Supporting Information

Copper Inhibition of Triplet-sensitized Phototransformation of Phenolic and Amine Contaminants

Yanheng Pan[†], Xiaoxue Ruan[†], Shikha Garg[‡], T. David Waite[‡], Yu Lei [†], Xin Yang^{†*}

[†] School of Environmental Science and Engineering, Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Sun Yat-sen University, Guangzhou 510275, China

[‡] School of Civil and Environmental Engineering, The University of New South Wales, Sydney, New South Wales 2052, Australia

* Corresponding author, Tel: +86-2039332690, email: yangx36@mail.sysu.edu.cn

33 Pages10 Figures3 Tables3 Schemes

Resubmitted to Environmental Science & Technology

Table of contents

Figure S1. Chemical structure of target contaminants used in this study					
Figure S2. Spectral irradiance from the solar simulator6					
Table S1 HPLC method parameters for detection of target contaminants					
Table S2. Model parameters for the inhibitory effects of Cu 8					
Figure S3. Photosensitized oxidation of target contaminants by CBBP10					
Figure S4. Inhibition factor for the ³ CBBP*-induced degradation of sorbic acid11					
Table S3. Estimated second-order reaction rate constants between radical					
intermediates and Cu(I)11					
Figure S5. Inhibition factor for ³ CBBP*-induced oxidation of target contaminants14					
Figure S6. Effect of SRNOM on the phototransformation of target contaminants15					
Figure S7. Effects of target contaminant addition on [Cu(I)]ss16					
Figure S8. Inhibition factor for triplet-induced oxidation of target contaminants16					
Text-S1. Description of chemicals used in the study17					
Text-S2. Detailed description of photochemical experimental setup18					
Text-S3. Detailed description of time-resolved laser spectroscopy19					
Text-S4. Measurement of steady-state concentrations of Cu(I)20					
Figure S9. [Cu(I)]ss generated on irradiation of CBBP and SRNOM systems21					
Text S5. Details of the kinetic model applied in CBBP systems					
Text S6. Details of the kinetic model applied in SRNOM systems without Cu25					
Text S7. Details of the kinetic model in SRNOM solutions containing Cu27					
Text S8. Derivation of Equation 9 in the main text					
Text S9. Rationale for pseudo-first-order kinetics in laser photolysis tests					
Figure S10. Transient absorption spectra of target contaminants					
REFERENCES					





(b)Amines





Figure S1. Chemical structure of target contaminants used in this study



Figure S2. Spectral irradiance from the solar simulator equipped with a Window-Q optical filter.

Compound	Eluent composition (%)		Flow rate	absorption	excitation	emission	
				(mL/min)	wavelength (nm)	wavelength (nm)	wavelength (nm)
	ACN	Water	10mM H ₃ PO ₄				
2,4,6-trimethylphenol	70		30	1		225	316
4-methylphenol	70		30	1		225	316
bisphenol A		50	50	1	276		
17β-estradiol	70	30		1		270	310
17α-ethinylestradiol	70	30		1		270	310
amoxicillin	20		80	0.8	230		
acetaminophen	40		60	1	238		
N,N-dimethyl-4-cyano	50	50		1		290	488
aniline							
4-cyanoaniline	30	70		1	273		
4-chloroaniline	40		60	1		246	345
mefenamic acid	80		20	1	288		
Trimethoprim	25		75	1	210		
Atenolol	25		75	1		228	342
Metoprolol	25		75	1		228	342
Propranolol	25		75	1		228	342
Sulfadiazine	30		70	1	266		
Sulfamerazine	30		70	1	266		
sulfachloropyridazine	30		70	1	266		
sulfamethoxazole	30		70	1	266		
Sulfathiazole	30		70	1	266		

 Table S1 HPLC method parameters for detection of target contaminants in this study

Table S2. Model parameters for the inhibitory effects of Cu on ³CBBP*or ³NOM*-induced oxidation of target contaminants

(a)

Photosensitizer CBBP ^a					
Target	[Cu]1/2 (nM)	f	adjusted R ^{2 e}	n ^f	
compound					
TMP	29.21 ± 4.35	0.86 ± 0.03	0.986	8	
4-MP	44.16 ± 1.43	0.89 ± 0.01	0.999	8	
BPA	88.73 ± 15.24	0.85 ± 0.04	0.983	8	
E2	101.16 ± 10.57	0.85 ± 0.03	0.994	8	
EE2	94.55 ± 13.78	0.81 ± 0.04	0.988	8	
AMX	112.66 ± 21.84	0.93 ± 0.06	0.981	8	
ACE	57.82 ± 7.18	0.86 ± 0.03	0.990	8	
DMABN	150.99 ± 33.34	0.97 ± 0.09	0.971	7	
ABN	61.19 ± 7.44	0.80 ± 0.02	0.990	8	
MFA	10.69 ± 1.76	0.72 ± 0.01	0.990	8	
TRI	93.34 ± 10.18	1	0.973	8	
PNL	15.01 ± 3.92	0.56 ± 0.02	0.968	8	
SMX	9.38 ± 1.94	0.79 ± 0.01	0.999	8	
STZ	15.15 ± 0.68	0.93 ± 0.01	0.999	8	

	Photosensitizer		SRNOM			
Data series	α (10 ⁻⁶ L	[NOM] _{1/2}	[Cu] _{1/2}	f	adjusted	\mathbf{n}^{f}
	$mgC^{-1}s^{-1}$)	(mgC/L)	(nM)	-	$\mathbf{R}^{2 e}$	
TMP+SRNOM ^b	55.9 ± 3.6	na ^g	na	na	0.984	5
TMP+SRNOM+Cu ^a	na	na	85.10 ± 5.18	0.98 ± 0.01	0.989	8
ABN+SRNOM ^c	2.96 ± 0.79	6.94 ± 0.64	na	0.76 ± 0.02	0.993	9
ABN+SRNOM+Cu ^d	na	6.94 (fixed)	26.68 ± 3.50	0.70 ± 0.03	0.951	8
TRI+SRNOM ^c	3.96 ± 0.61	4.44 ± 0.52	na	0.86 ± 0.04	0.988	9
TRI+SRNOM+Cu ^d	na	4.44 (fixed)	80.16 ± 14.51	0.80 ± 0.03	0.990	8

^a Results of data fitting to Eq 6 in the main text. ^b Results of data fitting to Eq S19 (SI-TextS6). ^c Results of data fitting to Eq S18 (SI-TextS6). ^d Results of data fitting to Eq 8 in the main text. ^e Correlation coefficient. ^f Number of data points included in data fitting. ^g na.: not applicable.



Figure S3. Photosensitized oxidation of target contaminants by CBBP in the absence and presence of Cu(II) under simulated sunlight irradiation. Conditions: [CBBP] = 45μ M, [contaminant]= 5μ M, pH = 5.2



Figure S4. Inhibition factor (IF) of Cu for the ³CBBP*-photosensitized degradation of sorbic acid. Conditions: [CBBP] = 45 μ M, [sorbic acid] =5 μ M, pH = 5.2

Table S3. Estimated second-order rate constants for the quenching of radical intermediates by Cu(I) ($k_{red,Cu(I)}$) derived from laser flash photolysis experiments.

$k_{red,Cu(I)}$
$(10^9 \text{ M}^{-1} \text{ s}^{-1})$
6.12 ± 0.39
6.84 ± 0.68
5.40 ± 1.05

Note: The effect of ionic strength on the rate constants for reactants involving two charged molecules (DMABN⁺⁺) was corrected employing the method reported previously.¹ No ionic strength correction was made for reactions involving a neutral molecule (TMP[•](-H) and BPA[•](-H)).







Figure S5. Inhibition Factor for ³CBBP*-induced oxidation of target contaminants as a function of total Cu concentration. Conditions: CBBP = 45 μ M, pH = 5.2. Curves represent nonlinear fits to Eq 6 in the main text.



Figure S6. Effect of SRNOM concentration on the pseudo-first-order phototransformation rate constant of (a) TMP, (b) ABN and (c) TRI (5 μ M initial concentration). Conditions: pH = 5.2. Curves represent nonlinear fits to Eq S18 and linear fits to Eq S19. All these rate constants were corrected for light screening caused by SRNOM.



Figure S7. Effects of target contaminant (TMP, ABN and TRI) addition on the steady-state concentration of Cu(I) generated on irradiation of Cu(II) in 10 mgC/L SRNOM solution. No amendments refer to no contaminant addition. Conditions: initial [Cu(II)] = 400 nM, [target contaminant] = 20 μ M, pH = 5.2



Figure S8. Inhibition Factor for induced oxidation of target contaminants by excited triplets of SRNOM and CBBP in the presence of 500nM Cu(II). Conditions: SRNOM=10 mgC/L or CBBP = 45μ M, pH = 5.2

Text-S1. Description of chemicals used in the study

All target organic contaminants were purchased from Sigma-Aldrich or TCI Chemicals. Triplet sensitizer 4-carboxybenzophenone (CBBP) was obtained from Sigma-Aldrich. Stock solutions of the above chemicals were prepared in water. Copper(II) sulfate pentahydrate (CuSO₄·5H₂O, >99.999%) and copper(I) chloride (CuCl, >99.99%) were obtained from Sigma-Aldrich. Cu(II) stock solutions (0.4 mM) were prepared weekly by dissolving an appropriate amount of copper(II) sulfate in a 1 mM H₂SO₄ solution. Cu(I) stock solutions (1 mM) were prepared daily according to methods described previously.² SRNOM (2R101N) was purchased from the International Humic Substances Society (IHSS). A 250 mg/L SRNOM stock solution was prepared by dissolving 25 mg of SRNOM in 0.1 litres of ultrapure water (18.2 MΩ·cm) and subsequently filtering through 0.45 µm cellulose acetate filters. Eluents (acetonitrile and phosphoric acid) used for high performance liquid chromatography (HPLC) were obtained from Fisher Scientific. All other reagents used were of reagent grade. All glassware were soaked in 5N HNO₃ for at least 3 days prior to use.

Text-S2. Detailed description of photochemical experimental setup

All irradiation experiments were conducted in a solar simulator (Q-SUN Xenon Test Chamber, Xe-1). The solar simulator was equipped with a Window-Q optical filter which cuts off light with wavelengths below 315 nm. The absolute irradiance of the solar simulator over the wavelength range 290–800 nm was recorded using an Ocean Optics USB-4000 spectrometer and is shown in Figure S2. The irradiation intensity at 300-400 nm was determined to be 73 W/m².

Solutions containing a single target contaminant (5 μ M), a photosensitizer (either 45 μ M CBBP or 10 mg C/L SRNOM) and varying Cu(II) concentrations (0–500 nM) were placed in a capped quartz vessel (inner diameter 5 cm, height 3 cm) and the initial solution pH adjusted to pH 5.2 using 1 mM H₂SO₄ or NaOH (buffers were not used in order to avoid any untoward interference). Note that Cu is mostly present in organically complexed form in the experimental system investigated here with the carboxylic and/or phenolic groups in SRNOM ^{3,4} and the carboxylic group in CBBP involved in Cu binding.⁵ The solutions were then irradiated for either 5 min (for the CBBP system) or 180–300 min (for the SRNOM system) and 500 μ L of samples were periodically withdrawn from the reactor for target contaminant measurement using HPLC. The variation in pH during each experiment was less than \pm 0.1 units. The temperature of samples during irradiation was maintained constant at 25.0 °C using a recirculating water bath.

Text-S3. Detailed description of time-resolved laser spectroscopy.

The experiments were performed using a LKS80 laser flash photolysis system (Applied Photophysics Ltd., the United Kingdom). The fourth harmonic mode of the Nd:YAG laser (266 nm, laser beam cross section of 0.5 cm², pulse duration of 4–6 ns) was used. A 150 W xenon lamp was used as the detecting light source. To minimize the oxidation of Cu(I) by oxygen, all samples were continuously sparged with nitrogen and contained 0.6 M NaCl since the presence of Cl⁻ inhibits Cu(I) oxygenation.² The radical intermediates (P⁺⁺ (or P⁺(-H))) were produced by direct photoexcitation of target contaminants at 266 nm according to the methods described previously in order to prevent the formation of halogen radicals..^{1, 6} The observed first-order decay rate constants of P⁺⁺ (or P⁺(-H)) were determined by tracking the decay traces at their maximum absorption peak (centered at 380 nm for TMP, 400 nm for BPA and 500 nm for DMABN).^{7, 8} Each sample was irradiated only once to minimize any potential effects of products.

Text-S4. Measurement of steady-state concentrations of Cu(I)

The steady-state Cu(I) concentration formed upon irradiation of solutions containing SRNOM and Cu(II) was measured using a modified bathocuproine method.⁹ For Cu(I) measurement, 5 mL of solution was irradiated in a 5 mL gas-tight Pyrex syringe (Hamilton, model 1005) in the solar simulator. Due to the low yield of Cu(I), an initial Cu(II) concentration of 400 nM was used to generate sufficient Cu(I) for measurement. Samples were irradiated for 15 min with this duration long enough for Cu(I) to reach a steady-state concentration.¹⁰ After irradiation, the sample was kept exposed to light and then injected into an amber bottle containing 5 mL of deaerated solution containing 0.05 mM bathocuproinedisulfonic acid disodium salt hydrate (BC) and 0.25 mM ethylenediaminetetraacetic acid (EDTA). The resultant solution containing the Cu(I)-BC complex was finally injected into a 1 m pathlength liquid waveguide capillary cell (LWCC 4100, World Precision Instruments) and the absorbance at 484 nm measured using an Ocean Optics spectrophotometry system equipped with a USB-4000 spectrometer and halogen lamp. The baseline drift was corrected by subtracting the absorbance at 690 nm. Calibration was performed prior to experiments by standard addition of Cu(I) to the experimental matrix. The detection limit of the method is ~0.6 nM Cu(I). The interference of the targer contanminants and NOM addition should be neglected since they have little absorbance over 400 nm.^{11, 12} Values for the parameter β (Eq 7 in the main text) are calculated to be 0.12 and 0.10 for CBBP and SRNOM systems, respectively.



Figure S9. The steady-state concentrations of Cu(I) generated on irradiation of Cu(II) in a 45 μ M CBBP solution and a 10 mg C/L SRNOM solution. Conditions: initial [Cu(II)] = 400 nM, pH = 5.2

Text S5. Details of the kinetic model applied in CBBP systems



Scheme S1. Major reaction pathways of target contaminant P phototransformation in CBBP solutions containing Cu. Triplet sensitizers (³Sen*) can oxidize target contaminant P to give (1) intermediates P[•]₁ (with yield f) undergoing inhibition by Cu, or (2) intermediates P[•]₂ (with yield 1-f) which are not affected by Cu. The intermediate P[•]₁ will then either get oxidized irreversibly (first-order rate constant $k_{1,ox}$) to give an oxidation product P_{1,ox}, or be reduced back by Cu(I) to the parent compounds P (second-order rate constant $k_{1,red,Cu(I)}$).

Equation 6 (main paper) can be derived from the kinetic model represented in Scheme S1, similar to the one developed by Canonica and co-workers who studied the role of NOM as a inhibitor.^{11, 13} According to the Scheme S1, the kinetic equations for P and P[•]₁ can be written as follows.

$$\frac{d[P]}{dt} = -k_{_{3}Sen^{*}}[^{3}Sen^{*}][P] + k_{red,Cu(I)}[P^{\bullet}_{1}] [Cu(I)]_{ss}$$
(S1)

$$\frac{d[\mathbf{P}^{\bullet}_{1}]}{dt} = fk_{{}^{3}Sen^{*}}[{}^{3}Sen^{*}][\mathbf{P}] - k_{1,red,Cu(I)}[\mathbf{P}^{\bullet}_{1}][Cu(\mathbf{I})]_{ss} - k_{1,ox}[\mathbf{P}^{\bullet}_{1}]$$
(S2)

where k_{3Sen*} was the second-order rate constant between excited triplets and target compound P.

In the model developed here, we assume that Cu(I) quickly reaches a steady-state concentration during irradiation as a result of the balance that is

established between the forward formation rate of Cu(I) (via ligand-to-metal charge transfer (LMCT) and superoxide-mediated reduction pathways) and the back oxidation rate of Cu(I) (via reaction with oxygen, superoxide, hydrogen peroxide and radical intermediates). As such, a factor β was introduced to simply express the proportionality between the steady-state concentration of the light-generated Cu(I) ([Cu(I)]_{ss}) and the total Cu concentration ([Cu]_{tot}) (Eq. S3).

$$[Cu(I)]_{ss} = \beta[Cu]_{tot}$$
(S3)

Also the steady-state concentration of P_1^{\bullet} was assumed in this model (d[P_1^{\bullet}]/dt=0) and, one obtained Eq. S4 from Eq. S2.

$$[\mathbf{P}_{1}](k_{I,ox} + k_{I,red,Cu(I)}\beta[\mathbf{Cu}]_{tot}) = fk_{{}^{3}Sen^{*}}[{}^{3}Sen^{*}][\mathbf{P}]$$
(S4)

After rearrangement of Eq. S4 and substitution into Eq. S1 one obtained

$$\frac{d[P]}{dt} = -k_{_{3}Sen^{*}}[^{3}Sen^{*}][P](1 - f \frac{k_{_{1,red,Cu(I)}}\beta[Cu]_{_{tot}}}{k_{_{1,ox}} + k_{_{1,red,Cu(I)}}\beta[Cu]_{_{tot}}})$$

$$= -k_{_{3}Sen^{*}}[^{3}Sen^{*}][P](\frac{fk_{_{1,ox}}}{k_{_{1,ox}} + k_{_{1,red,Cu(I)}}\beta[Cu]_{_{tot}}} + (1 - f))$$
(S5)

Thus, Eq. S6 expressed the pseudo-first-order rate constant for photooxidation of target compound P ($k_{\text{sen, Cu}}$).

$$k_{Sen, Cu} = k_{3Sen*} [^{3}Sen*] (\frac{fk_{1,ox}}{k_{1,ox} + k_{1,red, Cu(l)}\beta[Cu]_{tot}} + (1-f))$$
(S6)

Since
$$k_{Sen} = k_{Sen, Cu}([Cu]_{tot} = 0) = k_{3Sen*}[^{3}Sen*]$$
 (S7)

Then the "Inhibition Factor (IF)" was defined as dividing Eq. S6 by Eq. S7 as follows.

$$IF = \frac{k_{Sen, Cu}}{k_{Sen}} = \frac{fk_{I,ox}}{k_{I,ox} + k_{I,red, Cu(I)}\beta[Cu]_{tot}} + (1 - f)$$

$$= \frac{f}{1 + \frac{k_{I,red,Cu(l)}\beta}{k_{I,ox}} [Cu]_{tot}} + (1 - f)$$
(S8)

As in main paper, we introduce the concept of $[Cu]_{1/2}$ (= $k_{1,ox} / \beta k_{1,red,Cu(1)}$) (Eq. S9), which was the concentration of total Cu needed to halve the production of P_{1,ox} from P[•]₁. Substituting Eq. S9 in Eq. S8 and making a further rearrangement one obtained Eq S10, which corresponded to Eq. 6 in the main paper.

$$\frac{k_{I,ox}}{\beta k_{I,red,Cu(I)}} = [Cu]_{1/2}$$
(S9)

IF =
$$\frac{f}{1 + [Cu]_{tot}/[Cu]_{1/2}} + (1 - f)$$
 (S10)

Text S6. Details of the kinetic model applied in SRNOM systems without Cu



Scheme S2. Major photooxidation pathways of target contaminant P in only NOM solutions. Triplet NOM (³NOM*) can oxidize target contaminant P to give (1) intermediates P[•]₁ (with yield f) undergoing inhibition by NOM, or (2) intermediates P[•]₂ (with yield 1-f) which are not affected by Cu. The intermediate P[•]₁ will then

either get oxidized irreversibly (first-order rate constant $k_{1,ox}$) to give an oxidation product $P_{1,ox}$, or be reduced back by NOM to the parent compounds P (second-order rate constant $k_{1,red,NOM}$). Dashed line indicates reaction pathways that may be operative, depending on the specific contaminants (eg., amines).

Scheme S2 was previously proposed by Canonica and co-workers.¹¹ For the target contaminants exhibited an important inhibitory effect of NOM, the kinetic equations for P and P_1^{\bullet} can be written as follows.

$$k_{Sen}[P] = k_{3NOM*}[^{3}NOM*][P] - k_{1,red,NOM}[P^{\bullet}_{1}][NOM]$$
(S11)

$$\frac{d[\mathbf{P}^{\bullet}_{1}]}{dt} = fk_{{}^{3}NOM^{*}}[{}^{3}NOM^{*}][\mathbf{P}] - k_{I,red,NOM}[\mathbf{P}^{\bullet}_{1}][NOM] - k_{I,ox}[\mathbf{P}^{\bullet}_{1}]$$
(S12)

The steady-state concentration of P_1^{\bullet} was assumed in this model (d[P_1^{\bullet}]/dt=0) and, one obtains Eq. S13 from Eq. S12.

$$[\mathbf{P}^{\bullet}_{1}](k_{1,ox} + k_{1,red,NOM}[\text{NOM}]) = fk_{{}^{3}NOM^{*}}[{}^{3}NOM^{*}][\mathbf{P}]$$
(S13)

After rearrangement of Eq. S13 and substitution into Eq. S11 one obtains

$$k_{Sen}[P] = k_{3_{NOM*}}[^{3}NOM*][P](1 - f \frac{k_{1,red,NOM}[NOM]}{k_{1,ox} + k_{1,red,NOM}[NOM]})$$
$$= k_{3_{NOM*}}[^{3}NOM*][P](\frac{fk_{1,ox}}{k_{1,ox} + k_{1,red,NOM}[NOM]} + (1 - f))$$
(S14)

Then,

$$k_{Sen} = k_{3Sen*} [^{3}NOM^{*}][P](\frac{fk_{l,ox}}{k_{l,ox} + k_{l,red,NOM}[NOM]} + (1 - f))$$
(S15)

As in previous studies,⁴ the concept of $[NOM]_{1/2}$ (= $k_{1,ox} / k_{1,red,NOM}$) was introduced, which was the concentration of NOM needed to halve the production of P_{1,ox} from P[•]₁. Additionally, a factor α to express the proportionality between k_{3NOM*} ³NOM* and [NOM] was introduced as Eq. S17.

$$[\text{NOM}]_{1/2} = \frac{k_{1,ox}}{k_{1,red,NOM}}$$
(S16)

$$k_{{}^{3}NOM^{*}}[{}^{3}NOM^{*}] = \alpha[NOM]$$
(S17)

Thus,

$$k_{Sen} = \alpha[\text{NOM}](\frac{fk_{I,ox}}{k_{I,ox} + k_{I,red,NOM}[\text{NOM}]} + (1 - f))$$

= $\alpha[\text{NOM}](\frac{f}{1 + [\text{NOM}]/[\text{NOM}]_{1/2}} + (1 - f))$ (S18)

According to Eq. S18, for the target compound P (eg., TMP) exhibited the absence of inhibitory effect of NOM ([NOM]/[NOM]_{1/2}=0), Eq. S19 was obtained.

$$k_{Sen} = \alpha[\text{NOM}] \tag{S19}$$

Text S7. Details of the kinetic model in SRNOM solutions containing Cu



Scheme S3. Major photooxidation pathways of target contaminant P in NOM solutions containing Cu. Triplet NOM (³NOM*) can oxidize target contaminant P to give (1) intermediates P[•]₁ (with yield f) undergoing inhibition by NOM and Cu, or (2) intermediates P[•]₂ (with yield 1-f) which are not affected by NOM and Cu. The intermediate P[•]₁ will then either get oxidized irreversibly (first-order rate constant $k_{1,ox}$) to give an oxidation product P_{1,ox}, or be reduced back by NOM and/or Cu to the parent compounds P (second-order rate constant $k_{1,red,NOM}$ and $k_{1,Cu(I)}$). Dashed square indicates reaction pathways that may be operative, depending on the specific contaminants (eg., amines).

Scheme S3 was modified from Scheme S2 to take into account inhibition by Cu and NOM together. Similarly, for the target contaminants exhibited an important inhibitory effect of NOM, the kinetic equations for P and P[•]₁ can be written as follows.

$$k_{Sen,Cu}[P] = k_{3NOM*}[^{3}NOM*][P] - k_{1,red,NOM}[P^{\bullet}_{1}][NOM] - k_{1,red,Cu(l)}[P^{\bullet}_{1}][Cu(I)]_{ss}$$
(S20)

$$\frac{d[\mathbf{P}^{\bullet}_{1}]}{dt} = fk_{{}^{3}NOM^{*}}[{}^{3}NOM^{*}][\mathbf{P}] - k_{1,red,NOM}[\mathbf{P}^{\bullet}_{1}][NOM] - k_{1,red,Cu}[\mathbf{P}^{\bullet}_{1}][Cu(\mathbf{I})]_{ss} - k_{1,ox}[\mathbf{P}^{\bullet}_{1}]$$
(S21)

The steady-state concentration of P_1^{\bullet} was assumed in this model (d[P_1^{\bullet}]/dt=0) and, one obtained Eq. S22 from Eq. S21.

$$[\mathbf{P}^{\bullet}_{1}](k_{1,ox} + k_{1,red,NOM}[\text{NOM}] + k_{1,red,Cu}[\text{Cu}(\mathbf{I})]_{ss}) = fk_{3_{NOM}^{*}}[^{3}\text{NOM}^{*}][\mathbf{P}]$$
(S22)

After rearrangement of Eq. S22 and substitution into Eq. S20 one obtained

$$k_{Sen, Cu} = k_{3NOM*} [^{3}NOM*] (\frac{f}{1 + \frac{k_{I, red, NOM}}{k_{I, ox}} [NOM] + \frac{k_{I, red, Cu(I)}\beta}{k_{I, ox}} [Cu]_{tot}} + (1 - f))$$
(S23)

Since
$$[\text{NOM}]_{1/2} = \frac{k_{1,ox}}{k_{1,red,NOM}}, \frac{k_{1,ox}}{\beta k_{1,red,Cu(I)}} = [\text{Cu}]_{1/2}$$

$$k_{Sen, Cu} = k_{3NOM*} [^{3}NOM*] (\frac{f}{1 + [NOM] / [NOM]_{1/2} + [Cu]_{tot} / [Cu]_{1/2}} + (1 - f))$$
(S24)

Since

$$k_{Sen} = k_{Sen, Cu} ([Cu]_{tot} = 0) = k_{3NOM*} [^{3}NOM*] (\frac{f}{1 + [NOM] / [NOM]_{1/2}} + (1 - f))$$
(S25)

Thus,

$$IF = \frac{k_{Sen, Cu}}{k_{Sen}}$$

= $\frac{f + (1 - f) (1 + [NOM] / [NOM]_{1/2} + [Cu]_{tot} / [Cu]_{1/2})}{f + (1 - f) (1 + [NOM] / [NOM]_{1/2})} \times \frac{1 + [NOM] / [NOM]_{1/2}}{1 + [NOM] / [NOM]_{1/2} + [Cu]_{tot} / [Cu]_{1/2}}$ (S26)

According to Eq. S26, for the target compound P (eg., TMP) exhibited the absence of inhibitory effect of NOM ([NOM]/[NOM]1/2=0), Eq. S10 was obtained.

IF =
$$\frac{f}{1 + [Cu]_{tot}/[Cu]_{1/2}} + (1 - f)$$
 (S10)

Text S8. Derivation of Equation 9 in the main text.

Using the model developed here, the contribution of Cu(I) to the overall intermediate P[•]₁ reduction rate ($\Phi_{Cu(I)}$) in irradiated SRNOM solutions can be calculated as shown in Eq. S27.

$$\Phi_{Cu(l)} (\%) = \frac{[Cu(I)]_{ss} k_{l,red,Cu(l)}}{[Cu(I)]_{ss} k_{l,red,Cu(l)} + [NOM]k_{l,red,NOM}} \times 100 \%$$
(S27)

Since $[Cu(I)]_{ss} = \beta [Cu]_{tot}$,

$$\Phi_{Gu(I)}(\%) = \frac{\beta[Cu]_{tot} k_{I,red,Cu(I)}}{\beta[Cu]_{tot} k_{I,red,Cu(I)} + [NOM]k_{I,red,NOM}} \times 100\%$$
$$= \frac{[Cu]_{tot} \frac{\beta k_{I,red,Cu(I)}}{k_{I,ox}}}{[Cu]_{tot} \frac{\beta k_{I,red,Cu(I)}}{k_{I,ox}} + [NOM] \frac{k_{I,red,NOM}}{k_{I,ox}}} \times 100\%$$
(S28)

and $[NOM]_{1/2} = k_{1,ox} / k_{1,red,NOM}$, $[Cu]_{1/2} = k_{1,ox} / \beta k_{1,red,Cu(1)}$

$$\Phi_{Gu(I)}(\%) = \frac{[Cu]_{tot} \frac{\beta k_{I,red,Cu(I)}}{k_{I,ox}}}{[Cu]_{tot} \frac{\beta k_{I,red,Cu(I)}}{k_{I,ox}} + [NOM] \frac{k_{I,red,NOM}}{k_{I,ox}} \times 100\%$$
$$= \frac{[Cu]_{tot} / [Cu]_{1/2}}{[Cu]_{tot} / [Cu]_{1/2} + [NOM] / [NOM]_{1/2}} \times 100\%$$
(S29)

Rearranging, we get:

$$\Phi_{Gu(l)}(\%) = \frac{[\text{NOM}]_{1/2} [\text{Cu}]_{\text{tot}}}{[\text{NOM}]_{1/2} [\text{Cu}]_{\text{tot}} + [\text{Cu}]_{1/2} [\text{NOM}]} \times 100\%$$
(S30)

Text S9. Rationale for pseudo-first-order kinetics for radical intermediates in laser photolysis tests

In general, there are three main sinks for radical intermediates. Taking DMABN^{•+} as an example, the decay of DMABN^{•+} may occur via the following reactions:

DMABN⁺⁺
$$\rightarrow$$
 products k_1
DMABN⁺⁺ + $e_{aq}^- \rightarrow$ DMABN k_2

$$DMABN^{+} + O_2^{-} \rightarrow DMABN + O_2 \qquad k_3$$

where k_1 represents the first-order self-decay rate constant of DMABN⁺⁺ (including *e.g.* H-atom shift, deprotonation and hydrolysis) and k_2 and k_3 are the second-order rate constants for the reaction of DMABN⁺⁺ with hydrated electrons (e_{aq}^-) and O_2^- , respectively. The concentration of e_{aq}^- is quantified by monitoring its maximum absorption band at 600-700 nm. Based on the e_{aq}^- molar absorption coefficient (ε_{715} =19700 M⁻¹ cm⁻¹)¹⁴ and the measured absorbance (Figure S10), a maximum concentration of ~10⁻⁶ M is calculated for e_{aq}^- . Even if k_2 is a diffusion-limit rate constant (~10¹⁰ M⁻¹s⁻¹), the rate of decay of DMABN⁺⁺ via reaction with e_{aq}^- ($k_2[e_{aq}^-]$) is only about 10⁴ s⁻¹. As for the reaction between DMABN⁺⁺ and O2⁺⁻, the concentration of O2⁺⁻ should be less than the maximum concentration of e_{aq}^- since O_2^{+-} is derived from the reaction between e_{aq}^- and residual oxygen. Even if k_3 is a diffusion-limit rate constant, the rate of decay of DMABN⁺⁺ via reaction with O_2^{+-} , ($k_3[O_2^{+-}]$) is <10⁴ s⁻¹. However, the observed pseudo-first-order decay rate constant of DMABN⁺⁺ (k_{obs}) in the absence and presence of Cu(I) ranged from 2.50×10⁶-7.85×10⁶ s⁻¹, which is two orders of magnitude higher than that of $k_2[e_{aq}^{-1}]$

and $k_3[O_2^{-}]$ ($\leq 10^4$ s⁻¹). As such, the reaction with both e_{aq}^{-} and O_2^{-} played minor role in the decay of DMABN⁺⁺. The decay traces of radical intermediates fitted well with the first-order decay function (R²>0.95; Figure 2 in the main text). Thus, both the calculation data and experimental data support the hypothesis of pseudo-first-order decay kinetics of radical intermediates.



Figure S10. Transient absorption spectra obtained on 266 nm laser flash photolysis of 137 μ M DMABN, 367 μ M TMP and 438 μ M BPA in degassed conditions

REFERENCES

(1) Lei, Y.; Cheng, S.; Luo, N.; Yang, X.; An, T., Rate constants and mechanisms of the reactions of Cl[•] and Cl₂^{•–} with trace organic contaminants. *Environmental Science & Technology* **2019**, *53*(19), 11170-11182.

(2) Yuan, X.; Pham, A. N.; Xing, G.; Rose, A. L.; Waite, T. D., Effects of pH, chloride, and bicarbonate on Cu(I) oxidation kinetics at circumneutral pH. *Environmental Science & Technology* **2012**, *46*(3), 1527-1535.

(3) Chen, W.; Habibul, N.; Liu, X. Y.; Sheng, G. P.; Yu, H. Q., FTIR and synchronous fluorescence heterospectral two-dimensional correlation analyses on the binding characteristics of copper onto dissolved organic matter. *Environmental Science & Technology* **2015**, *49*(4), 2052-2058.

(4) Hur, J.; Lee, B.-M., Characterization of binding site heterogeneity for copper within dissolved organic matter fractions using two-dimensional correlation fluorescence spectroscopy. *Chemosphere* **2011**, *83*(11), 1603-1611.

(5) Yan, M.; Han, X.; Zhang, C., Investigating the features in differential absorbance spectra of NOM associated with metal ion binding: A comparison of experimental data and TD-DFT calculations for model compounds. *Water Research* **2017**, *124*, 496-503.

(6) Cheng, S.; Lei, Y.; Lei, X.; Pan, Y.; Lee, Y.; Yang, X., Coexposure degradation of purine derivatives in the sulfate radical-mediated oxidation process. *Environmental Science & Technology* **2020**, *54*(2), 1186-1195.

(7) Leresche, F.; Ludvíková, L.; Heger, D.; Klán, P.; von Gunten, U.; Canonica, S., Laser flash photolysis study of the photoinduced oxidation of 4-(dimethylamino)benzonitrile (DMABN). *Photochemical & Photobiological Sciences* **2019**, *18*(2), 534-545.

(8) Spanget-Larsen, J.; Gil, M.; Gorski, A.; Blake, D. M.; Waluk, J.; Radziszewski, J. G., Vibrations of the phenoxyl radical. *Journal of the American Chemical Society* **2001**, *123*(45), 11253-11261.

(9) Pan, Y.; Garg, S.; Waite, T. D.; Yang, X., Copper inhibition of triplet-induced reactions involving natural organic matter. *Environmental Science & Technology* **2018**, *52*(5), 2742-2750.

(10) Buerge-Weirich, D.; Sulzberger, B., Formation of Cu(I) in estuarine and marine waters: Application of a new solid-phase extraction method to measure Cu(I). *Environmental Science & Technology* **2004**, *38*(6), 1843-1848.

(11) Leresche, F.; von Gunten, U.; Canonica, S., Probing the photosensitizing and inhibitory effects of dissolved organic matter by using N,N-dimethyl-4-cyanoaniline (DMABN). *Environmental Science & Technology* **2016**, *50*(20), 10997–11007.

(12) Pham, A. N.; Rose, A. L.; Waite, T. D., Kinetics of Cu(II) reduction by natural organic matter. *Journal of Physical Chemistry A* **2012**, *116*(25), 6590-6599.

(13) Wenk, J.; Von Gunten, U.; Canonica, S., Effect of dissolved organic matter on the transformation of contaminants induced by excited triplet states and the hydroxyl radical. *Environmental science & technology* **2011**, *45*(4), 1334-1340.

(14) Torche, F.; Marignier, J.-L., Direct evaluation of the molar absorption \$32

coefficient of hydrated electron by the isosbestic point method. *The Journal of Physical Chemistry B* **2016**, *120*(29), 7201-7206.