Supporting Information for

## Prediction of Photochemically Produced Reactive Intermediates in Surface Waters via Satellite Remote Sensing

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#### **Text S1: Preparation of stock solutions and analytical standards**

The 2,4,6-trimethylphenol (TMP) stock solution for analytical standards (stock 1) was prepared by dissolving 5 µM TMP in a 2% acetonitrile (ACN) solution in a volumetric flask and further diluted with ultrapure water to the desired concentrations. An aqueous TMP stock solution for spiking into water samples (stock 2) was prepared by mixing solid TMP in ultrapure water and centrifuging the solution for 15 min to remove any undissolved solids prior to spiking, to reach an approximate concentration of 2.5 mM. Using the calibration curve obtained using stock 1, the concentration of TMP was calculated to be 4.81  $\mu$ M if 50  $\mu$ L aliquot of stock 2 was spiked into aliquots of 25 mL water. As a result, 52  $\mu$ L of stock 2 was added into 25 mL lake water samples to obtain an initial TMP concentration of ~5 µM. Similarly, analytical standards of 4-carboxybenzophenone (CBP) were prepared by dissolving 0.1 mM CBP in 20% ACN and subsequently diluting with ultrapure water. A stock solution used to spike CBP into water samples was prepared by dissolving CBP in 10 mM borate buffer (10 mM borax mixed with 10 mM boric acid; pH adjusted to 8.0 using 36–38 % hydrochloric acid) with a target concentration of 1 mM, and undissolved solids were removed from the stock solution by centrifugation for 15 min. A terephthalic acid (TPA) stock solution was prepared by adding solid into ultrapure water to achieve a concentration of 10 mM and heating in water bath until dissolved. The TPA stock was stored in the dark to minimize exposure to light.

#### **Text S2: PPRI probes**

**<sup>3</sup>DOM**<sup>\*</sup>. TMP was used to measure the apparent quantum yield ( $\Phi_{app, 3DOM^*}$ , mol molphotons<sup>-1</sup>), rate of formation ( $R_{f, 3DOM^*}$ , M s<sup>-1</sup>), and steady-state concentration ([<sup>3</sup>DOM<sup>\*</sup>]<sub>ss</sub>, M) of <sup>3</sup>DOM<sup>\*</sup>. To measure the rate constant for TMP loss ( $k_{obs,TMP}$ , s<sup>-1</sup>), the desired amount of aqueous TMP stock 2 (52 µL) was added into 25 mL volumetric flasks and filled to the mark with water sample to reach an initial concentration of ~5 µM. Previous studies demonstrated that this is the appropriate concentration to measure <sup>3</sup>DOM<sup>\*</sup> production from analysis of the pseudo-first order kinetics of TMP.<sup>1,2</sup> The TMP-containing solutions were irradiated in the solar simulator for 60- to 90-minute time periods.

Previous studies<sup>3–9</sup> reported that the second order rate constant for the reaction between <sup>3</sup>DOM\* and TMP ( $k_{3DOM*,TMP}$ , M<sup>-1</sup> s<sup>-1</sup>) varies in different natural waters, with a range of  $0.81 \times 10^9$  to  $10 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. To obtain  $k_{3DOM*,TMP}$ , concentrations of [TMP]<sub>0</sub> of 50, 250, 500 and 750 µM were dissolved in a subset of lake samples with varying DOC levels (Island Lake, South Sturgeon Lake, Lake Winnibigosh, Upper Red Lake #2, and Lake of the Woods (Fourmile Bay)) and stirred continuously for 7 days in the dark. The solutions were then centrifuged for 15 min to remove undissolved TMP solids prior to irradiation. TMP loss was monitored for 60 to 180 minutes in the solar simulator. The data were fit to equation S1 to obtain the formation rate of <sup>3</sup>DOM\* ( $R_{f_{c}, ^3DOM^*}$ ):<sup>6</sup>

$$\frac{1}{k_{obs,TMP}} = \frac{[TMP]_0}{R_{f, 3DOM^*}} + \frac{k_q}{R_{f, 3DOM^*} * k_{3DOM^*,TMP}}$$
(S1)

where  $k_q$  is the pseudo-first order rate constant for all deactivation processes acting on <sup>3</sup>DOM<sup>\*</sup>. A value of  $3.13 \times 10^5$  s<sup>-1</sup> was chosen for  $k_q$ .<sup>4</sup> A plot of  $1/k_{obs,TMP}$  vs. [TMP]<sub>0</sub> yields a slope of  $1/R_{f_1, 3DOM^*}$ , and  $k_{3DOM^*,TMP}$  was obtained from the y-intercept.

The pseudo-first order loss rate constant of TMP ( $k_{obs,TMP}$ ) the product of  $k_{3DOM^*,TMP}$ and [ $^{3}DOM^{*}$ ]<sub>ss</sub>.<sup>1,5,10,11</sup> Thus, TMP loss is given by equation S2:

$$\frac{d[TMP]}{dt} = -k_{obs,TMP}[TMP] = -k_{3_{DOM^*,TMP}}[TMP][\ ^3DOM^*]_{ss}$$
(S2)

Additionally, photodegradation of TMP by <sup>3</sup>DOM<sup>\*</sup> may be inhibited by the DOC.<sup>7,12,13</sup> The inhibition factor (IF), for TMP photodegradation was measured using CBP as triplet sensitizer in selected waters. Details are in Text S3.

<sup>1</sup>O<sub>2</sub>. To obtain the rate of formation ( $R_{f, 1O_2}$ , M s<sup>-1</sup>) and steady-state concentration ([<sup>1</sup>O<sub>2</sub>]<sub>ss</sub>, M) of <sup>1</sup>O<sub>2</sub>, an aqueous stock solution of 5 mM FFA was added into 25 mL volumetric flasks and filled with a lake water sample to reach an initial FFA concentration of 20  $\mu$ M.<sup>14</sup> The solutions were transferred to triplicate quartz tubes and irradiated under the same conditions as the TMP experiments. FFA loss was monitored up to 7 h in the solar simulator, and data were fit using pseudo-first order kinetics to obtain  $k_{obs,FFA}$  (s<sup>-1</sup>).

The formation rate of  ${}^{1}O_{2}(R_{f_{-1}O_{2}}, M s^{-1})$  was computed from:

$$\frac{R_{f, 1O_2}}{k_{obs, FFA}} = [FFA]_0 + \frac{k_{d,S}}{k_{S, FFA}}$$
(S3)

where  $k_{S,FFA}$  (M<sup>-1</sup> s<sup>-1</sup>), the second order rate constant for the reaction between <sup>1</sup>O<sub>2</sub> and FFA, was calculated to be  $1.22 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup> at 30 °C.<sup>15</sup>  $k_{d,S}$  (s<sup>-1</sup>) is the pseudo-first order rate constant for the decay of <sup>1</sup>O<sub>2</sub> in water (2.81×10<sup>5</sup> s<sup>-1</sup>).<sup>4</sup>

•OH. •OH formation was quantified by measuring the production of the fluorescent hydroxyterephthalic acid (hTPA) produced from the reaction of •OH and TPA<sup>16,17</sup> Each 25 mL volumetric flask of water sample was dosed with 10  $\mu$ M TPA and irradiated up to 8 h in the solar simulator. Samples were taken periodically, and the formation of hydroxyterephthalic acid (hTPA) by HPLC was monitored to quantify •OH formation.

#### Text S3. Measurement of inhibition factor (IF)

The reaction rate constants of TMP using pseudo-first order kinetics were obtained in four different solutions: (1)  $k_0$ , 10 mM borate buffer at pH 8; (2)  $k_{CBP}$ , 10 mM borate buffer at pH 8 with CBP present; (3)  $k_{DOM}$ , selected water samples; and (4)  $k_{CBP,DOM}$ , selected water samples with CBP present.<sup>18</sup> Seven samples including Island Lake, South Sturgeon Lake, Lake Vermilion (Pike Bay), Lake Winnibigosh, Upper Red Lake #2, Lake of the Woods (Fourmile Bay) and Lake Saint Croix were selected out of twenty-four samples as representatives.  $k_0 = 0$  because direct photolysis of TMP is not significant. Thus,  $k_{CBP}$  did not need to be corrected for the direct photolysis of TMP.  $k_{DOM}$  was used to correct  $k_{CBP,DOM}$ to compensate for the <sup>3</sup>DOM<sup>\*</sup>-induced depletion of TMP. IF was then computed as the ratio of the corrected rate constant with the existence of both CBP and DOM and the corrected rate constant with the existence of CBP only:

$$k_{CBP}^{corr} = k_{CBP} - k_0 \tag{S4}$$

$$k_{CBP,DOM}^{corr} = k_{CBP,DOM} - k_{DOM} \tag{S5}$$

$$IF = \frac{k_{CBP,DOM}^{corr}}{k_{CBP}^{corr}}$$
(S6)

It has been reported that 1/IF was linearly dependent on DOC level. A plot of 1/IF versus [DOC] was drawn to calculate the IF values for 24 water samples. The  $k_{obs,TMP}$  value for each sample can then be normalized by its IF to obtain  $k_{obs,TMP}^{corr}$ .

# Text S4. Determination of Steady-State Concentrations and Quantum Yields of PPRIs

The steady state concentration of <sup>3</sup>DOM<sup>\*</sup> is:

$$[{}^{3}DOM^{*}]_{ss} = \frac{k_{obs,TMP}}{k_{{}^{3}DOM^{*},TMP}}$$
(S7)

Where  $k_{obs,TMP}$ , (s<sup>-1</sup>), is the rate constant for TMP loss and  $k_{3DOM*,TMP}$  (M<sup>-1</sup> s<sup>-1</sup>) is the second order rate constant for reaction between <sup>3</sup>DOM\* and TMP (see equation S2).

FFA loss was modeled as pseudo-first order reaction, and the steady state concentration of  ${}^{1}O_{2}$  is:

$$[{}^{1}O_{2}]_{ss} = \frac{k_{obs,FFA}}{k_{s,FFA}}$$
(S8)

Where  $k_{obs,FFA}(s^{-1})$  is the rate constant for FFA loss, and  $k_{S,FFA}(M^{-1}s^{-1})$  is the second order rate constant for the reaction between  ${}^{1}O_{2}$  and FFA.

TPA reaction with •OH to form hTPA ( $R_{f,hTPA}$ , M s<sup>-1</sup>) follows pseudo-zero order kinetics:

$$R_{f,hTPA} = \frac{\Delta[hTPA]}{\Delta t} \tag{S9}$$

Photodegradation of hTPA in the solar simulator was less than 5%, and DOM slows its loss via light screening.<sup>19</sup> Thus,  $R_{f,hTPA}$  was not corrected by the direct photolysis rate of hTPA. The steady-state concentration of •OH was estimated as:

$$[\bullet OH]_{ss} = \frac{R_{f,hTPA}}{Yk_{\bullet OH,TPA} [TPA]}$$
(S10)

where *Y* is the efficiency of hTPA production when oxygen is the oxidant, which is 35%;<sup>20,21</sup> and *k*<sub>•OH,TPA</sub> is  $4.4\times10^9$  M<sup>-1</sup> s<sup>-1</sup>.<sup>16</sup> [TPA] was assumed to be constant because TPA loss was minimal.<sup>6</sup>

Under state-state conditions, the rate of formation of •OH ( $R_{f,•OH}$ , M s<sup>-1</sup>) is equal to its rate of loss ( $R_{l,•OH}$ , M s<sup>-1</sup>), and this value is:

$$R_{f,\bullet OH} = R_{l,\bullet OH}$$

$$= [\bullet OH]_{ss} (k_{\bullet OH,HCO_3} [HCO_3^{-}] + k_{\bullet OH,CO_3} [CO_3^{2-}] + k_{\bullet OH,DOC} [DOC] + k_{\bullet OH,TPA} [TPA])$$
(S11)

where:  $k_{\cdot OH,HCO3}$  (8.5×10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>),  $k_{\cdot OH,CO3}$  (3.9×10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>), and  $k_{\cdot OH,DOC}$  (2.0×10<sup>4</sup> L mgC<sup>-1</sup> s<sup>-1</sup>)<sup>22,23</sup> are the second order rate constants for the reactions of •OH with HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and DOC, respectively. In addition, halide ions were reported to be scavengers of •OH in previous studies,<sup>24,25</sup> especially the Br ion, which can significant quench •OH, converting •OH to radical reactive halogen species (RHS), leading to ineffective treatment of saline waters. However, in our case, the Br ion should have minor effect on the formation rate of •OH due to its low level in freshwaters.

Quantum yields of the PPRIs ( $\Phi_{app, {}^{3}DOM^{*}}$ ,  $\Phi_{app, {}^{1}O_{2}}$ , and  $\Phi_{app, {}^{0}OH}$ ; mol molphotons<sup>-1</sup>) are defined as the ratio of PPRI formation rate ( $R_{f}$ ) to the rate of light absorption by the water sample ( $R_{a}$ , mol-photons L<sup>-1</sup> s<sup>-1</sup>). Following the method of Sharpless et al.,<sup>11</sup>  $R_{a}$  was determined to calculate quantum yields and quantum yield coefficients of PPRIs. A bimolecular actinometer solution of 9.8 µM p-nitroanisole/5.5 mM pyridine (PNA/PYD) was used to estimate the spectral irradiance of the lamp ( $I_{\lambda}$ , mol-photons L<sup>-1</sup> s<sup>-1</sup>).<sup>6,11</sup>  $R_{a}$  was calculated from  $I_{\lambda}$ :

$$R_a = \sum_{275nm}^{600nm} I_{\lambda} \left( 1 - 10^{-a_{\lambda,dec}z} \right) \tag{S12}$$

Where  $a_{\lambda,dec}$  (m<sup>-1</sup>) is the decadic absorption coefficients of the water sample for each wavelength;<sup>6</sup> and *z* (m) is the average optical pathlength through the reaction vessels, with a value of  $1.12 \times 10^{-2}$  m for  $13 \times 100$  mm test tubes.<sup>26</sup> The integration range we chose is from 275 to 600 nm, which captures the full light absorption spectrum of CDOM.<sup>27,28</sup>

The quantum yield coefficient for  ${}^{3}\text{DOM}^{*}$  ( $f_{\text{TMP}}$ , L mol-photons<sup>-1</sup>) was calculated by equation S13:

$$f_{TMP} = \frac{k_{obs,TMP}}{R_a} \tag{S13}$$

The apparent quantum yield of  ${}^{3}\text{DOM}^{*}$  ( $\Phi_{app, {}^{3}DOM^{*}}$ , mol mol-photons<sup>-1</sup>) was then calculated:<sup>6</sup>

$$\Phi_{app,\ ^{3}DOM^{*}} = f_{TMP}\left([TMP]_{0} + \frac{k_{q}}{k_{\ ^{3}DOM^{*},TMP}}\right)$$
(S14)

The apparent quantum yield of  ${}^{1}O_{2}$  ( $\Phi_{app, {}^{1}O_{2}}$ , mol mol-photons<sup>-1</sup>) was determined using equation S12:

$$\Phi_{app, \ ^1O_2} = k_{d,S}$$

$$\times \frac{[\ ^1O_2]_{ss}}{R_a}$$
(S15)

The apparent quantum yield for the formation of •OH ( $\Phi_{app,\bullet OH}$ , mol mol-photons<sup>-1</sup>) was computed by dividing the rate of loss of •OH ( $R_{l,\bullet OH}$ , M s<sup>-1</sup>) by  $R_a$ :

$$\Phi_{app,\bullet OH} = \frac{R_{l,\bullet OH}}{R_{a}}$$

$$= \frac{[\bullet OH]_{ss} (k_{\bullet OH,HCO_{3}}[HCO_{3}^{-}] + k_{\bullet OH,CO_{3}}[CO_{3}^{2-}] + k_{\bullet OH,DOC}[DOC] + k_{\bullet OH,TPA}[TPA])}{R_{a}}$$
(S16)

Where  $k_{\bullet OH,HCO3}$  (8.5×10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>),  $k_{\bullet OH,CO3}$  (3.9×10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>), and  $k_{\bullet OH,DOC}$  (2.0×10<sup>4</sup> L mgC<sup>-1</sup> s<sup>-1</sup>)<sup>22,23</sup> are the second order rate constants for the reactions of •OH with HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and DOC, respectively.

#### Text S5. Correction for DOC-induced inhibition.

Similar with previous studies,<sup>7</sup> our results using CBP as a model for <sup>3</sup>DOM<sup>\*</sup> demonstrated that the inhibition of TMP photodegradation is likely due to the reduction of

TMP reaction intermediates. The experimental IF ranged from 0.62 to 1.18 with an average of 1.01. Consistent with previous research, IF<sup>-1</sup> linearly correlated with DOC ( $\mathbb{R}^2 = 0.93$ ; Figure S10). To correct for the DOC-induced inhibition, the  $k_{obs,TMP}$  values were normalized to  $k_{obs,TMP}^{corr}$  by IF (eq. S6). Splitting the data into two groups, low to moderately colored waters ( $a_{440} \le 11 \text{ m}^{-1}$ ) and high color waters ( $a_{440} > 11 \text{ m}^{-1}$ ), an average 6.22% decrease in  $k_{obs,TMP}^{corr}$  for low to moderately colored waters was observed, while  $k_{obs,TMP}^{corr}$  of high color waters increased by 65.72%. The average increase in  $k_{obs,TMP}$  with IF correction was 2.77% (Figure S5).

The  $k_{obs,TMP}^{corr}$  values were used to find  $R_{f, 3DOM^*}$  with a [TMP]<sub>0</sub> value of 5  $\mu$ M using equation S1. Experiments measuring  $k_{obs,TMP}^{corr}$  as a function of [TMP]<sub>0</sub> provided the value of  $k_{3DOM^*,TMP}$  to be  $1.72 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , similar a reported value of  $1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . <sup>7</sup> Corrected  $R_{f, 3DOM^*}$  were then computed to range from  $2.33 \times 10^{-8}$  to  $1.75 \times 10^{-7} \text{ M s}^{-1}$  with a mean of  $6.41 \times 10^{-8} \text{ M s}^{-1}$  (Table S4).

#### Text S6. Hypothesis of TMP oxidation by produced <sup>3</sup>DOM\*.

Because the energy gap between ground state O<sub>2</sub> and <sup>1</sup>O<sub>2</sub> is relatively small (94 kJ mol<sup>-1</sup>), ground state O<sub>2</sub> is capable of reacting with both high-energy <sup>3</sup>DOM\* (> 250 kJ mol<sup>-1</sup>) and low-energy <sup>3</sup>DOM\* (94 to 250 kJ mol<sup>-1</sup>) to generate <sup>1</sup>O<sub>2</sub>. However, the oneelectron oxidation potential of TMP is 1.22 V, meaning that TMP oxidation by low-energy <sup>3</sup>DOM\* (< 1.22 V) is thermodynamically unfavorable. Because high-energy <sup>3</sup>DOM\* only accounts for 15–53% of the total <sup>3</sup>DOM\* pool,<sup>8</sup> TMP samples a smaller fraction of <sup>3</sup>CDOM\* than ground state O<sub>2</sub>, leading to a lower value of  $\Phi_{app, ^3DOM^*}$  than  $\Phi_{app, {}^{1}O_{2}}$  (calculated efficiency > 100%). As stated in the main text, another explanation is different pools of <sup>3</sup>DOM\* that react via different processes.

#### Text S7. Models for generating maps.

The correlations between  $R_a$ , steady-state concentrations and formation rates of PPRIs with  $a_{440}$  were used to create lake average level and pixel level maps (Figures 5&S11-14).

$$R_a (mol - photons \ L^{-1} \ s^{-1}) = 1.67 \times 10^{-6} \cdot a_{440} \ (m^{-1}) + 1.77 \times 10^{-6}$$
(S17)

$$R_{f, 3_{DOM^*}} (M s^{-1}) = 3.75 \times 10^{-9} \cdot a_{440} (m^{-1}) + 4.22 \times 10^{-8}$$
(S18)

$$R_{f, {}^{1}O_{2}} (M s^{-1}) = 1.70 \times 10^{-8} \cdot a_{440} (m^{-1}) + 7.30 \times 10^{-8}$$
(S19)

$$R_{f,\bullet OH} (M s^{-1}) = 3.04 \times 10^{-11} \cdot a_{440} (m^{-1}) + 1.12 \times 10^{-11}$$
(S20)

$$\left[ {}^{3}DOM^{*} \right]_{ss} (M) = 1.17 \times 10^{-14} \cdot a_{440} (m^{-1}) + 1.32 \times 10^{-13}$$
(S21)

$$\left[ {}^{1}O_{2} \right]_{ss} (M) = 5.99 \times 10^{-14} \cdot a_{440} (m^{-1}) + 2.58 \times 10^{-13}$$
(S22)

$$[\bullet OH]_{ss} (M) = 2.69 \times 10^{-16} \cdot \ln a_{440} (m^{-1}) + 1.79 \times 10^{-16}$$
(S23)

The estimated first-order rate constants for reactions of diuron and propiconazole were obtained following the equations of Zeng et.al 2013:<sup>19</sup>

$$k_{obs,diuron} (s^{-1}) = 7.8 \times 10^9 \cdot \left[ {}^{3}DOM^* \right]_{ss} (M)$$
  
= 7.8 × 10<sup>9</sup> · (1.17 × 10<sup>-14</sup> · a<sub>440</sub> (m<sup>-1</sup>) + 1.32 × 10<sup>-13</sup>) (S24)

 $k_{obs,propiconazole} (s^{-1}) = 3.9 \times 10^6 \cdot \left[ {}^{1}O_2 \right]_{ss} (M)$ 

$$= 3.9 \times 10^{6} \cdot (5.99 \times 10^{-14} \cdot a_{440} \ (m^{-1}) + 2.58 \times 10^{-13}) \tag{S25}$$

Thus,

$$k_{obs,diuron} (s^{-1}) = 9.13 \times 10^{-5} \cdot a_{440} (m^{-1}) + 1.03 \times 10^{-3}$$
(S26)

$$k_{obs,propiconazole} (s^{-1}) = 2.34 \times 10^{-7} \cdot a_{440} (m^{-1}) + 1.01 \times 10^{-6}$$
 (S27)

The half-lives were calculated based on the rate law for a first-order reaction,

$$t_{1/2,diuron}(s) = 0.693/k_{obs,diuron}(s^{-1})$$

$$= \frac{0.693}{9.13 \times 10^{-5} \cdot a_{440} (m^{-1}) + 1.03 \times 10^{-3}}$$
$$= \frac{1}{1.32 \times 10^{-4} \cdot a_{440} (m^{-1}) + 1.49 \times 10^{-3}}$$
(S28)

 $t_{1/2, propiconazole}\left(s\right) = 0.693/k_{obs, propiconazole}\left(s^{-1}\right)$ 

$$= \frac{0.693}{2.34 \times 10^{-7} \cdot a_{440} (m^{-1}) + 1.01 \times 10^{-6}}$$
$$= \frac{1}{3.38 \times 10^{-7} \cdot a_{440} (m^{-1}) + 1.46 \times 10^{-6}}$$
(S29)

Compound	Acronym	Supplier	Purity
2,4,6-Trimethylphenol	TMP	Acros Organics	99%
4-Carboxybenzophenone	CBP	Sigma-Aldrich	99%
p-Nitroanisole	PNA	Acros Organics	> 99%
Pyridine	PYD	Sigma-Aldrich	≥99%
Furfuryl alcohol	FFA	Sigma-Aldrich	98%
Terephthalic acid	TPA	Acros Organics	99%
Hydroxyterephthalic acid	hTPA	TCI	98%
Boric acid	H <sub>3</sub> BO <sub>3</sub>	VWR International	≥99.5%
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	Fisher Scientific	≥85% wt
Sodium phosphate monobasic	NaH <sub>2</sub> PO <sub>4</sub>	J.T.Baker	99%
Sodium phosphate dibasic	Na <sub>2</sub> HPO <sub>4</sub>	J.T.Baker	99%
Acetonitrile	ACN	Fisher Scientific	≥99.93%

Table S1. Chemical suppliers and purities.

**Table S2.** HPLC analysis methods for compound detection: 2,4,6-trimethylphenol (TMP), furfuryl alcohol (FFA), hydroxyterephthalic acid (hTPA), and p-nitroanisole (PNA).

Compound	Column	Mobile Phase	Flow Rate (mL/min)	Detection λ (nm) <sup>a</sup>	Retention time (min)			
ТМР	Ascentis RP-Amide (Supelco, 150×4.6 mm, 5 µm particles) Ascentis RP-Amide	50% Acetonitrile 50% 0.1% Phosphoric Acid	1	$\lambda_{\rm UV}=205$	7.3			
FFA	(Supelco, $150 \times 4.6$ mm, 5 µm particles)	100% Milli-Q H <sub>2</sub> O	1	$\lambda_{\rm UV}=219$	5			
TMP+CBP	Ascentis RP-Amide (Supelco, 150×4.6 mm, 5 μm particles)	<ul><li>35 % Acetonitrile</li><li>65 % Acetate buffer pH</li><li>4.75</li></ul>	1	λ <sub>UV,TMP</sub> = 200, 254 λ <sub>UV,CBP</sub> = 265	TMP = 10.9 CBP = 3.3			
PNA	Ascentis RP-Amide (Supelco, 150×4.6 mm, 5 μm particles)	60% Acetonitrile 40% 10 mM Phosphate Buffer (pH 3, 10% Acetonitrile)	1	$\lambda_{\rm UV}=313$	3.3			
hTPA	Ascentis RP-Amide (Supelco, 150×4.6 mm, 5 µm particles)	70% 10mM Phosphate buffer (pH 2) 30% Acetonitrile	1	$\lambda ex = 312$ $\lambda em = 428$	7			
<sup>a</sup> $\lambda_{UV}$ = ultraviolet light detection, $\lambda ex/\lambda em$ = fluorescence detection								

Site Name	Ecoregion	Latitude	Longitude	рН	<i>a</i> 440 (m <sup>-1</sup> )	DOC (mg L <sup>-1</sup> )	SUVA254 (L mg <sup>-1</sup> m <sup>-1</sup> )	DIC (mg/L)	E2/E3	NO3 <sup>-</sup> (mg L <sup>-1</sup> ) <sup>a</sup>	[HCO3 <sup>-</sup> ] (M)	[CO3 <sup>2-</sup> ] (M)
Lake Bemidji	NLF	47.4700	-94.8629	8.43	1.15	6.28	3.66	37.4	12.00	< 0.008	6.11E-04	7.58E-06
Blandin Reservoir	NLF	47.2369	-93.5668		3.68	11.0	3.18	29.6	6.29	0.057		
Burntside Lake	NLF	47.9483	-91.9442	8.76	0.78	5.49	1.99	2.09	8.31	< 0.008	3.37E-05	8.95E-07
Gull Lake	NLF	46.4236	-94.3602	7.76		5.97		23.1		< 0.008	3.70E-04	9.81E-07
Island Lake	NLF	46.9356	-95.5224		0.78	6.51	1.97	29.3	9.11	< 0.008		
Lake Itasca	NLF	47.2149	-95.182	8.31	0.41	6.54	1.34	35.4	10.56	< 0.008	5.79E-04	5.45E-06
Mille Lacs Lake	NLF	46.1541	-93.4842	7.49	2.53	6.03	1.61	15.1	5.32	< 0.008	2.34E-04	3.34E-07
Rainy Lake	NLF	48.6166	-93.3481	7.79	4.15	10.1	3.18	3.41	5.82	< 0.008	5.47E-05	1.55E-07
Shagawa Lake	NLF	47.9240	-91.9133	7.57	1.70	6.76	2.87	5.77	6.74	< 0.008	9.06E-05	1.55E-07
South Sturgeon Lake	NLF	47.6369	-93.0645	7.96	27.9	36.2	4.85	2.73	4.53	0.079	4.42E-05	1.86E-07
Sturgeon Lake	NLF	47.6696	-93.0565		2.30	8.46	2.26	6.32	7.30	< 0.008	9.52E-05	9.39E-08
Lake Vermilion (Big Bay)	NLF	47.8473	-92.3078	7.34	3.22	12.0	3.05	7.48	6.77	< 0.008	1.13E-04	1.14E-07
Lake Vermilion (Pike Bay)	NLF	47.8224	-92.308	7.41	24.2	28.9	5.05	9.96	4.46	0.070	1.52E-04	1.81E-07
White Iron Lake - South	NLF	47.8608	-91.8173	7.77	8.75	14.3	4.63	3.43	5.01	< 0.008	5.49E-05	1.49E-07
Lake Winnibigosh	NLF	47.4285	-94.057	8.47	0.92	7.37	1.79	28.6	10.62	< 0.008	4.66E-04	6.35E-06
Upper Red Lake #1	NMW	48.1711	-94.5409	8.58		13.4		27.3		< 0.008	4.44E-04	7.79E-06
Upper Red Lake #2	NMW	48.1743	-94.5173	7.09	27.2	47.6	4.2	19.1	5.04	0.079	2.69E-04	1.52E-07
Lake of the Woods (Muskeg Bay)	NMW	48.9940	-95.0627	7.53	5.30	11.6	3.26	9.28	5.65	< 0.008	1.45E-04	2.26E-07
Lake of the Woods (Fourmile Bay)	NMW	48.8506	-94.6974	8.62	6.68	13.7	3.85	6.55	5.40	< 0.008	1.07E-04	2.05E-06
Crystal Lake	NCHF	46.6241	-95.9611	8.74	0.51	6.33	1.61	41.1	11.78	< 0.008	6.65E-04	1.69E-05
Detroit Lake	NCHF	46.7764	-95.8403	8.64	0.83	7.02	2.1	40.2	10.24	0.106	6.53E-04	1.32E-05
Mississippi River	NCHF	45.0434	-93.2817	7.73	2.99	9.35	3.32	47.7	6.21	1.368	7.61E-04	1.89E-06
Vadnais Lake	NCHF	45.0517	-93.0937	7.94	1.84	11.3	2.36	31.4	7.69	0.138	5.07E-04	2.04E-06
Lake Saint Croix	WCBP	44.7499	-92.8086	8.08	5.07	10.0	4.26	18.7	5.18	0.652	3.05E-04	1.69E-06

**Table S3.** Water quality and spectral parameters measured for the collected water samples.

<sup>a</sup> The limit of detection (LOD) for  $NO_3^{2-}$  was 0.008 mg/L.

Site Name	<i>R<sub>a</sub></i> (mol-photons <sup>-1</sup> L <sup>-1</sup> s <sup>-1</sup> )	k <sub>obs,TMP</sub> <sup>corr</sup> (s <sup>-1</sup> )	f <sub>TMP</sub> (L mol-photons <sup>-1</sup> )	$R_{f, 3_{DOM^*}}$ (M s <sup>-1</sup> )	k <sub>obs,FFA</sub> (s <sup>-1</sup> )	$R_{f, 10_2}$ (M s <sup>-1</sup> )	$\begin{array}{c} R_{f,\bullet 0H} \\ (\mathrm{M} \ \mathrm{s}^{-1}) \end{array}$
Lake Bemidji	2.32E-06	2.40E-04	1.03E+02	4.49E-08	3.17E-05	7.36E-08	3.99E-11
Blandin Reservoir	8.74E-06	3.62E-04	4.15E+01	6.76E-08	7.50E-05	1.74E-07	
Burntside Lake	3.16E-06	1.30E-04	4.12E+01	2.43E-08	2.33E-05	5.42E-08	0
Gull Lake	2.67E-06	2.22E-04	8.33E+01	4.15E-08	3.17E-05	7.36E-08	4.16E-11
Island Lake	2.11E-06	1.25E-04	5.94E+01	2.34E-08	2.17E-05	5.03E-08	
Lake Itasca	1.85E-06	1.39E-04	7.49E+01	2.59E-08	2.33E-05	5.42E-08	0
Mille Lacs Lake	2.01E-06	1.25E-04	6.22E+01	2.33E-08	1.67E-05	3.87E-08	0
Rainy Lake	8.47E-06	3.51E-04	4.14E+01	6.55E-08	5.83E-05	1.36E-07	1.42E-10
Shagawa Lake	5.13E-06	2.14E-04	4.18E+01	4.00E-08	4.17E-05	9.68E-08	7.37E-11
South Sturgeon Lake	4.83E-05	4.97E-04	1.03E+01	9.28E-08	1.98E-04	4.61E-07	4.53E-10
Sturgeon Lake	4.05E-06	2.05E-04	5.06E+01	3.82E-08	3.50E-05	8.13E-08	6.33E-11
Lake Vermilion (Big Bay)	8.21E-06	3.86E-04	4.71E+01	7.21E-08	7.33E-05	1.70E-07	1.37E-10
Lake Vermilion (Pike Bay)	3.95E-05	7.87E-04	1.99E+01	1.47E-07	2.05E-04	4.76E-07	6.90E-10
White Iron Lake - South	1.95E-05	4.16E-04	2.13E+01	7.77E-08	1.00E-04	2.32E-07	2.88E-10
Lake Winnibigosh	2.69E-06	2.17E-04	8.05E+01	4.04E-08	2.67E-05	6.20E-08	0
Upper Red Lake #1	3.50E-06	3.75E-04	1.07E+02	7.01E-08	4.83E-05	1.12E-07	6.68E-11
Upper Red Lake #2	4.77E-05	9.40E-04	1.97E+01	1.75E-07	2.58E-04	6.00E-07	1.28E-09
Lake of the Woods (Muskeg Bay)	9.28E-06	3.73E-04	4.01E+01	6.95E-08	7.83E-05	1.82E-07	1.79E-10
Lake of the Woods (Fourmile Bay)	1.64E-05	4.03E-04	2.46E+01	7.52E-08	8.17E-05	1.90E-07	2.74E-10
Crystal Lake	2.22E-06	1.62E-04	7.31E+01	3.03E-08	2.33E-05	5.42E-08	3.05E-11
Detroit Lake	2.70E-06	2.82E-04	1.05E+02	5.27E-08	3.50E-05	8.13E-08	4.26E-11
Mississippi River	8.82E-06	4.67E-04	5.29E+01	8.71E-08	9.00E-05	2.09E-07	2.06E-10
Vadnais Lake	5.67E-06	4.01E-04	7.08E+01	7.49E-08	6.83E-05	1.59E-07	4.10E-11
Lake Saint Croix	1.19E-05	4.27E-04	3.59E+01	7.96E-08	9.67E-05	2.25E-07	1.92E-10

### Table S4. A summary of photodegradation kinetics.

Site Name	[ <sup>3</sup> CDOM <sup>*</sup> ]ss (M)	${oldsymbol{\Phi}_{app,\ ^{3}DOM^{*}}}\ ({ m mol\ mol\ -photons^{-1}})$	[ <sup>1</sup> O <sub>2</sub> ]ss (M)	$\Phi_{app, {}^{1}O_{2}}$ (mol mol-photons <sup>-1</sup> )	[•OH]ss (M)	Φ <sub>app,•OH</sub> (mol mol-photons <sup>-1</sup> )
Lake Bemidji	1.40E-13	1.88E-02	2.60E-13	3.14E-02	2.24E-16	1.72E-05
Blandin Reservoir	2.11E-13	7.53E-03	6.15E-13	1.98E-02	5.91E-16	
Burntside Lake	7.56E-14	7.48E-03	1.91E-13	1.70E-02	0	0
Gull Lake	1.29E-13	1.51E-02	2.60E-13	2.73E-02	2.49E-16	1.56E-05
Island Lake	7.29E-14	1.08E-02	1.78E-13	2.37E-02	0	
Lake Itasca	8.06E-14	1.36E-02	1.91E-13	2.91E-02	0	0
Mille Lacs Lake	7.27E-14	1.13E-02	1.37E-13	1.91E-02	0	0
Rainy Lake	2.04E-13	7.52E-03	4.78E-13	1.59E-02	5.76E-16	1.68E-05
Shagawa Lake	1.25E-13	7.59E-03	3.42E-13	1.87E-02	4.09E-16	1.44E-05
South Sturgeon Lake	2.89E-13	1.87E-03	1.63E-12	9.46E-03	5.91E-16	9.39E-06
Sturgeon Lake	1.19E-13	9.18E-03	2.87E-13	1.99E-02	2.96E-16	1.56E-05
Lake Vermilion (Big Bay)	2.25E-13	8.55E-03	6.01E-13	2.06E-02	4.80E-16	1.66E-05
Lake Vermilion (Pike Bay)	4.57E-13	3.62E-03	1.68E-12	1.20E-02	1.11E-15	1.75E-05
White Iron Lake - South	2.42E-13	3.88E-03	8.20E-13	1.18E-02	8.70E-16	1.48E-05
Lake Winnibigosh	1.26E-13	1.46E-02	2.19E-13	2.28E-02	0	0
Upper Red Lake #1	2.18E-13	1.95E-02	3.96E-13	3.18E-02	2.10E-16	1.91E-05
Upper Red Lake #2	5.46E-13	3.58E-03	2.12E-12	1.25E-02	1.28E-15	2.68E-05
Lake of the Woods (Muskeg Bay)	2.17E-13	7.29E-03	6.42E-13	1.94E-02	6.46E-16	1.93E-05
Lake of the Woods (Fourmile Bay)	2.34E-13	4.46E-03	6.69E-13	1.15E-02	8.59E-16	1.67E-05
Crystal Lake	9.44E-14	1.33E-02	1.91E-13	2.42E-02	1.67E-16	1.37E-05
Detroit Lake	1.64E-13	1.90E-02	2.87E-13	2.99E-02	2.18E-16	1.58E-05
Mississippi River	2.71E-13	9.61E-03	7.38E-13	2.35E-02	8.64E-16	2.33E-05
Vadnais Lake	2.33E-13	1.29E-02	5.60E-13	2.78E-02	1.49E-16	7.24E-06
Lake Saint Croix	2.48E-13	6.51E-03	7.92E-13	1.87E-02	7.76E-16	1.61E-05

 Table S5. A summary of the steady-state concentrations and quantum yields of PPRIs.



Figure S1. Map showing locations of 24 inland waters sampled throughout Minnesota.



**Figure S2.** Correlations of E2/E3 with  $a_{440}$ . The regression equation is E2/E3 = 7.96  $\cdot \exp(-0.54 \cdot a_{440} \text{ (m}^{-1})) + 4.84$ .



**Figure S3.** Time course of TMP photodegradation in Lake Bemidji, FFA photodegradation in Lake Bemidji, and hTPA formation in Lake Saint Croix.



**Figure S4.** Correlations of  $k_{obs,TMP}$  and  $k_{obs,FFA}$  with  $a_{440}$ . The regression equations are (a)  $k_{obs,TMP}$  (s<sup>-1</sup>) = 0.0043  $\cdot a_{440}$  (m<sup>-1</sup>) + 0.015; (b)  $k_{obs,FFA}$  (s<sup>-1</sup>) = 0.0004  $\cdot a_{440}$  (m<sup>-1</sup>) + 0.0019.



**Figure S5.** The correlations of  $k_{obs,TMP}$  versus DOC before and after correction using the inhibition factor, IF. The regression equation after correction is  $k_{obs,TMP}$  (s<sup>-1</sup>) = 1.68×10<sup>-5</sup> · DOC (mg/L) + 1.98×10<sup>-6</sup>.



**Figure S6**. Plots of formation of <sup>3</sup>DOM<sup>\*</sup>, <sup>1</sup>O<sub>2</sub> and •OH versus  $R_a$ . The slope from the origin to each point is the (apparent) quantum yield for the given water sample. The small range in slopes implies a small range of (apparent) quantum yields.



**Figure S7.** Relationships between (a)  $\Phi_{app, {}^{3}DOM^{*}}$  and  $a_{440}$ ; (b)  $\Phi_{app, \bullet OH}$  and  $a_{440}$ .



**Figure S8.** Correlations of E2/E3 with  $f_{\text{TMP}}$ . The regression equation is:  $f_{\text{TMP}}$  (L molphotons<sup>-1</sup>) = 9.28 (± 1.19) · E2/E3 – 16.7 (± 9.11).



**Figure S9.** Correlations of E2/E3 with  $\Phi_{app, {}^{3}DOM^{*}}$  and  $\Phi_{{}^{1}O_{2}}$ . The regression equations are (a)  $\Phi_{app, {}^{3}DOM^{*}}$  (mol mol-photons<sup>-1</sup>) = 0.0017 (± 0.0002) · E2/E3 – 0.0030 (± 0.0017); (b)  $\Phi_{app, {}^{1}O_{2}}$  (mol mol-photons<sup>-1</sup>) = 0.0021 (± 0.0003) · E2/E3 – 0.0046 (± 0.0026). (c) shows the relationship between E2/E3 and  $\Phi_{app, {}^{\bullet}OH}$ .



**Figure S10.** Correlations of SUVA<sub>254</sub> with  $\Phi_{app, {}^{3}DOM^{*}}$  and  $\Phi_{{}^{1}O_{2}}$ . The regression equations are (a)  $\Phi_{app, {}^{3}DOM^{*}}$  (mol mol-photons<sup>-1</sup>) =  $-0.0028 (\pm 0.0007) \cdot \text{SUVA}_{254}$  (L mg<sup>-1</sup> m<sup>-1</sup>) + 0.0178 (± 0.0022); (b)  $\Phi_{app, {}^{1}O_{2}}$  (mol mol-photons<sup>-1</sup>) =  $-0.0036 (\pm 0.0009) \cdot \text{SUVA}_{254}$  (L mg<sup>-1</sup> m<sup>-1</sup>) + 0.0309 (± 0.0030). (c) shows the relationship between SUVA<sub>254</sub> and  $\Phi_{app, {}^{\bullet}OH}$ .



**Figure S11.**  $\Phi_{app, {}^{1}O_{2}}$  versus  $\Phi_{app, {}^{3}DOM^{*}}$ . The slope of the linear relationship with/without the intercept forced through 0 is 1.92 and 1.23, respectively.



**Figure S12.** Relationship between  $f_{TMP}$  and  $\Phi_{app,\bullet OH}$ .



**Figure S13.** Minnesota 2015 and 2016 mean CDOM distribution for all measured waterbodies by ecoregion. This figure is fromref.<sup>29</sup> and is reproduced with permission from Elsevier.



Figure S14. Correlation of  $IF^{-1}$  with DOC. The regression equation is  $IF^{-1} = 0.025 (\pm 0.003) \cdot DOC (mg/L) + 0.71 (\pm 0.08).$ 



**Figure S15**. Distribution of estimated  $R_a$ , steady-state concentrations and formation rates of PPRIs, the first-order photodegradation rate constants and half-lives of pesticides in Minnesota lakes, based on pixel-level  $a_{440}$  values in 2015. A zoom in of the NLF ecoregion in northeast Minnesota is shown in the inset figure.



**Figure S16**. Distribution of estimated  $R_a$ , steady-state concentrations and formation rates of PPRIs, the first-order photodegradation rate constants and half-lives of pesticides in Minnesota lakes, based on lake average  $a_{440}$  values in 2016. A zoom in of the NLF ecoregion in northeast Minnesota is shown in the inset figure.



**Figure S17**. Distribution of estimated  $R_a$ , steady-state concentrations and formation rates of PPRIs, the first-order photodegradation rate constants and half-lives of pesticides in Minnesota lakes, based on pixel-level  $a_{440}$  values in 2016. A zoom in of the NLF ecoregion in northeast Minnesota is shown in the inset figure.



**Figure S18**. Distribution of estimated  $R_a$ , steady-state concentrations and formation rates of PPRIs, the first-order photodegradation rate constants and half-lives of pesticides in Minnesota lakes, based on average of lake average  $a_{440}$  values in 2015 and 2016. A zoom in of the NLF ecoregion in northeast Minnesota is shown in the inset figure.



**Figure S19**. Pixel-level  $a_{440}$  distribution in Upper and Lower Red Lake based on satellite imagery collected in (a) 2015 and (b) 2016. A zoom in of the Red Lake in 2015 and 2016 are shown in (c) and (d). Inflow of highly colored water from the Tamarack River at the northeast end of Upper Red Lake accounts for the high  $a_{440}$  values in the eastern part of the lake. High values along the shorelines of both lakes likely reflect interference from bottom and emergent vegetation effects.



**Figure S20**. Pixel-level  $a_{440}$  distribution in South and North White Iron Lake near Ely, Minnesota based on satellite imagery collected in (a) 2015 and (b) 2016.



**Figure S21.** Comparison of estimated (satellite) and measured values of (a)  $a_{440}$ , (b)  $R_a$ ; (c)  $R_{f, 3DOM^*}$ ; and (d)  $[^{3}DOM^*]_{ss}$ . The dashed line is a 1:1 line. Mississippi River and Upper Red #2 (at the mouth of the Tamarack River) were excluded because the riverine flows create highly dynamic conditions that are not suitable for comparisons with relatively infrequent satellite imagery.

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