

**Electronic Supplementary Information: Rapid, High-Sensitivity Analysis of Oxyhalides by Non-Suppressed Ion Chromatography-Electrospray Ionization-Mass Spectrometry: Application to  $\text{ClO}_4^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$ , and  $\text{BrO}_3^-$  Quantification During Sunlight/Chlorine Advanced Oxidation**

**Text S1. Detailed Description of Experimental Setup and Reactor Configurations for FAC only and sunlight/FAC Treatments.**

*Simulated sunlight experiments.* Experiments were undertaken in 28-mL quartz tubes in duplicate, and thermostated at 10 °C in a circulating water bath below the lamp in the Atlas solar simulator. Sample tubes were inclined at an angle of 35° from the horizontal in test tube racks that can each hold 10 tubes. Two racks were placed within the water bath during each experiment with tubes angled outward from the center and parallel to the lamp.

Ten-mM phosphate buffer was used to control pH at either pH 6.0 or 8.0±0.1 in Milli-Q reagent water, or at the native pH of natural water samples (Table S2). Bromide concentrations in phosphate-buffered reagent waters were either 0 or 200 µg/L, and specified natural water samples were dosed with an additional 200 µg/L of bromide beyond native concentrations. Stock free available chlorine (FAC) concentrations were standardized spectrophotometrically (at pH 11) at  $\lambda = 292 \text{ nm}$  using  $\epsilon_{292\text{nm},\text{OCl}^-} = 350 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>1</sup>

Sunlight/FAC experiments were initiated by dosing FAC (targeting an initial concentration of ~8 mg/L as  $\text{Cl}_2$ ) into quartz tubes containing the prepared water matrix. Solutions within quartz tubes were manually mixed after FAC addition by inverting the tubes three times. After FAC addition and mixing, a 2 mL sample was collected and immediately amended with 0.2 mM ethylene diamine (EDA) to sequester FAC for later quantification of  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ , and  $\text{BrO}_3^-$  introduced from the chlorine stock at the initiation of the sunlight/FAC experiments.

The tubes containing sunlight/FAC experimental solutions were immediately placed in one of the two racks submerged in the thermostated water bath within the solar simulator (with up to 20 tubes arranged in parallel at 35° inclination from the horizontal). Sunlight/FAC experiment sets were concluded after a pre-defined irradiation time (0, 20, or 45 minutes), at which point residual FAC in all tubes was sequestered with a two-fold molar excess of EDA for subsequent analysis of  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ , and  $\text{BrO}_3^-$ . Irradiation times and FAC concentrations were selected to reflect conditions previously found to yield 1- to 3- $\log_{10}$  inactivation of *Cryptosporidium* spp. oocysts and/or *Bacillus subtilis* spores during sunlight/FAC treatment.<sup>2, 3</sup>

*FAC only experiments.* Dark chlorination (FAC only) experiments were initiated by dosing FAC (targeting an initial concentration of ~8 mg/L as  $\text{Cl}_2$ ) into amber glass vials containing the prepared water matrix, with continuous mixing using PTFE-coated magnetic stir bars. After chlorine addition and mixing, a 2 mL sample was collected and immediately amended with 0.2 mM EDA to sequester FAC for later analysis of  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ , and  $\text{BrO}_3^-$  introduced from the chlorine stock at the initiation of the FAC only experiments.

The FAC only experiments were then allowed to proceed up to a reaction time sufficient to reach the same target  $CT_{\text{FAC}}$  as the 45-minute-irradiated sunlight/FAC experiments described above (with  $CT_{\text{FAC}}$  determined according to equation 8 in the main text), at which point residual FAC in all tubes was sequestered with a two-fold molar excess of EDA for subsequent analysis of  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ , and  $\text{BrO}_3^-$ .

*Natural water samples.*  $\text{Cl}^-$  concentrations were quantified in filtered natural water samples and the collected tap water using ion chromatography (IC) with suppressed conductivity detection on a Dionex ICS-3000 system equipped with a Thermo Scientific Dionex IonPac AS9-HC carbonate form column operated with a gradient spanning carbonate concentrations of 5–20

mM. Low concentrations of bromide were quantified by means of non-suppressed ion chromatography with mass spectrometry detection using LC-MS/MS System 1, but with an isocratic method employing a fully aqueous mobile phase containing 200 mM methylamine. Dissolved organic carbon concentrations were quantified using a Shimadzu TOC-L<sub>CSH</sub> high-temperature catalytic combustion system.<sup>4</sup> An Orion 5 Star meter with Orion ROSS Ultra pH electrode was used to measure native pH of natural water samples or while adjusting the pH of phosphate buffer solutions (using 1 mol/L NaOH or 500 mmol/L H<sub>2</sub>SO<sub>4</sub> for pH adjustment). Selected water quality parameters for each sample are listed in Table S2.

### **Text S2. Spectroradiometry and *para*-Nitroanisole/Pyridine Actinometry Measurements.**

Incident spectral irradiance measurements for simulated sunlight were obtained using a USB2000+ XR spectroradiometer (Ocean Optics; Dunedin, FL) equipped with a 200  $\mu\text{m}$  x 2 m optical fiber and a CC-3-UV-S cosine corrector. A representative incident spectral irradiance curve is depicted in Figure S2 for the Atlas solar simulator output compared with the ASTM standard G173-03 for solar radiation (hemispherical on a 37° tilted surface) at sea level.<sup>5</sup> Measured incident irradiance spectra were obtained in the present work at the surface of the quartz tubes containing the reaction solutions, with the plane of the spectroradiometer's cosine corrector facing directly (perpendicular) toward the light source.

Effective in situ fluence rates,  $F_{\text{tot},\lambda}$ , from 290-400 nm were determined for simulated solar irradiation experiments by means of *para*-nitroanisole (pNA)/pyridine actinometry.<sup>6, 7</sup> Actinometer solutions containing 1  $\mu\text{M}$  pNA and 10 mM pyridine were prepared in Milli-Q water. These actinometer solutions were then transferred into the same 28-mL quartz tubes as used for sunlight/FAC experiments (Text S1). The actinometer solutions were kept in the dark

until the start of each experiment, after which they were exposed to light for similar durations as utilized in the sunlight/FAC experiments. Samples were obtained from the irradiated actinometer solutions at pre-defined time intervals for pNA analysis. pNA concentrations were measured on an UltiMate3000 HPLC-UV system (Thermo Scientific/Dionex), using isocratic elution (0.2 mL/min) on a Supelco Ascentis C18 column (150 × 2.1 mm, 3 μm), with 50:50 CH<sub>3</sub>CN:10-mM H<sub>3</sub>PO<sub>4</sub> as mobile phase.  $F_{\text{tot},\lambda}$  was in turn determined to be 59.8 W/m<sup>2</sup> from pNA degradation rates in accord with established procedures,<sup>8</sup> using recently reported updated quantum yield data for pNA photolysis.<sup>7</sup>

### **Text S3. Influence of Mobile Phase Composition on Methylamine Base Strength.**

Acetonitrile has a high proton solvation energy relative to water and other common solvents such as methanol, which can result in large increases in the pK<sub>a</sub>s of acids and bases when dissolved in mobile phases comprising high acetonitrile to water ratios.<sup>9</sup> The effective pK<sub>a</sub>s for organic bases (e.g., methylamine) typically decrease at low proportions of organic solvent, but then increase substantially at higher acetonitrile percentages (>70%), with an expected pK<sub>a</sub> = 18.3 for methylamine in 100% acetonitrile.<sup>9, 10</sup> With a higher pK<sub>a</sub>, a higher proportion of methylamine will be protonated in the 20% A + 80% B phase compared to in fully aqueous methylamine, resulting in increased OH<sup>-</sup> concentrations and hence, increased mobile phase pH, for a given concentration of methylamine at high acetonitrile to water ratios.

**Table S1.** Summary of chlorine photolysis reactions and quantum yields

	$\Phi(254 \text{ nm})$	$\Phi(313 \text{ nm})$	$\Phi(365 \text{ nm})$
$\text{HOCl} + h\nu \rightarrow \text{HO}^\bullet + \text{Cl}^\bullet$	0.46–1.4 <sup>11-13</sup>	1 <sup>a 14</sup>	NA
$\text{OCl}^- + h\nu \rightarrow \text{O}^{\bullet-} + \text{Cl}^\bullet$	0.28 <sup>15</sup>	0.13 <sup>15</sup>	0.08 <sup>15</sup>
$\text{OCl}^- + h\nu \rightarrow \text{O}(^3\text{P}) + \text{Cl}^-$	0.074 <sup>15</sup>	0.075 <sup>15</sup>	0.28 <sup>15</sup>

<sup>a</sup> At approximately 310 nm, NA = not available

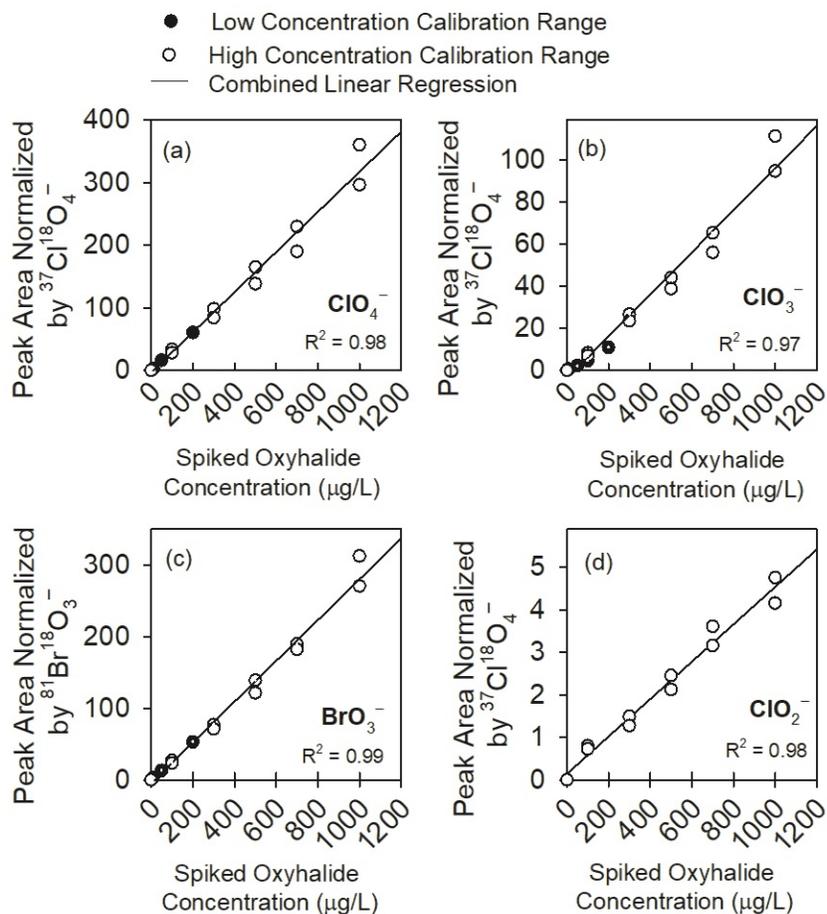
**Table S2.** Characteristics of natural water samples

	pH	$\text{Br}^-$ Conc. ( $\mu\text{g/L}$ )	$\text{Cl}^-$ Conc. ( $\text{mg/L}$ )	DOC Conc. ( $\text{mg}_\text{C}/\text{L}$ )
Tap water	7.6	20	5	0.4
Local Reservoir	8.1	25	3	0.5
Lake Washington	8.1	24	3	2.4
Groundwater	7.4	320	132	1.4

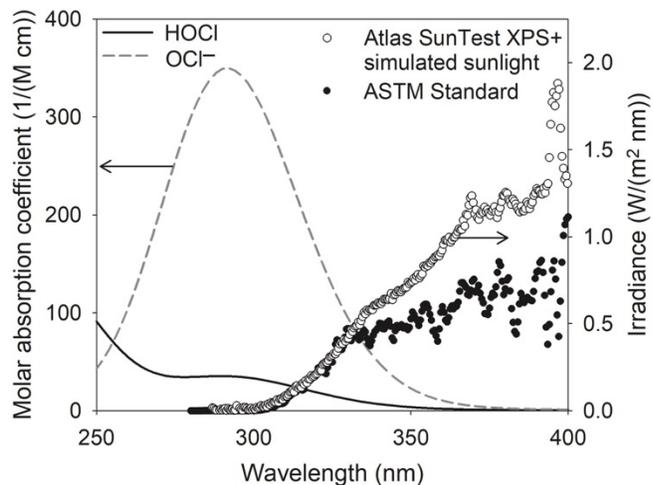
**Table S3.** Retention times (in minutes) for 10 µg/L oxyhalide standards in various matrixes over sequential 100 µL injections, with isocratic elution from a 250 × 2 mm, 9 µm, AS16 column at 20% A + 80% B and 0.25 mL/min, using LC-MS/MS System 1.<sup>a</sup>

Injection #	Milli-Q Water	in 10 mM Phosphate Buffer			in Milli-Q water <sup>b</sup>				
		No Ba <sup>2+</sup>	Ba <sup>2+</sup> pH 12	Ba <sup>2+</sup> pH 8	Cl <sup>-</sup>	Br <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>	SRNOM
ClO <sub>4</sub> <sup>-</sup>									
1	5.6	4.9	5.3	5.3	5.4	5.9	5.6	5.3	5.2
2	5.6	4.8	5.4	5.3	5.5	5.5	5.6	5.3	5.2
3	5.5	4.7	5.4	5.3	5.5	5.5	5.5	5.2	5.2
4	5.4	4.6	5.4	5.3	5.6	5.5	5.5	5.2	5.2
5	5.3	-	5.4	5.4	5.9	5.6	5.4	5.2	5.2
ClO <sub>3</sub> <sup>-</sup>									
1	7.8	6.4	7.5	7.4	7.0	8.0	7.4	6.8	6.7
2	8.0	6.2	7.6	7.4	7.3	7.2	7.4	6.7	6.7
3	7.8	5.9	7.6	7.5	7.5	7.2	7.3	6.7	6.7
4	7.7	5.6	7.6	7.5	7.9	7.2	7.2	6.6	6.7
5	7.5	-	7.6	7.5	8.1	7.3	7.0	6.5	6.8
BrO <sub>3</sub> <sup>-</sup>									
1	10.4	8.2	10.0	9.8	9.0	10.1	9.5	8.6	8.4
2	10.1	7.8	10.1	9.8	9.8	9.2	9.5	8.5	8.4
3	10.7	7.3	10.1	9.9	10.7	9.2	9.4	8.5	8.4
4	10.4	6.9	10.1	10.0	11.7	9.3	9.2	8.4	8.5
5	10.1	-	10.1	10.1	11.5	9.4	8.9	8.2	8.4
ClO <sub>2</sub> <sup>-</sup>									
1	11.0	8.7	10.8	10.5	9.1	10.5	10.2	9.1	8.9
2	10.8	8.3	10.9	10.5	9.2	9.8	10.1	9.0	8.9
3	10.5	7.7	10.9	10.7	9.1	10.0	10	9.0	8.9
4	11.2	7.2	10.9	10.7	9.2	10.0	9.9	8.9	9.0
5	10.7	-	10.8	10.8	9.2	10.0	9.4	8.7	NA <sup>c</sup>

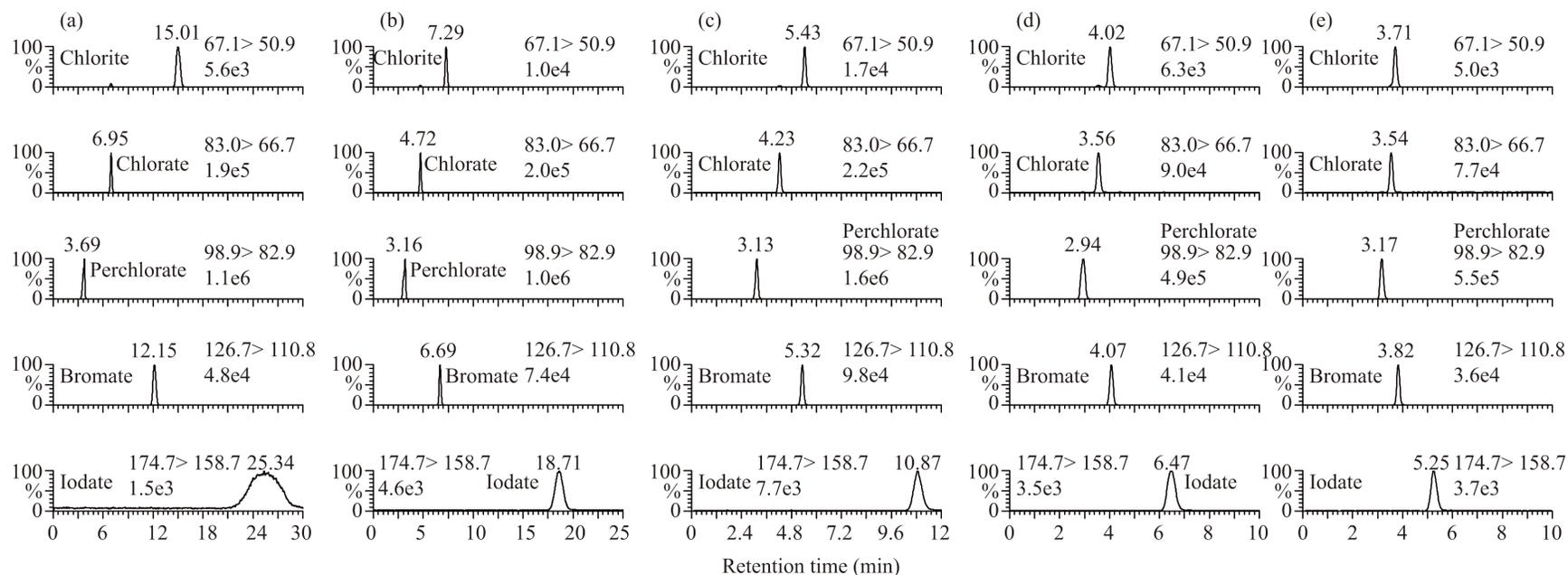
<sup>a</sup> Standards prepared in Milli-Q water (Milli-Q Water), untreated 10-mM phosphate buffer at pH 8 (No Ba<sup>2+</sup>), or Ba(OH)<sub>2</sub> treated 10-mM phosphate buffer – either left at pH 12 following Ba(OH)<sub>2</sub> addition or post-adjusted to pH 8 with H<sub>2</sub>SO<sub>4</sub> (Ba<sup>2+</sup> pH 12 or Ba<sup>2+</sup> pH 8, respectively). Following treatment with 15 mM Ba(OH)<sub>2</sub>, measured phosphate in samples was < 17 µM PO<sub>4</sub><sup>3-</sup>. <sup>b</sup> Oxyhalide standards prepared in Milli-Q water amended with Cl<sup>-</sup> (18, 36, 71, 178, 355 mg/L), Br<sup>-</sup> (0.01, 0.05, 0.1, 0.5, 1 mg/L), HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> (0.5, 1, 2, 5, 10 mM), SO<sub>4</sub><sup>2-</sup> (5, 10, 50, 100, 500 mg/L), or SRNOM (1, 1.5, 2, 5, 10 mg/L), with concentrations increasing from injections 1-5. <sup>c</sup> Due to interference of SRNOM with ClO<sub>2</sub><sup>-</sup> analyses, ClO<sub>2</sub><sup>-</sup> could not be measured at the 10 mg/L SRNOM concentration.



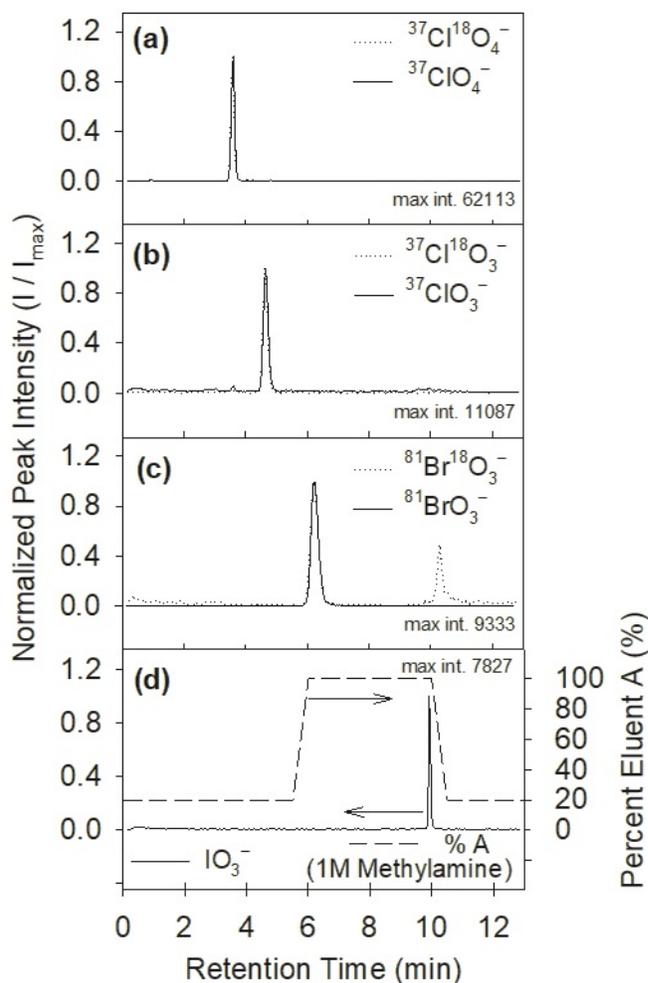
**Figure S1.** Calibration curves of (a)  $\text{ClO}_4^-$ , (b)  $\text{ClO}_3^-$ , (c)  $\text{BrO}_3^-$ , and (d)  $\text{ClO}_2^-$  standards diluted in Milli-Q water.  $\text{ClO}_4^-$ ,  $\text{ClO}_3^-$ , and  $\text{ClO}_2^-$  peak areas were normalized to peak area of the 10  $\mu\text{g/L}$   $^{37}\text{Cl}^{18}\text{O}_4^-$  internal standard, and  $\text{BrO}_3^-$  peak areas were normalized to peak area of the 10  $\mu\text{g/L}$   $^{81}\text{Br}^{18}\text{O}_3^-$  internal standard. Samples were analyzed on LC-MS/MS System 2 – a Waters Acquity UPLC H Class Quaternary HPLC interfaced with an AB Sciex API 4000 QTRAP mass spectrometer, using a modified NS-IC-MS/MS method incorporating a 30 second gradient transition from 20% A + 80% B to fully aqueous conditions (100% A) at  $t = 5.5$  minutes, with elution from a  $250 \times 2$  mm,  $9 \mu\text{m}$ , AS16 column at a flow rate of 0.25 mL/min.



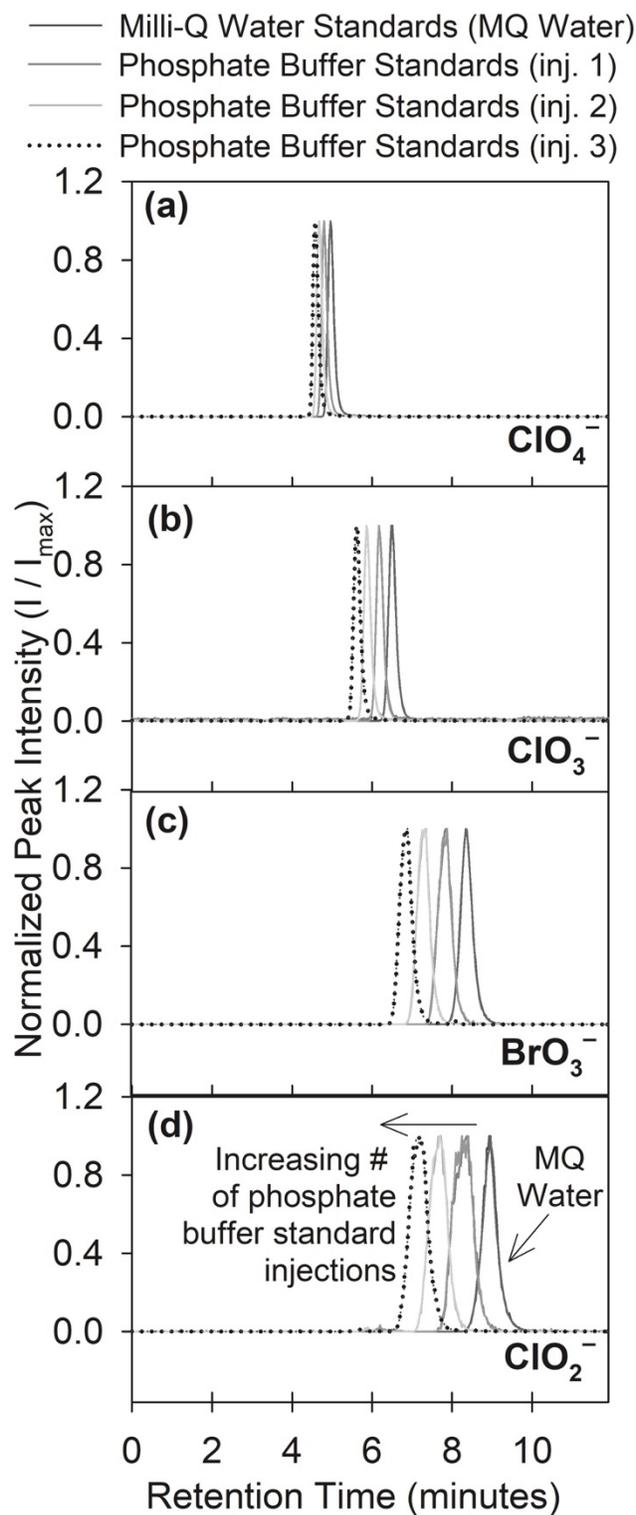
**Figure S2.** Molar extinction coefficients of HOCl and OCl<sup>-</sup> (left y-axis), and incident spectral irradiance from 290-400 nm for the ASTM G173-03 solar irradiance standard (hemispherical on a 37° tilted surface) at sea level and for the Atlas XLS+ Solar Simulator (equipped with daylight filter and infrared radiation filter) at the surface of irradiated reactor solutions (right y-axis), versus wavelength. Spectroradiometric measurements were taken using an Ocean Optics USB2000+ XR spectroradiometer equipped with a 200 μm × 2 m optical fiber and a CC-3-UV-S cosine corrector.



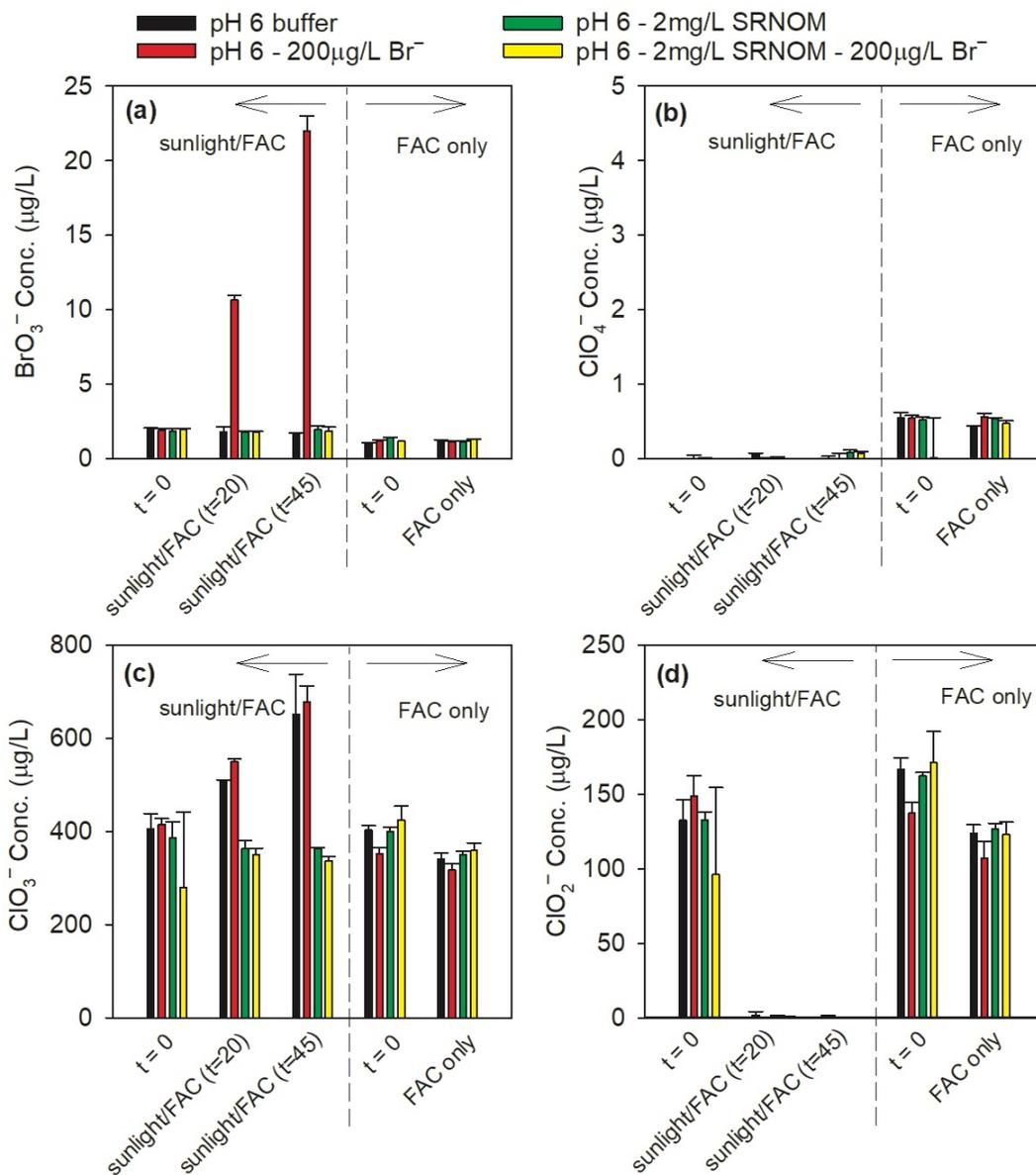
**Figure S3.** Oxyhalide chromatographs for isocratic NS-IC-MS/MS analyses of 10  $\mu$ L injections of 5  $\mu$ g/L standards prepared in Milli-Q water using varying percentages of 1 M methylamine (A) and acetonitrile (B) with (a) 15% A + 85% B (150 mM methylamine overall), (b) 20% A + 80% B (200 mM methylamine overall), (c) 25% A + 75% B (250 mM methylamine overall), (d) 30% A + 70% B (300 mM methylamine overall), and (e) 35% A + 65% B (350 mM methylamine overall), with elution from a 250  $\times$  2 mm, 9  $\mu$ m, AS16 column at a flow rate of 0.25 mL/min, using LC-MS/MS System 3.



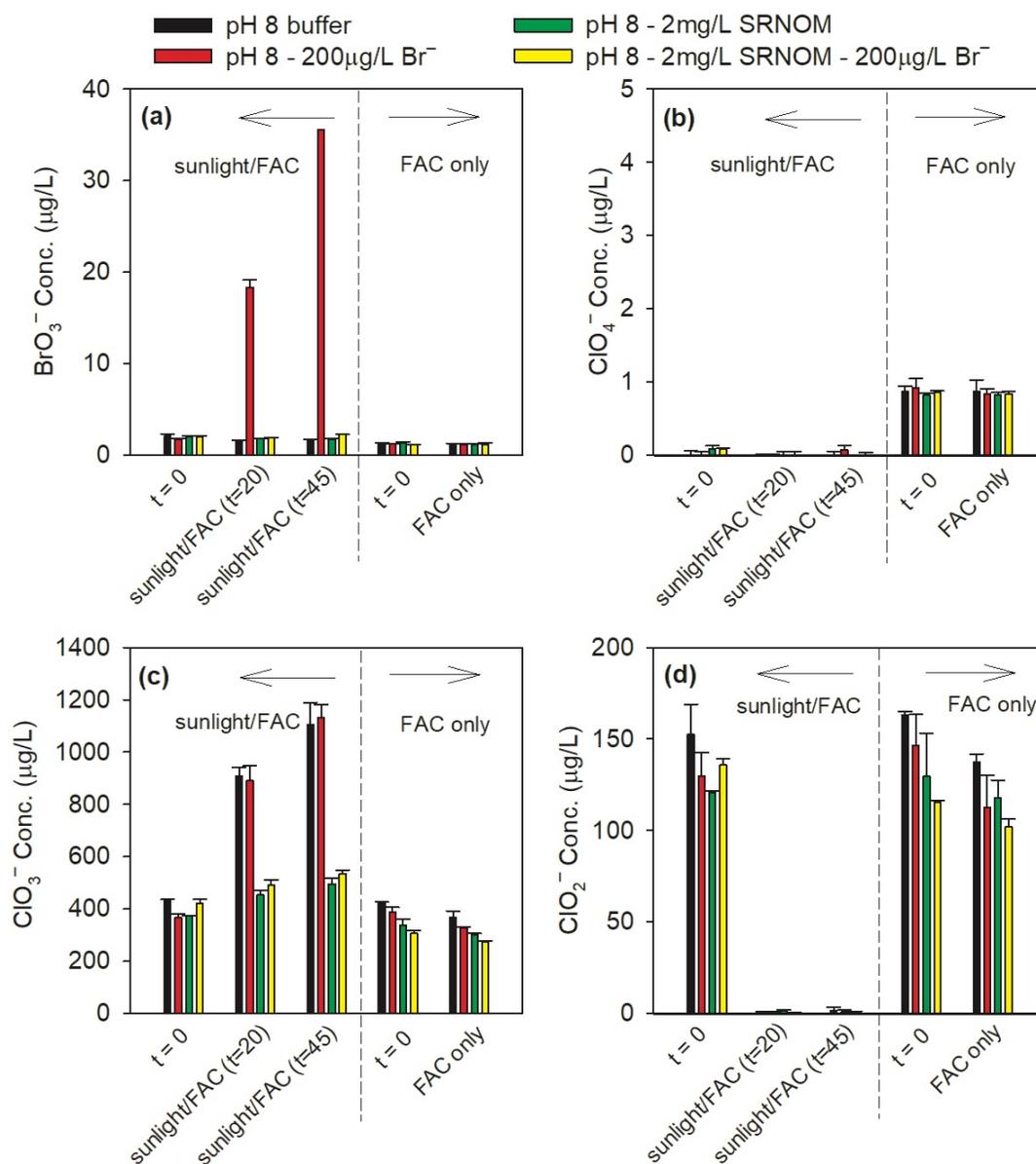
**Figure S4.** Normalized extracted ion chromatograms (EICs) for 10  $\mu\text{L}$  injections of (a)  $\text{ClO}_4^-$ , (b)  $\text{ClO}_3^-$ , (c)  $\text{BrO}_3^-$ , and (d)  $\text{IO}_3^-$  standards (100  $\mu\text{g/L}$ ) prepared in Milli-Q water, during analysis with a modified NS-IC-MS/MS method incorporating a 30 second gradient transition from 20% A + 80% B to fully aqueous conditions (100% A) at  $t = 5.5$  minutes, with elution from a  $250 \times 2$  mm, 9  $\mu\text{m}$ , AS16 column at a flow rate of 0.25 mL/min. The dashed line in plot (d) depicts % A, with the remainder representing % B. Note: The shorter retention times depicted in Figure S4 relative to those depicted in Figure 1 reflect differences in instrument configurations and fluidics for LC-MS/MS System 2 (used in these analyses) compared to System 1 (used in nearly all other analyses) (e.g., flow in System 1 was routed from the HPLC through a UV/Vis detector prior to the MS detector, whereas in System 2, flow was routed directly from the HPLC to the MS detector).  $\text{ClO}_2^-$  was not included in the mixed oxyhalide standards injected for these analyses due to the presence of  $\text{ClO}_3^-$  as a contaminant of the  $\text{NaClO}_2$  stock.



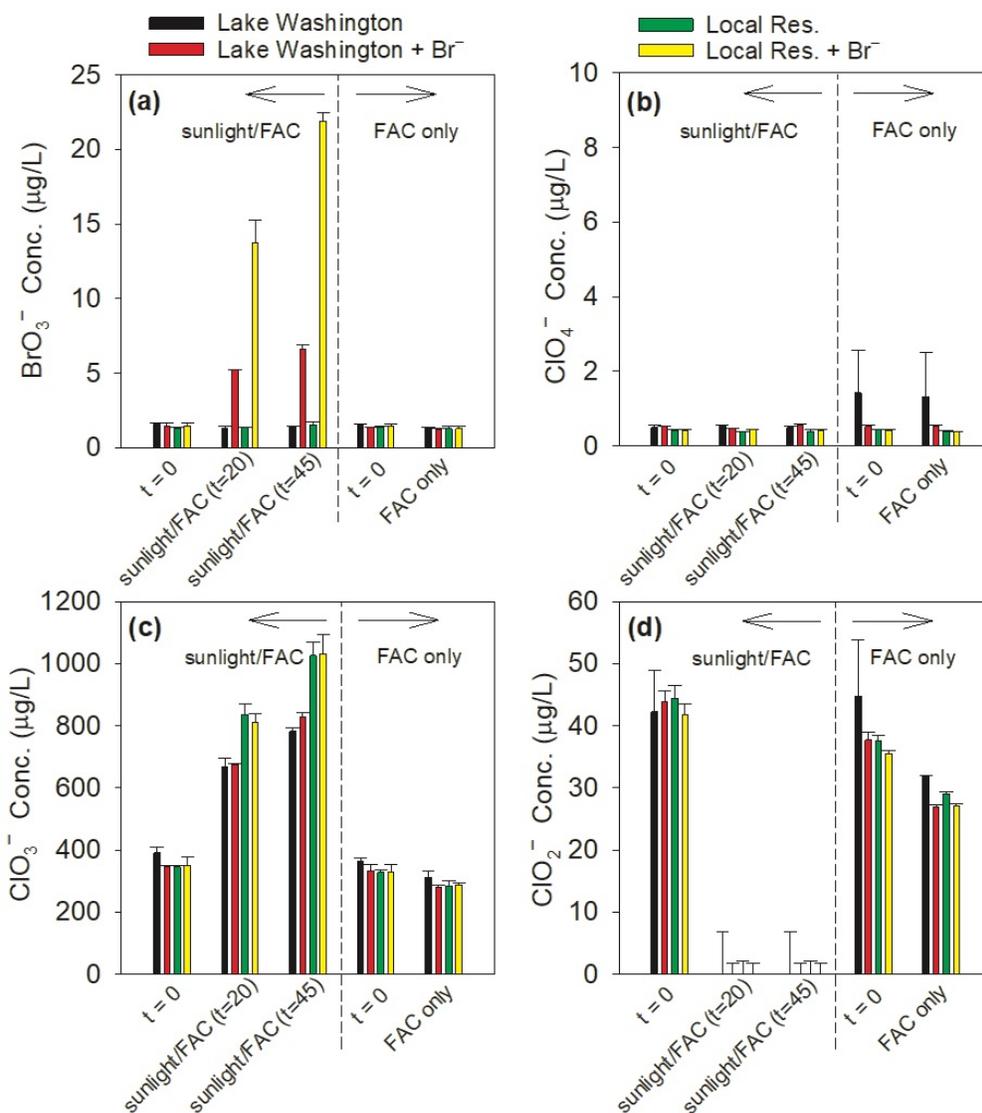
**Figure S5.** Extracted ion chromatograms (XICs) for 100  $\mu\text{L}$  injections of (a)  $\text{ClO}_4^-$ , (b)  $\text{ClO}_3^-$ , (c)  $\text{BrO}_3^-$ , and (d)  $\text{ClO}_2^-$  standards (10  $\mu\text{g/L}$ ) prepared in Milli-Q water followed by three sequential injections of the corresponding standards prepared in 10-mM phosphate buffer, with elution from a  $250 \times 2$  mm, 9  $\mu\text{m}$ , AS16 column by 20% A + 80% B at 0.25 mL/min



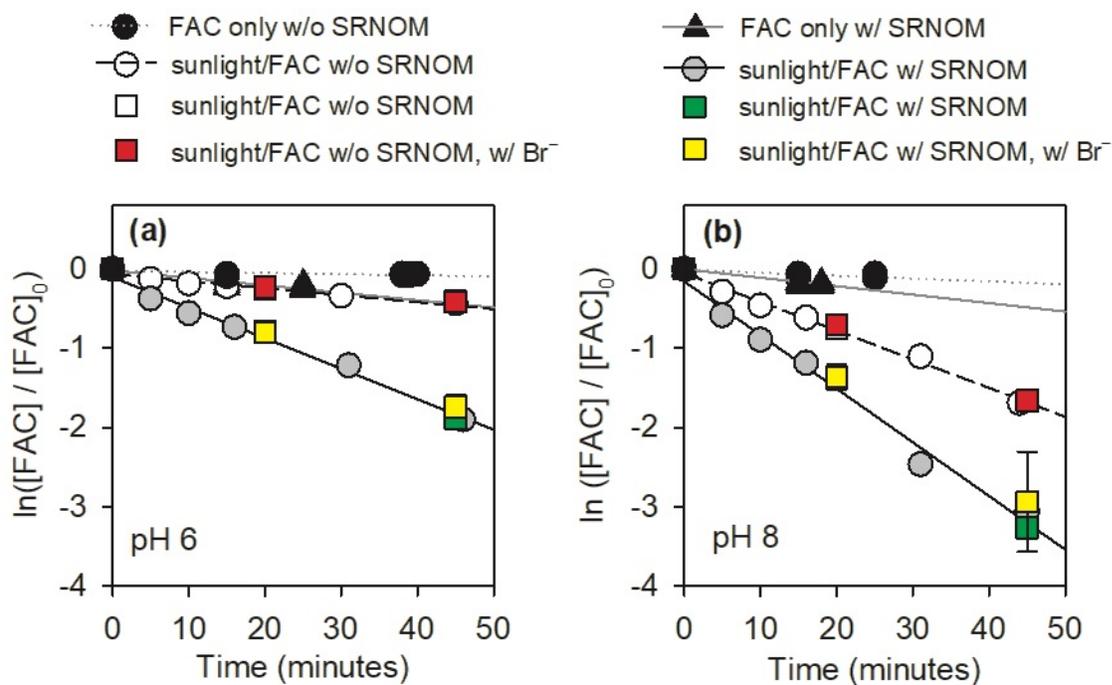
**Figure S6.** Concentrations of (a) BrO<sub>3</sub><sup>-</sup>, (b) ClO<sub>4</sub><sup>-</sup>, (c) ClO<sub>3</sub><sup>-</sup>, and (d) ClO<sub>2</sub><sup>-</sup> in 10-mM phosphate buffered Milli-Q water solutions subjected to dark chlorination (FAC only) and sunlight/FAC treatment at pH 6. In sunlight/FAC experiments, samples were irradiated for 20 or 45 minutes (290-400 nm fluence = 7.2 or 16.1 J/cm<sup>2</sup>). FAC only experiments were conducted in the dark until the  $CT_{\text{FAC}}$  matched the measured  $CT_{\text{FAC}}$  for the 45-minute irradiated sunlight/FAC samples. Note that all FAC-containing samples contained initial background concentrations of ~300-400 µg/L ClO<sub>3</sub><sup>-</sup>, ~100-150 µg/L ClO<sub>2</sub><sup>-</sup>, and ~2 µg/L BrO<sub>3</sub><sup>-</sup> originating from the NaOCl stock use in preparing FAC solutions (indicated by the “t = 0” data sets). All experiments were conducted at 10 °C, with [FAC]<sub>0</sub> ~8 mg/L as Cl<sub>2</sub>. Error bars represent one standard deviation about the mean for duplicate samples.



**Figure S7.** Concentrations of (a) BrO<sub>3</sub><sup>-</sup>, (b) ClO<sub>4</sub><sup>-</sup>, (c) ClO<sub>3</sub><sup>-</sup>, and (d) ClO<sub>2</sub><sup>-</sup> in 10-mM phosphate buffered Milli-Q water solutions subjected to dark chlorination (FAC only) and sunlight/FAC treatment at pH 8. In sunlight/FAC experiments, samples were irradiated for 20 or 45 minutes (290-400 nm fluence = 7.2 or 16.1 J/cm<sup>2</sup>). FAC only experiments were conducted in the dark until the  $CT_{\text{FAC}}$  matched the measured  $CT_{\text{FAC}}$  for the 45-minute irradiated sunlight/FAC samples. Note that all FAC-containing samples contained initial background concentrations of ~300-400 μg/L ClO<sub>3</sub><sup>-</sup>, ~100-150 μg/L ClO<sub>2</sub><sup>-</sup>, and ~2 μg/L BrO<sub>3</sub><sup>-</sup> originating from the NaOCl stock use in preparing FAC solutions (indicated by the “t = 0” data sets). All experiments were conducted at 10 °C, with [FAC]<sub>0</sub> ~8 mg/L as Cl<sub>2</sub>. Error bars represent one standard deviation about the mean for duplicate samples.



**Figure S8.** Concentrations of (a)  $\text{BrO}_3^-$ , (b)  $\text{ClO}_4^-$ , (c)  $\text{ClO}_3^-$ , and (d)  $\text{ClO}_2^-$  in natural water samples subjected to dark chlorination (FAC only) and sunlight/FAC treatment. Natural water samples were buffered with 10-mM phosphate at their native pH of 8.1, at native and fortified  $\text{Br}^-$  concentrations (where “+  $\text{Br}^-$ ” corresponds to amendment with 200  $\mu\text{g/L}$   $\text{Br}^-$  in addition to native  $\text{Br}^-$  levels). In sunlight/FAC experiments, samples were irradiated for 20 or 45 minutes (290-400 nm fluence = 7.2 or 16.1  $\text{J}/\text{cm}^2$ ). FAC only experiments were conducted in the dark until the  $CT_{\text{FAC}}$  matched the measured  $CT_{\text{FAC}}$  for the 45-minute irradiated sunlight/FAC samples. Note that all FAC-containing samples contained initial background concentrations of  $\sim 300$ -400  $\mu\text{g/L}$   $\text{ClO}_3^-$ ,  $\sim 35$ -45  $\mu\text{g/L}$   $\text{ClO}_2^-$ , and  $\sim 2$   $\mu\text{g/L}$   $\text{BrO}_3^-$  originating from the  $\text{NaOCl}$  stock use in preparing FAC solutions (indicated by the “ $t = 0$ ” data sets). All experiments were conducted at 10  $^\circ\text{C}$ , with  $[\text{FAC}]_0 \sim 8$   $\text{mg/L}$  as  $\text{Cl}_2$ . The lower background  $\text{ClO}_2^-$  levels in “ $t = 0$ ” data sets for each natural water compared to “ $t = 0$ ” phosphate buffer solutions (Figures S6 and S7) may have been due to reactions with redox-active moieties of the DOM in each water. Error bars represent one standard deviation about the mean for duplicate samples.



**Figure S9.** FAC decay during FAC only and sunlight/FAC treatment of (a) 10-mM phosphate buffered Milli-Q water at pH 6, and (b) 10-mM phosphate buffered Milli-Q water at pH 8. All experiments were conducted at 10 °C, with  $[FAC]_0 \sim 8$  mg/L as  $Cl_2$ . Samples w/ NOM contained 2 mg<sub>C</sub>/L SRNOM, and samples w/ Br<sup>-</sup> contained 200 μg/L Br<sup>-</sup>. Error bars represent one standard deviation about the mean for duplicate samples.

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