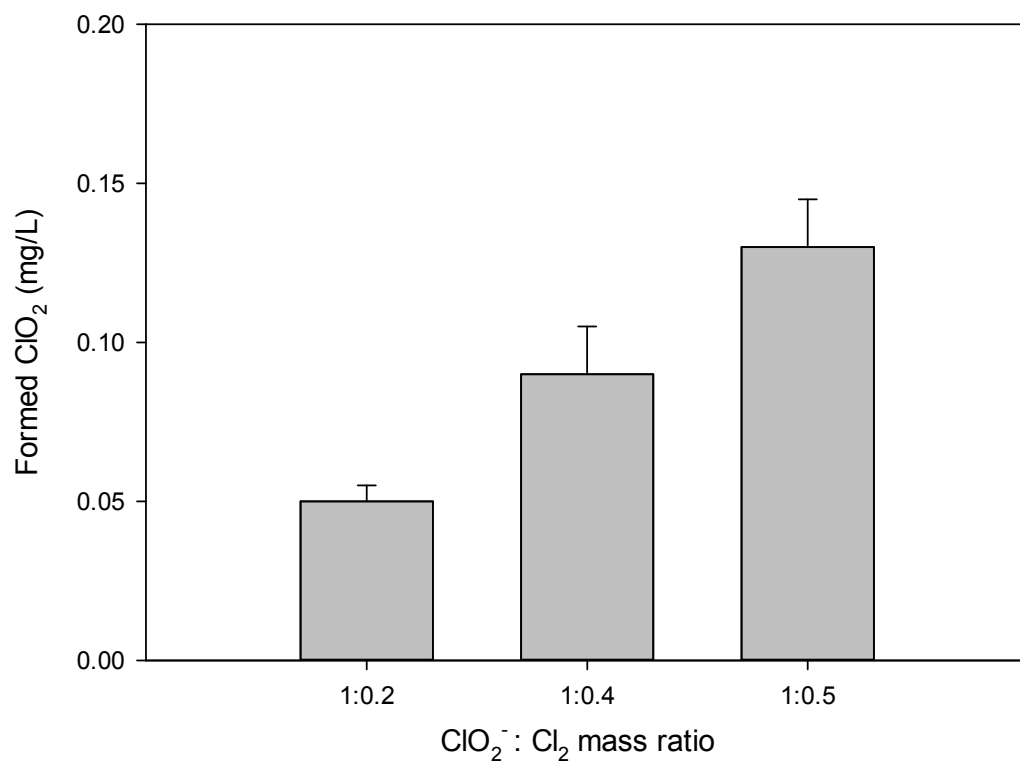Fig. S2. The chlorine dioxide formed form reaction between chlorite (5 mg/L) and chlorine (1-2.5 mg/L) at pH 7 (The error bars represents error bars represent the difference in concentration of the two duplicate samples).
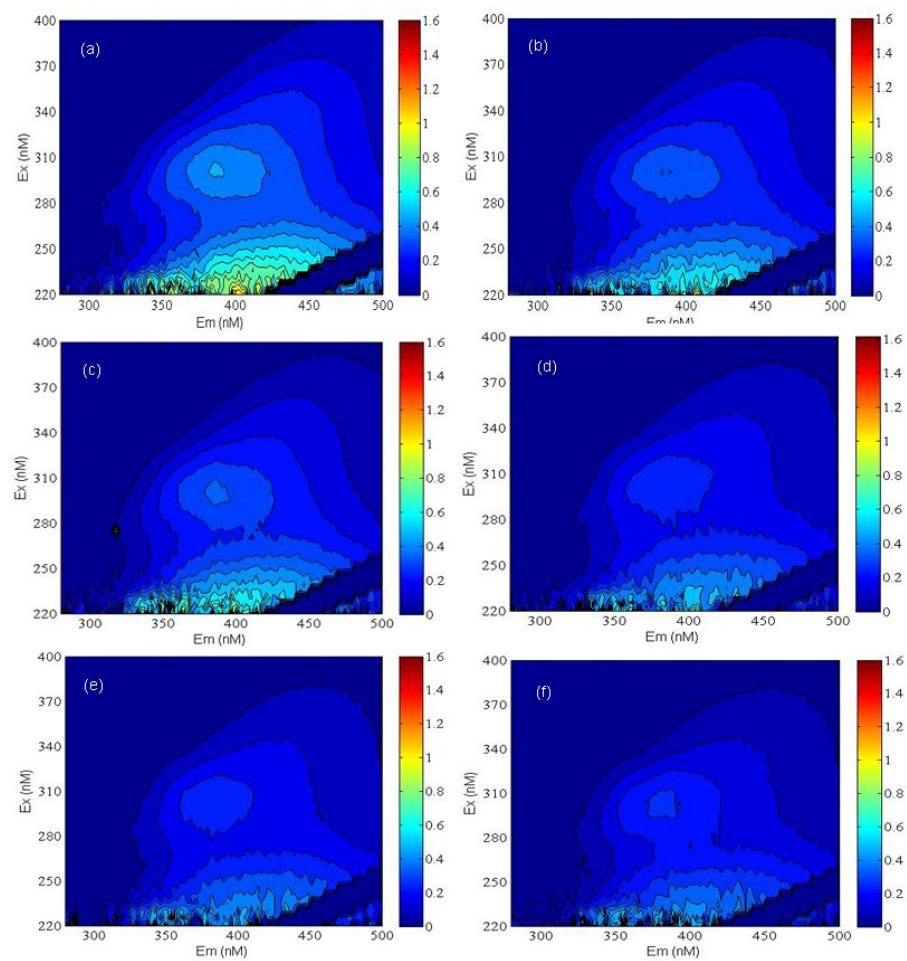
Fig. S3. Fluorescence EEMs of: (a) HS, (b) HS+ 1 mg/L ClO_2 pre-oxidation, (c-f) HS+ mixed oxidant pre-oxidation (1 mg/L ClO_2 mixed with 0.2, 0.5, 0.8 and 1 mg/L Cl_2).
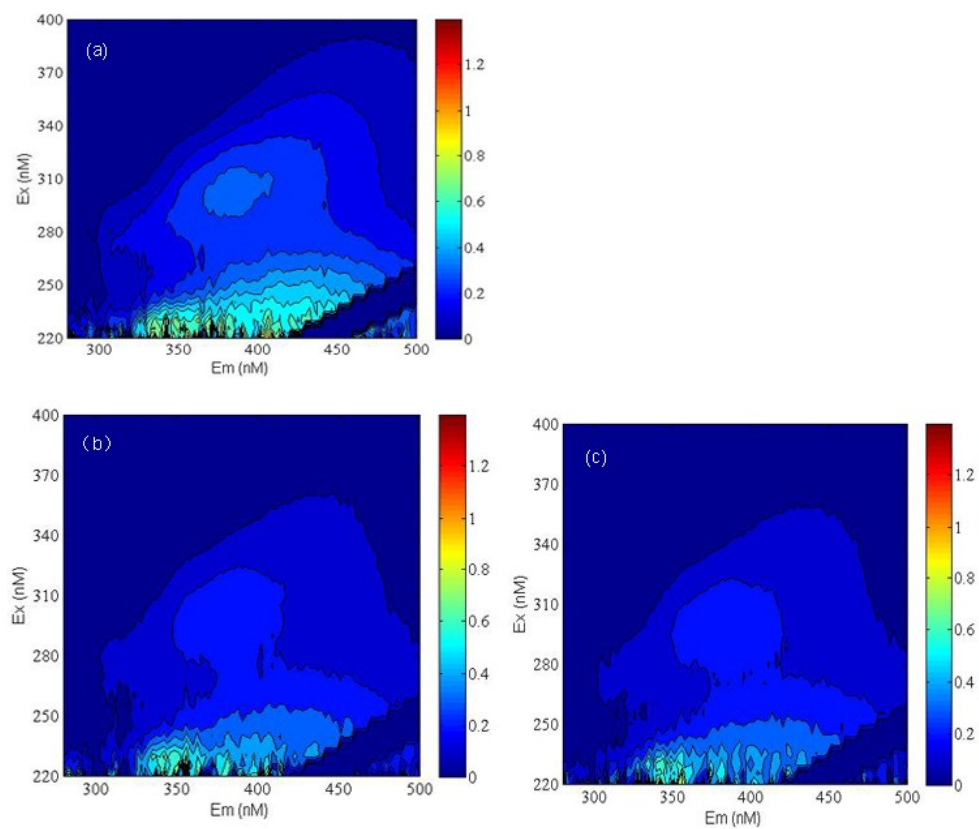
Fig. S4. Fluorescence EEMs of: (a) GM, (b) GM+ 1 mg/L ClO_2 pre-oxidation, (c) GM+ mixed oxidant at mass ratio of 1:0.5 (ClO_2/Cl_2).
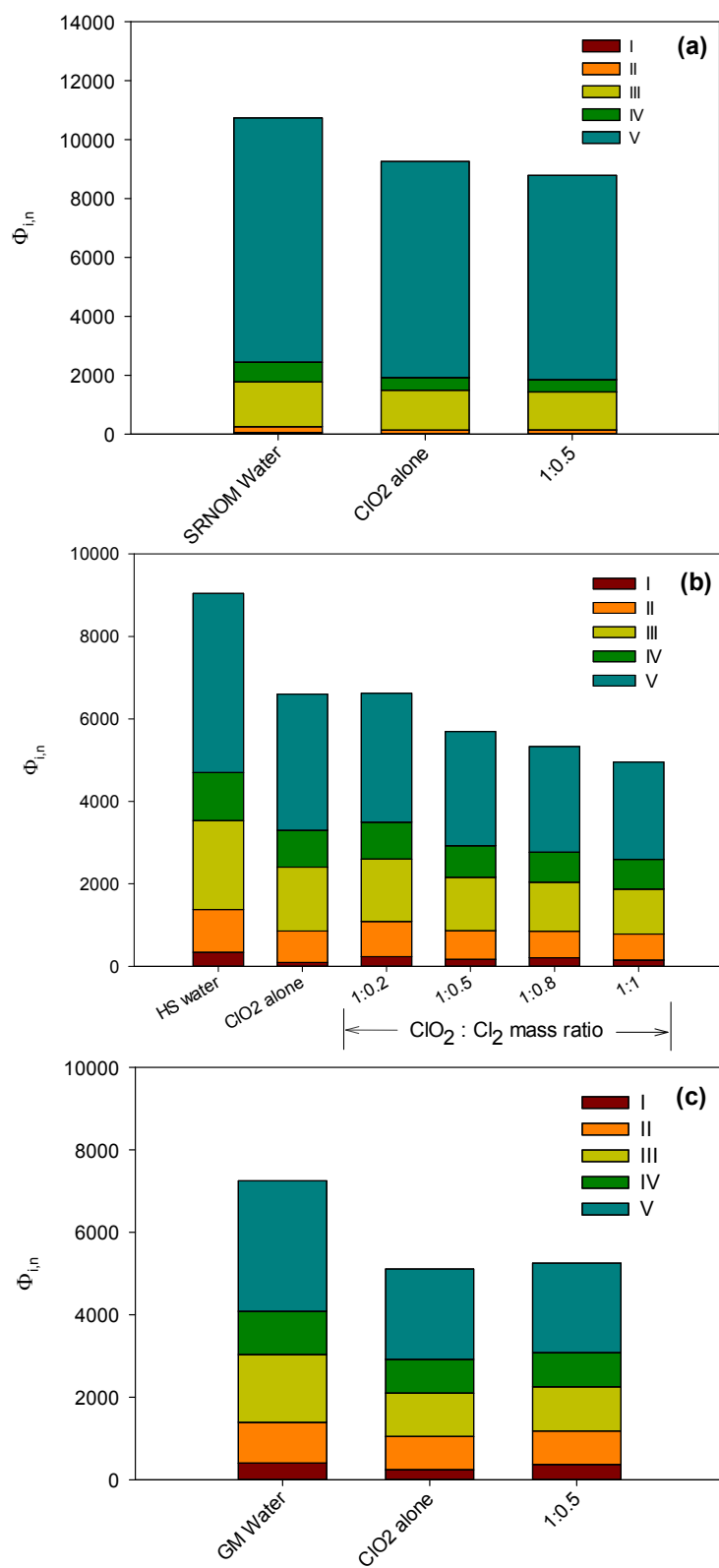
Fig. S5. The changes of fluorescence intensity of five excitation-emission regions with and without pre-oxidation in (a) SRNOM; (b) HS and (c) GM.