

**Reaction of chlorine dioxide with organic matter**

**- Formation of inorganic products –**

**- Electronic Supplementary Information (ESI) -**

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## Material and Methods

**Table S1:** All used chemicals

| Chemical   | Molecular formula   | Purity                   | Producer   |
|--|---|--------------------------|--|
| <b>Sodium dihydrogen phosphate monohydrate</b>   | NaH <sub>2</sub> PO <sub>4</sub> *H <sub>2</sub> O  | 99.0 – 102.0%            | AppliChem GmbH (Darmstadt, Germany)              |
| <b>Di-potassium hydrogen phosphate anhydrous</b> | K <sub>2</sub> HPO <sub>4</sub>   | min. 99%                 | AppliChem GmbH (Darmstadt, Germany)              |
| <b>Sulfuric acid</b>                             | H <sub>2</sub> SO <sub>4</sub>  | > 95%                    | Fisher Scientific GmbH (Schwerte, Germany)       |
| <b>Sodium hydroxide solution (1 M)</b>           | NaOH  | Not available            | Bernd Kraft GmbH (Duisburg, Germany)             |
| <b>Sodium chlorite</b>                           | NaClO <sub>2</sub>  | 80%                      | Sigma Aldrich (Darmstadt, Germany)               |
| <b>Potassium chlorate</b>                        | KClO <sub>3</sub>   | ≥ 99.0%                  | Sigma Aldrich (Darmstadt, Germany)               |
| <b>Sodium persulfate</b>                         | Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>   | ≥ 99.0%                  | Sigma Aldrich (Darmstadt, Germany)               |
| <b>Potassium iodide</b>                          | KI  | 99%                      | Thermo Fisher (Kandel) GmbH (Karlsruhe, Germany) |
| <b>Sodium carbonate</b>                          | Na <sub>2</sub> CO <sub>3</sub>   | ≥ 99.5% p.a.             | Die Carl Roth GmbH + Co. KG (Karlsruhe, Germany) |
| <b>Sodium chloride</b>                           | NaCl  | ≥ 99.5%                  | Bernd Kraft GmbH (Duisburg, Germany)             |
| <b>Nitrogen</b>                                  | N <sub>2</sub>  | > 99%                    | Air liquid (Oberhausen, Germany)                 |
| <b>Argon</b>                                     | Ar  | > 99%                    | Air liquid (Oberhausen, Germany)                 |
| <b>Methanol</b>                                  | H <sub>3</sub> COH  | ≥ 99.8%                  | VWR International GmbH (Darmstadt, Germany)      |
| <b>Hydrochloric acid</b>                         | HCl   | ~ 37%                    | Fisher Scientific GmbH (Schwerte, Germany)       |
| <b>Vanillin</b>                                  | C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>  | 99%                      | Sigma Aldrich (Darmstadt, Germany)               |
| <b>Indigo trisulfonic acid tripotassium salt</b> | C <sub>16</sub> H <sub>7</sub> K <sub>3</sub> N <sub>2</sub> O <sub>11</sub> S <sub>3</sub> | Ozone scavenging reagent | Sigma Aldrich (Darmstadt, Germany)               |
| <b>Glycine</b>                                   | C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>   | ≥ 99.0%                  | Sigma Aldrich (Darmstadt, Germany)               |
| <b>Sodium hypochlorite</b>                       | NaOCl   | 11 – 15%                 | Alfa Aesar (Germany)                             |
| <b>Natural organic matter</b>                    | Suwannee River  | RO isolate (2R101N)      | International Humic Substances Society (IHSS)    |
| <b>Hydroquinone</b>                              | C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>  | ≥ 99.0%                  | Sigma Aldrich (Darmstadt, Germany)               |
| <b>Ammonium molybdate (para) tetrahydrate</b>    | (NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> × 4H <sub>2</sub> O         | 99 %                     | Alfa Aesar (Karlsruhe, Germany)                  |
| <b>TOC standard</b>                              | Not available   | (1000 ± 10) mg/L         | Sigma Aldrich (Darmstadt, Germany)               |
| <b>Formic acid</b>                               | CH <sub>2</sub> O <sub>2</sub>  | ~ 98%                    | Sigma Aldrich (Darmstadt, Germany)               |
| <b>2-methoxybenzo-1,4-quinone</b>                | C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>  | Not available            | Sigma Aldrich (Darmstadt, Germany)               |

**Table S2:** All used instruments

| <b>Instrument</b>                | <b>Component</b>   | <b>Specification</b>                            | <b>Manufacturer</b>                         |
|----------------------------------|--------------------|---|---|
| <b>UV-VIS-spectrophotometer</b>  | Hardware           | UV-1800   | Shimadzu<br>(Duisburg, Germany)             |
|                                  | Software           | UVProbe   | Shimadzu<br>(Duisburg, Germany)             |
| <b>Ultra-pure water facility</b> | -                  | Purelab Ultra                                   | ELGA<br>(Celle, Germany)                    |
| <b>HPLC-UV</b>                   | Degasser           | Shimadzu<br>DGU-20A <sub>5R</sub>               | Shimadzu Europa GmbH<br>(Duisburg, Germany) |
|                                  | High pressure Pump | Shimadzu Liquid Chromatograph<br>LC-10AT VP     | Shimadzu Europa GmbH<br>(Duisburg, Germany) |
|                                  | Autosampler        | Shimadzu Auto Injector<br>SIL-10AD VP           | Shimadzu Europa GmbH<br>(Duisburg, Germany) |
|                                  | Detector           | Shimadzu Diode Array<br>Detector<br>SPD-M10A VP | Shimadzu Europa GmbH<br>(Duisburg, Germany) |
|                                  | Column             | 5 µm EVO C18 100A;<br>100 x 2.1 mm (1 x ID)     | Phenomenex<br>(Aschaffenburg, Germany)      |
| <b>IC</b>                        | Equipment          | 881 Compact IC pro                              | Metrohm<br>(Filderstadt, Germany)           |
|                                  | Pump               | Standard  |   |
|                                  | Autosampler        | 863 Compact                                     |   |
|                                  | Detector           | IC Conductivity detector<br>UV-Detector         |   |
|                                  | Column             | Metrosep ASupp 7<br>(250/4.0)                   |   |
|                                  | Sample Loop        | 1 mL<br>Injection volume:<br>100 µL             |   |
| Software                         | MagicIC Net        |   |   |
| <b>Ozone generator</b>           | -                  | BMT 802X  | BTM Messtechnik<br>(Berlin, Germany)        |
| <b>Dispenser-system</b>          | -                  | Dispensette                                     | Brand GMBH + CO KG<br>(Wertheim, Germany)   |
| <b>pH-Meter</b>                  | -                  | 827 pH lab                                      | Metrohm<br>(Essen, Germany)                 |
| <b>TOC analyser</b>              | Equipment          | TOC-L   | Shimadzu Europa GmbH<br>(Duisburg, Germany) |
|                                  | Auto-sampler       | ASI-L   |   |
|                                  | Software           | TOC Control -L                                  |   |

**Table S3:** All used methods

| <b>Compound</b>                                  | <b>Instrument</b>   | <b>Conditions</b>  |
|--|---|--|
| <b>Chloride, chlorite, chlorate, formic acid</b> | IC with conductivity detector<br>Column: Metrohm A Supp 7 (250/4.0)                 | Eluent: 1.6 mM Na <sub>2</sub> CO <sub>3</sub><br>Flow: 0.8 mL min <sup>-1</sup><br>Injection volume: 100 µL   |
| <b>N-chloroglycine</b>                           | IC with post-column reaction and UV-detector  | Post Column Reaction (PCR)<br>1. Potassium iodide (270 mM)<br>2. Ammonium molybdate (50 µM) and sulfuric acid (100 mM)<br>Flow: 0.2 mL min <sup>-1</sup><br>Injection volume: 100 µL |
| <b>Vanillin, 2-methoxybenzo-1,4-quinone</b>      | HPLC with UV-detector<br>Column: Kinetex 5 µm EVO C18 100 A 100 x 3 mm (Phenomenex) | Mobile phase: isocratic<br>20% Methanol/80% H <sub>2</sub> O pH 2 (adjusted with HCl)<br>Flow: 0.5 mL min <sup>-1</sup><br>Injection volume: 75 µL<br>Wavelength: 347 nm             |
| <b>Hydroquinone, p-benzoquinone</b>              | HPLC with UV-detector<br>Column: Kinetex 5 µm EVO C18 100 A 100 x 3 mm (Phenomenex) | Mobile phase: isocratic<br>1% Methanol/99% H <sub>2</sub> O (pH 2 (adjusted with HCl))<br>Flow: 0.5 mL min <sup>-1</sup><br>Injection volume: 75 µL<br>Wavelength: 288 nm            |
| <b>Indigo-trisulfonate</b>                       | UV-VIS-spectrometer   | Wavelength: 600 nm<br>Cuvette: 1 cm<br>For checking the purity concentration was also calculated with the extinction coefficient of 20000 M <sup>-1</sup> cm <sup>-1</sup>           |

**Table S4:** Reaction rate constants of used compounds at defined pH  
(if available/applicable)

| Reaction                              | $k$ [ $M^{-1} s^{-1}$ ]     | pH    | Reference |
|---------------------------------------|-----------------------------|-------|-----------|
| glycine + HOCl                        | $1.5 \times 10^5$           | 7     | 2         |
| glycine + ClO <sub>2</sub>            | $1 \times 10^{-3}$          | 8     | 3         |
| vanillin + ClO <sub>2</sub>           | $5 \times 10^3$             | 8     | 3         |
| hydroquinone + ClO <sub>2</sub>       | $(8.8 \pm 0.4) \times 10^5$ | 6.93  | 4         |
| indigotrisulfonate + ClO <sub>2</sub> | $2.5 \times 10^5$           | 8     | 3         |
| Dimedone + ClO <sub>2</sub>           | $\sim 2 \times 10^4$        | 2 - 5 | 3         |
| galic acid + HOCl                     | $(1.5 \pm 0.1) \times 10^4$ | 7     | 5         |
| hydroquinone + HOCl                   | $21.6 \pm 0.3$              | 7     | 5         |

### Text S1: Production of ClO<sub>2</sub>

ClO<sub>2</sub> was produced by mixing sodium persulfate and sodium chlorite (reaction 1) (persulfate-chlorite method). This method was firstly described and performed by Gates (1998)<sup>6</sup>.

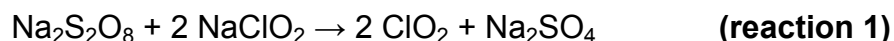
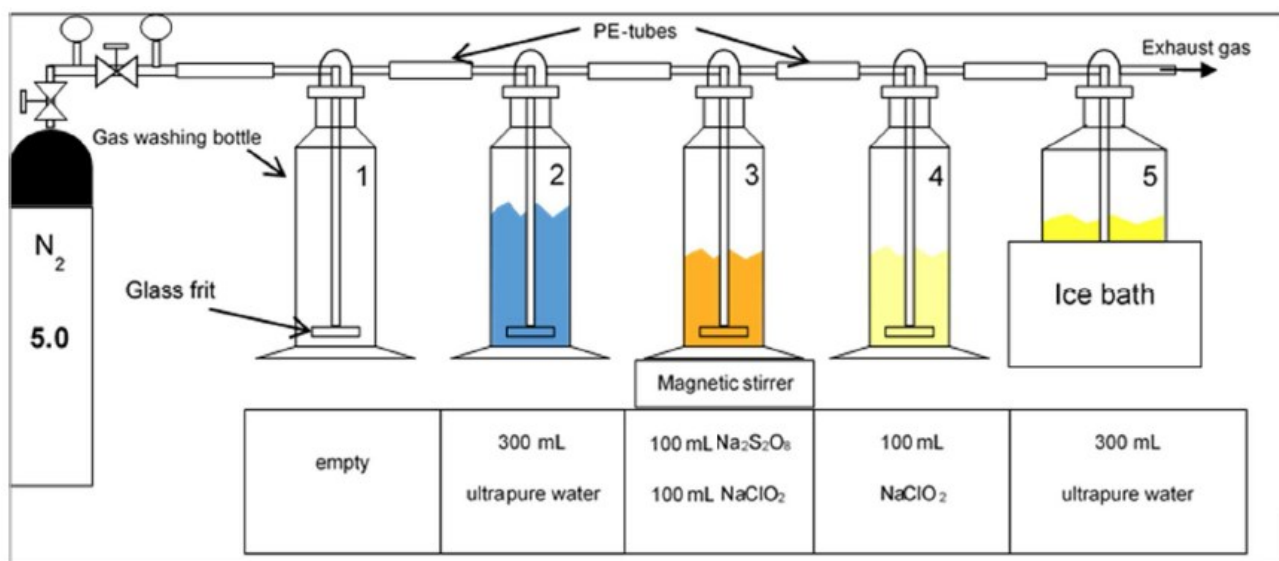


Figure S1 shows the experimental setup for the ClO<sub>2</sub> production. The principle of this setup is that ClO<sub>2</sub> is produced using the chlorite persulfate method combined with a purification step<sup>7</sup>. Therefore, five gas washing bottles connected *via* PE-tubes and a nitrogen-gas supply are needed. The empty bottle 1 is used for avoiding pressure effects after turning on/off gas supply, bottle 2 (ultrapure water) for washing the used nitrogen gas and in bottle 3 ClO<sub>2</sub> is produced according to reaction 1. Bottle 4 (NaClO<sub>2</sub>) is used for scavenging FAC which might be formed during the production. ClO<sub>2</sub><sup>-</sup> present in excess can scavenge FAC because it reacts with HOCl to ClO<sub>2</sub>, H<sub>2</sub>O and Cl<sup>-</sup> in an acid catalysed reaction ( $k = 1.06 \times 10^6 M^{-2} s^{-1}$ )<sup>8</sup>. In bottle 5 the produced ClO<sub>2</sub> is absorbed in ice cooled water. Before starting the production, all

bottles were cleaned with ultrapure water. First, bottle 2 and 5 were filled with 300 mL ultrapure water, bottle 4 was filled with 100 mL of 0.111 M NaClO<sub>2</sub> solution and bottle 3 was filled with 100 mL of 0.885 M NaClO<sub>2</sub> solution. For starting the reaction 100 mL of 0.168 M Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added to bottle 3. During the production the reaction solution (bottle 3) was continuously stirred.



**Figure S1:** Experimental setup of ClO<sub>2</sub> production (modified from Terhalle et al.)<sup>7</sup>

The ClO<sub>2</sub> stock solution was stored dark and cool in brown glass conical shoulder bottles with minimum headspace.

### Usage of ClO<sub>2</sub> solutions

ClO<sub>2</sub> stock solution was kept cool in an ice bath throughout the whole experiment to suppress gas transfer losses of ClO<sub>2</sub>. The concentration of the produced ClO<sub>2</sub> stock solution (bottle 5) was measured via UV-VIS- spectrometry. Therefore, the stock solution was diluted 1:30 (100 µL stock solution and 2.9 mL ultrapure water) in a 1 cm cuvette and turned over carefully two times for mixing. To avoid losses of ClO<sub>2</sub> via headspace during dosage of ClO<sub>2</sub>, hamilton syringes were used. The dilution of the stock solution ensure that the absorbance was below 1 cm<sup>-1</sup> and therefore in the



linear range of the photometer. The absorbance of the diluted stock solutions at wavelength 359 nm was between 0.4 and 0.84 cm<sup>-1</sup> (1 – 2.1 x 10<sup>-2</sup> M ClO<sub>2</sub>). The concentrations were calculated with the extinction coefficient of ClO<sub>2</sub> ( $\epsilon_{359\text{ nm}} = 1200\text{ M}^{-1}\text{ cm}^{-1}$ )<sup>9</sup> via the Lambert-Beer-law (equation S1).

$$E_{359\text{ nm}} = \epsilon_{359\text{ nm}} \times c \times d \quad \text{(equation S1)}$$

$E_{359\text{ nm}}$ : Extinction at 359 nm

$\epsilon_{359\text{ nm}}$ : molar extinction coefficient for ClO<sub>2</sub> at 359 nm [M<sup>-1</sup> s<sup>-1</sup>]

$c$ : concentration of ClO<sub>2</sub> [M]

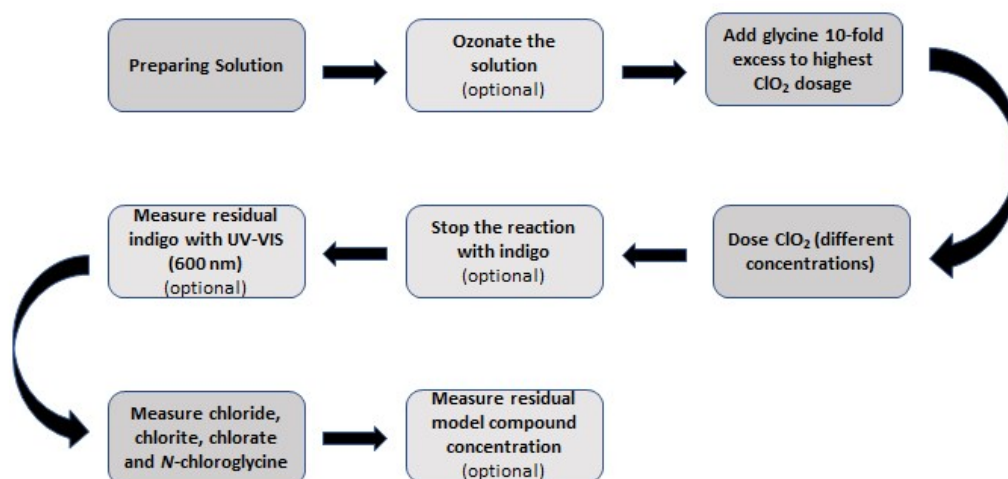
$d$ : optical path length [cm] (in present work 1 cm)

### Text S2: Production of O<sub>3</sub>

O<sub>3</sub> gas was produced with an BMT 802X ozone generator and purged in ice cooled ultrapure water. After about 1 – 2 hours purging, the concentration of O<sub>3</sub> was measured via a UV-Vis-spectrometer at wavelength of 258 nm ( $\epsilon_{258\text{ nm}, \text{O}_3} = 2950\text{ M}^{-1}\text{ cm}^{-1}$ )<sup>1</sup> and calculated with the Lambert-Beer law (see equation S1). Therefore, the O<sub>3</sub> stock solution was diluted 1:6 (2.5 mL ultrapure water and 0.5 mL O<sub>3</sub> stock solution) and was measured five times. In case the standard deviation of these measurements was > 5% the concentration of ozone in the stock solution may not be saturated and measurement was repeated at a later time. Transfer of O<sub>3</sub> stock solution was done by Hamilton syringes and the ozone gas was continuously bubbled into the stock solution to ensure that the ozone concentrations remains constant. The concentration of O<sub>3</sub> stock solution was measured near-term before each dosage.

**Table S5:** Composition and ClO<sub>2</sub> dosages of the investigated compounds for the oxidation experiments

| Compound  | Composition reaction solution   | ClO <sub>2</sub> dosages [μM] |
|---|---|-------------------------------|
| <b>Vanillin and hydroquinone</b>                          | <ul style="list-style-type: none"> <li>• 100 μM compound</li> <li>• 2 mM glycine</li> <li>• 5 mM phosphate buffer</li> <li>• pH 7 ± 0.05</li> </ul>   | 0, 25, 50, 75, 100, 150, 200  |
| <b>Indigotrisulfonate</b>                                 | <ul style="list-style-type: none"> <li>• 86 μM compound</li> <li>• 2 mM glycine</li> <li>• 5 mM phosphate buffer</li> <li>• pH 7 ± 0.05</li> </ul>  | 0, 25, 50, 75, 100, 150, 200  |
| <b>Dimedone</b>   | <ul style="list-style-type: none"> <li>• 100 μM compound</li> <li>• 2 mM glycine</li> <li>• 5 mM phosphate buffer</li> <li>• pH 7 ± 0.05</li> </ul>   | 0, 50, 100, 150, 200          |
| <b>SRNOM and pre-ozonated SRNOM (40 μM O<sub>3</sub>)</b> | <ul style="list-style-type: none"> <li>• 5 mg DOC L<sup>-1</sup> SRNOM</li> <li>• 0.8 mM glycine (added after ozonation)</li> <li>• 5 mM phosphate buffer</li> <li>• pH 7 ± 0.05</li> </ul> | 0, 15, 30, 40, 50, 60, 70, 80 |
| <b>Pre-ozonated SRNOM (80 μM O<sub>3</sub>)</b>           | <ul style="list-style-type: none"> <li>• 5 mg DOC L<sup>-1</sup> SRNOM</li> <li>• 0.8 mM glycine (added after ozonation)</li> <li>• 5 mM phosphate buffer</li> <li>• pH 7 ± 0.05</li> </ul> | 0, 15, 30, 40, 50, 60         |



**Figure S2:** Workflow of the oxidation experiments

**Table S6:** Reaction time of the investigated compounds with ClO<sub>2</sub>

| Compound  | Reaction time with ClO <sub>2</sub>  |
|---|--|
| <b>SRNOM and pre-ozonated SRNOM (40 μM O<sub>3</sub>)</b>       | 90 min (15 μM ClO <sub>2</sub> ), 130 min (30 μM ClO <sub>2</sub> ), 170 min (40 μM ClO <sub>2</sub> ), 210 min (50 μM ClO <sub>2</sub> ), 250 min (60 μM ClO <sub>2</sub> ), 290 min (70 μM ClO <sub>2</sub> ) and 330 min (80 μM ClO <sub>2</sub> ), reaction time is composed of 90 min plus the wait-time of the sample in the autosampler |
| <b>Pre-ozonated SRNOM (80 μM O<sub>3</sub>)</b>                 | After 180 min the reaction was stopped by adding indigo-trisulfonate   |
| <b>Vanillin, indigo-trisulfonate and hydroquinone, dimedone</b> | at least 30 min  |

**Table S7:** Limits of detection (LOD) and limits of quantification (LOQ) of the measured compounds of the used methods

| Compound                           | LOD [μM] | LOQ [μM] | Injection volume     |
|------------------------------------|----------|----------|----------------------|
| <b>Cl<sup>-</sup></b>              | 0.50     | 1.47     | 100 μL               |
| <b>ClO<sub>2</sub><sup>-</sup></b> | 0.54     | 1.59     | 100 μL               |
| <b>ClO<sub>3</sub><sup>-</sup></b> | 1.07     | 2.89     | 100 μL               |
| <b>N-Chloroglycine (FAC)</b>       | 1.98     | 5.48     | 100 μL               |
| <b>Vanillin</b>                    | 1.85     | 5.33     | 75 μL                |
| <b>Hydroquinone</b>                | 0.16     | 0.49     | 75 μL                |
| <b>Indigo-trisulfonate</b>         | 1.40     | 4.09     | 3 mL in 1 cm cuvette |

**Table S8:** Concentrations of the recovery experiments *N*-chloroglycine (FAC) for the oxidation of vanillin or dimedone (100  $\mu\text{M}$ ) with  $\text{ClO}_2$ , 5 mM phosphate buffer, pH  $7 \pm 0.05$ , reaction time 30 min, room temperature

| Compound | $[\text{ClO}_2]$ [ $\mu\text{M}$ ] | [Glycine] [mM] | [HOCl] [ $\mu\text{M}$ ] | [Cl-gly] [ $\mu\text{M}$ ] |
|----------|------------------------------------|----------------|--------------------------|----------------------------|
| Vanillin | 0                                  | 2              | 100                      | 0                          |
|          | 0                                  | 20             | 100                      | 0                          |
|          | 0                                  | 2              | 100                      | 100                        |
|          | 50                                 | 2              | 100                      | 0                          |
|          | 50                                 | 20             | 0                        | 0                          |
|          | 50                                 | 20             | 100                      | 0                          |
|          | 50                                 | 2              | 0                        | 100                        |
|          | 50                                 | 2              | 100                      | 100                        |
|          | Dimedone                           | 0              | 0                        | 0                          |
| 50       |                                    | 0              | 0                        | 0                          |
| 100      |                                    | 0              | 0                        | 0                          |
| 150      |                                    | 0              | 0                        | 0                          |
| 200      |                                    | 0              | 0                        | 0                          |

### Text S3: Depletion experiments

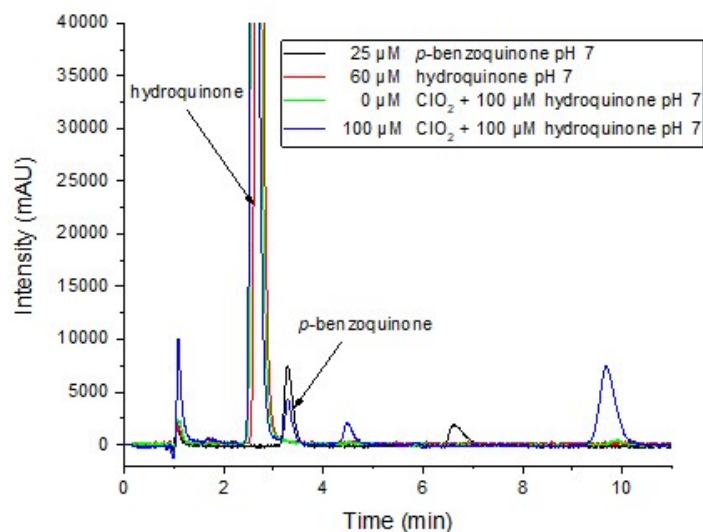
Before the  $\text{ClO}_2$  and  $\text{O}_3$  was dosed, the dispenser was rinsed three times with the SRNOM solution and two reference sample ( $t = 0$  s, before addition of 80  $\mu\text{M}$   $\text{ClO}_2$ , 40  $\mu\text{M}$  or 80  $\mu\text{M}$   $\text{O}_3$ ) were taken. Then  $\text{ClO}_2$  or  $\text{O}_3$  was dosed and the solution was mixed for 10 seconds and following a predefined time protocol samples were taken by adding 10 mL of the sample into reaction tubes prefilled with small amounts (i.e.  $\leq 1$  mL) of indigotrisulfonate working solution ( $C_{\text{indigo}}$  (sample + indigotrisulfonate) =  $1 \times 10^{-4}$  M for  $\text{ClO}_2$  depletion and  $8.7 \times 10^{-5}$  M and for  $\text{O}_3$  depletion). The remaining indigotrisulfonate concentration was calculated by the Lambert-Beer-law

using absorbance at 600 nm ( $\epsilon_{600 \text{ nm, indigotrisulfonate}} = 20000 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>1</sup>. For the ClO<sub>2</sub> depletion the extinction factor was divided by factor 2 (= 10000 M<sup>-1</sup> cm<sup>-1</sup>) because 2 mol ClO<sub>2</sub> are required to deplete one mol indigotrisulfonate. The amount of indigo dye bleaching was determined by subtracting oxidant containing samples from the average of the references (no oxidant).

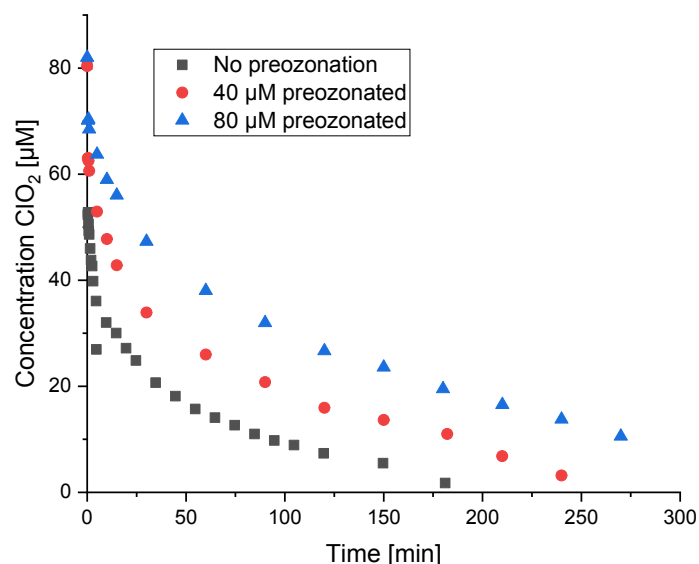
**Table S9:** Composition of the indigotrisulfonate working solutions for the depletion of ClO<sub>2</sub> and O<sub>3</sub>

| Measured oxidant | Composition of indigo working solution                                       |
|------------------|--|
| ClO <sub>2</sub> | 1 mM indigotrisulfonate<br>11 mM glycine<br>5 mM phosphate buffer<br>pH 7    |
| O <sub>3</sub>   | 1.25 mM indigotrisulfonate<br>65 mM H <sub>3</sub> PO <sub>4</sub><br>pH < 4 |

## Results and Discussion



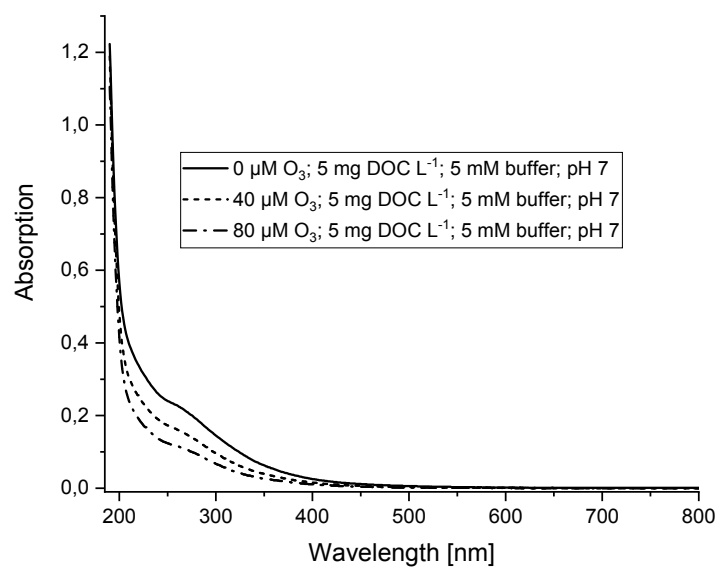
**Figure S3:** Chromatograms of 25  $\mu\text{M}$  p-benzoquinone (5 mM phosphate buffer pH 7  $\pm$  0.05) (black), 60  $\mu\text{M}$  hydroquinone (5 mM phosphate buffer pH 7  $\pm$  0.05) (red), 100  $\mu\text{M}$  hydroquinone (2 mM glycine and 5 mM phosphate buffer pH 7  $\pm$  0.05) (green), 100  $\mu\text{M}$  hydroquinone oxidised with 100  $\mu\text{M}$   $\text{ClO}_2$  (2 mM glycine and 5 mM phosphate buffer pH 7  $\pm$  0.05) (blue) measured with HPLC-UV at wavelength 288 nm (99%/1% methanol/water pH 2 flow 0.5 mL/min)



**Figure S4:** Depletion of  $\text{ClO}_2$  (80  $\mu\text{M}$ ) in 5 mg  $\text{DOC L}^{-1}$ , 5 mM phosphate buffer and 0.8 mM glycine pH 7  $\pm$  0.05 (no pre-ozonation (grey), 40  $\mu\text{M}$  pre-ozonated (red) and 80  $\mu\text{M}$  pre-ozonated (blue)), depletion was measured with the indigo method

**Table S10:** Reference values of yields of inorganic chlorine by-products per  $\text{ClO}_2$  consumed for the reaction with  $\text{ClO}_2$  with selected compounds

| Compound                | Yields per $\text{ClO}_2$ consumed  | Conditions  | Reference                    |
|-------------------------|---|---|------------------------------|
| <b>Phenol</b>           | <ul style="list-style-type: none"> <li>• 60% <math>\text{ClO}_2^-</math></li> <li>• 40% HOCl</li> </ul>   | 1 mM Compound<br>pH 7<br>5 mM phosphate buffer<br>10 mM bromide       | Terhalle et al. <sup>7</sup> |
| <b>Vanillic acid</b>    | <ul style="list-style-type: none"> <li>• 50% <math>\text{ClO}_2^-</math></li> </ul>   | 100 $\mu\text{M}$ compound<br>pH 7<br>2 mM phosphate buffer           | Gan et al. <sup>10</sup>     |
| <b>Hydroquinone</b>     | <ul style="list-style-type: none"> <li>• 80% <math>\text{ClO}_2^-</math></li> </ul>   | scavenging of HOCl after reaction                                     |                              |
| <b>Vanillyl alcohol</b> | <ul style="list-style-type: none"> <li>• 5% <math>\text{ClO}_2^-</math></li> <li>• 20% <math>\text{Cl}^-</math></li> <li>• 70% <math>\text{ClO}^-</math></li> </ul> | Pulp bleaching conditions   | Ni et al. <sup>11</sup>      |
| <b>SRNOM</b>            | <ul style="list-style-type: none"> <li>• 71% - 82% <math>\text{ClO}_2^-</math></li> <li>• 22% - 25% FAC</li> <li>• 1% - 15% <math>\text{ClO}_3^-</math></li> </ul>  | 2 $\text{mgC L}^{-1}$ SRNOM<br>pH 6.5 – 8.1<br>10 mM phosphate buffer | Rouge et al. <sup>12</sup>   |



**Figure S5:** UV-Vis spectra of SRNOM (5 mg DOC L<sup>-1</sup>) with 5 mM phosphate buffer at pH 7 oxidized with different ozone (O<sub>3</sub>) concentrations (0 μM, 40 μM and 80 μM) (reaction time 30 min)



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