

# Humic Substances Enhance Chlorothalonil Phototransformation via Photoreduction and Energy Transfer

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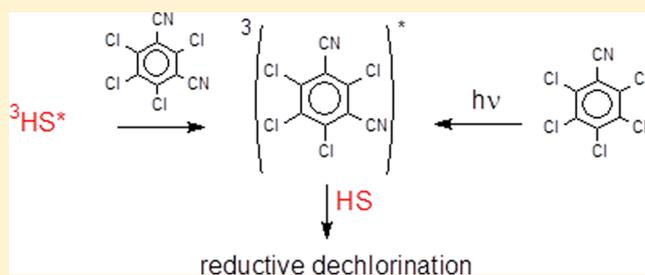
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**S** Supporting Information

**ABSTRACT:** The photodegradation of chlorothalonil, a polychlorinated aromatic fungicide widely used in agriculture, was investigated under ultraviolet–visible irradiation in the presence and absence of different humic substances that significantly enhance the chlorothalonil phototransformation. On the basis of a kinetic model, an analytical study, the effect of scavengers, the chlorothalonil phosphorescence measurement, and varying irradiation conditions, it was possible to demonstrate that this accelerating effect is due to their capacity to reduce the chlorothalonil triplet state via H-donor reaction and to energy transfer from the triplet humic to ground state chlorothalonil. Energy transfer occurs at wavelengths below 450 nm and accounts for up to 30% of the reaction in deoxygenated medium upon irradiation with polychromatic light (300–450 nm). This process is more important with Elliott humic and fulvic acids and with humic acids extracted from natural carbonaceous material than with Nordic NOM and Pahokee peat humic acids. The obtained results are of high relevance to understanding the processes involved in chlorothalonil phototransformation and the photoreactivity of humic substances. Chlorothalonil is one of the rare molecules shown to react by energy transfer from excited humic substances.



## INTRODUCTION

The causes of water contamination are numerous and range from the massive contents of fertilizers and pesticides in agricultural runoff to improper use of household chemicals and prescription drugs. In the environment, chemicals or waste products can undergo solar-light-induced photodegradation. The presence of colored dissolved organic matter in water, i.e., humic substances (HS), can play an important role in the light-induced phototransformation of organic contaminants.<sup>1–4</sup> This effect is generally initiated by light absorption of the HS. This absorption induces many electronic processes that lead to the formation of reactive species such as excited triplet states <sup>3</sup>HS\*, singlet oxygen <sup>1</sup>O<sub>2</sub>, superoxide ion O<sub>2</sub><sup>-</sup>, and hydroxyl radicals.<sup>5–11</sup> On the basis of different studies, the photochemical properties of HS were proposed to result in part from intramolecular charge-transfer interactions between hydroxyaromatic donors and quinoid (or other) acceptors, which are formed through the partial oxidation of lignin and possibly other partially oxidized hydroxyaromatics, i.e., polyphenols, tannins, and melanins.<sup>12,13</sup>

The <sup>3</sup>HS\* species play a key role in the photoreactivity of humic substances. They produce singlet oxygen via energy transfer to ground-state oxygen.<sup>5</sup> These species can also directly react with substrates in photoredox reactions, and reduction of <sup>3</sup>HS\* and oxidation of the substrate describes the most

documented reaction by far.<sup>3,4,6,14–17</sup> In this case, <sup>3</sup>HS\* display oxidant properties similar to those of carbonyl compounds.<sup>6</sup> Oxidation of the <sup>3</sup>HS\* and reduction of the substrate involving <sup>3</sup>HS\* with reductant properties should also be possible, but this type of reaction is rarely reported. HS were found to enhance the photodechlorination of the insecticide mirex; however, this reaction was shown to involve photoejected electrons rather than <sup>3</sup>HS\*.<sup>18,19</sup> A recent work proposed that intramolecular electron transfer occurs between humic constituents themselves, from the short-lived excited states of electron donors to the ground-state electron acceptors, leading to hydrogen peroxide formation.<sup>20</sup> Additionally, <sup>3</sup>HS\* can transfer energy to ground-state substrates as it transfers energy to ground state oxygen. Again, few examples of this reaction exist in the literature. The first reason is that the energy transfer process is restricted to molecules that fulfill specific conditions, and the second is that producing strong evidence of energy transfer is difficult in the case of HS. Indeed, quantum yields are low, and the direct detection of the triplet excited state of an acceptor via time-resolved spectroscopy is not possible. Conjugated dienes

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**Table 1. Absorption Characteristics of HSs (5 mg L<sup>-1</sup>); Rates of Photodegradation of CT Alone, ( $r_{CT}$ )<sup>aerated</sup>, or in the Presence of HSs (5 mg L<sup>-1</sup>), ( $r_{CT}$ )<sup>aerated</sup><sub>HS</sub>, in Air-Saturated Medium and pH 8; Effect of Desoxygenation; Apparent Quantum Yield of Singlet Oxygen Production of HSs ( $\Phi_{SO}$ ); Irradiations in Polychromatic Light**

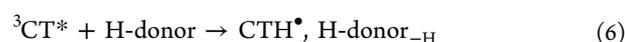
HS	$A^{300}$ in m <sup>-1</sup> L mg <sup>-1</sup> <sup>a</sup>	spectral slope <sup>290-450</sup>	( $r_{CT}$ ) <sup>aerated</sup> <sub>HS</sub> in M s <sup>-1</sup>	( $r_{CT}$ ) <sup>argon</sup> <sub>HS</sub> /( $r_{CT}$ ) <sup>aerated</sup> <sub>HS</sub>	$\Phi_{SO}$
none			(4.0 ± 0.5) × 10 <sup>-11</sup> <sup>b</sup>	20 ± 3 <sup>c</sup>	
HA <sub>E</sub>	4.3	0.0079	(1.1 ± 0.2) × 10 <sup>-10</sup>	88 ± 22	(1.4 ± 0.2) × 10 <sup>-2</sup>
FA <sub>E</sub>	1.3	0.013	(3.1 ± 0.2) × 10 <sup>-10</sup>	52 ± 7	(3.4 ± 0.3) × 10 <sup>-2</sup>
HA <sub>CM</sub>	3.3	0.0093	(2.6 ± 0.3) × 10 <sup>-10</sup>	69 ± 9	(1.4 ± 0.2) × 10 <sup>-2</sup>
HA <sub>peat</sub>	2.2	0.011	(1.4 ± 0.3) × 10 <sup>-10</sup>	88 ± 25	(5.1 ± 0.5) × 10 <sup>-3</sup>
NOM	0.89	0.013	(1.7 ± 0.4) × 10 <sup>-10</sup>	59 ± 12	(8.6 ± 0.7) × 10 <sup>-3</sup>
2-propanol (0.5%)			(3.1 ± 0.3) × 10 <sup>-10</sup> <sup>d</sup>	20 ± 2	

<sup>a</sup>Uncertainty of 5%. <sup>b</sup>( $r_{CT}$ )<sup>aerated</sup>. <sup>c</sup>( $r_{CT}$ )<sup>argon</sup>/<sub>HS</sub>/( $r_{CT}$ )<sup>aerated</sup>. <sup>d</sup>No HS added.

are good <sup>3</sup>HS\* quenchers and energy acceptors,<sup>5,21</sup> and their photoisomerization when they are irradiated in the presence of HS ensures that the reaction involves energy transfer. The phototransformation of Monuron (a chloro-substituted phenyl urea) in the presence of HS was proposed to take place via energy transfer from <sup>3</sup>HS\* to the ground-state Monuron.<sup>22</sup>

Another important property of HS that has been more recently underlined is their ability to play the role of antioxidant and to act as ground-state electrons or as H-donor molecules.<sup>23-28</sup> Dissolved organic matter of terrestrial origin is a more effective reductor than dissolved organic matter of aquatic origin,<sup>23</sup> and phenolic moieties are the major electron donating groups.<sup>27</sup>

The aim of this work was to investigate the main reactive species that contribute to the photodegradation of chlorothalonil in the presence of HS. Chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile, CT) is a fungicide commonly applied in a large number of agricultural crops, especially in vegetables and fruits.<sup>29</sup> Chlorothalonil has been reported to be resistant to hydrolysis and photolysis in surface water.<sup>29</sup> Interestingly, HS were found to enhance its photodegradation,<sup>30,31</sup> but the mechanism of this reaction remains unknown. In an organic solvent such as *n*-heptane, the photoexcitation of chlorothalonil generates the triplet excited state <sup>3</sup>CT\* (reactions 1 and 2) that deactivates (reaction 3), produces photoproducts (reaction 4), or reacts with oxygen (reaction 5).<sup>32</sup> The <sup>3</sup>CT\* is also trapped by H-donor molecules (reaction 6)<sup>32</sup> to yield the reduced CTH• radical that also leads to photoproducts. The bimolecular reaction rate constant (e.g., with phenol) was measured as 1.8 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>. The same processes are observed in water.<sup>33</sup>



In this work, we attempted to explain the accelerating effect of HS on CT photolysis. To this end, we studied the influence of HS on CT decay under different conditions of irradiation and oxygenation. Scavengers were also used to delineate the role of the possible reactive species.

## EXPERIMENTAL SECTION

**Chemicals.** Elliott humic acids (HA<sub>E</sub>, 1S102H) and fulvic acids (FA<sub>E</sub>, 2S102F), Pahokee peat (1S103H), and the aquatic natural organic matter known as Nordic lake (1R108N) were received from the International Humic Substances Society (IHSS). The humic acid sample known as HA<sub>CM</sub> was extracted in the laboratory from an air-modified low-rank coal from the Amagá region in Colombia. Chlorothalonil (99.3%) was supplied by Sigma-Aldrich. Furfuryl alcohol (FFA) and 2,4,6-trimethylphenol (TMP) were of the highest grade available and were used as received. Water was purified using a Millipore Milli-Q device. Acetonitrile (Chromasolv gradient grade, >99.9%) was provided by Sigma-Aldrich. Argon used for deoxygenation was of ultrapure quality (Air Products), and 4-hydroxychlorothalonil was purchased from Dr. Ehrenstorfer GmbH.

**HA<sub>CM</sub> Extraction.** Powder from the air-modified coal was stirred for 24 h in 0.5 M NaOH at room temperature under a nitrogen atmosphere, and the suspension was subsequently centrifuged for 20 min at 1500 rpm. The solution was filtered to remove insoluble materials and acidified with HCl to reach pH < 2 and to allow precipitation of humic acids. The mixture was centrifuged for 20 min to separate the humic acids and fulvic acids (supernatant). The entire procedure was repeated a second time. The humic extract was demineralized by stirring in HCl and HF solutions of 0.1 and 0.3 M, respectively, for 36 h at room temperature under a nitrogen atmosphere. Finally, the humic acids were washed with deionized water, freeze-dried, and labeled as HA<sub>CM</sub>. The spectral properties of the HSs studied in this work are given in Table 1.

**Solution Preparation.** The HSs stock solutions of 40 mg L<sup>-1</sup> were prepared in phosphate buffered solution (10<sup>-3</sup> M) at pH 8 and filtered through 0.45- $\mu$ m sterile cellulose acetate filters prior to use. Because CT is poorly soluble in pure water (0.6 mg L<sup>-1</sup> or 2.2 × 10<sup>-6</sup> M at 25 °C<sup>34</sup>), acetonitrile was used as a cosolvent. The CT stock solutions (10<sup>-3</sup> M) were prepared in acetonitrile and stored at 4 °C. The final solutions of CT and HSs were prepared in a mixture of water and acetonitrile (pH 8, 95:5, v/v). Unless otherwise specified, the concentrations were 5 × 10<sup>-6</sup> M and 5 mg L<sup>-1</sup>, respectively. We verified that the aqueous CT solutions are stable at room temperature for several days in the dark in the absence or in the presence of HSs. The binding of CT to HSs is expected to be quite low based on the octanol–water partition coefficient ( $K_{ow} = 10^{2.9}$ ; ref 35). Because the binding constant of solute to dissolved HSs  $K_{DOC}$  is close to  $K_{ow}$ ,<sup>36</sup> and taking an averaged DOC content of 2.5 × 10<sup>-6</sup> kg L<sup>-1</sup>, we determined that the fraction of CT bound to HS is  $\sim 2 \times 10^{-3}$ , i.e., negligible. In accordance, the

absorption spectrum of the mixture CT + HSs is the exact sum of the individual compounds.

**Photochemical Experiments.** Polychromatic irradiations were conducted in a device equipped with six fluorescent tubes (TLAD 15W05 Philips) emitting wavelengths between 300 and 450 nm (see the emission spectrum in Supporting Information (SI) Figure S1) and a cylindrical Pyrex tube. For irradiations in air-saturated medium, the 15-mL solution was maintained in contact with air during the reaction, and aliquots were withdrawn after selected irradiation times. Monochromatic irradiations were performed in a quartz cuvette using a xenon lamp equipped with a Schoeffel monochromator. Irradiations were performed at 382, 406, 433, 454, and 505 nm with a bandwidth at midheight of 6 nm for selective excitation of HSs. Filters were used to cut off any light with a wavelength below 365 nm. In this case, unique sampling was carried out, and the entire solution was renewed for each irradiation period. Deoxygenation of solutions was achieved by purging argon into the solutions for 20 min prior to irradiation. In the case of monochromatic irradiations, the cuvette was sealed with a Teflon tap just before the irradiation. For the experiments in the reactor with polychromatic light, argon bubbling was maintained during irradiation. By recording the UV spectra of the CT solutions before and after argon bubbling, we verified that CT was not lost by volatilization. A QE65000 radiometer from Ocean Optics was employed to measure the photon fluence rate. For polychromatic irradiations, the light intensity absorbed by each HS,  $I_a^{HS}$ , was calculated using eq 1:

$$I_a^{HS} = \sum_{290}^{450} I_0^{\lambda_i} (1 - 10^{-A_{HS}^{\lambda_i}}) \quad (1)$$

where  $I_0^{\lambda_i}$  is the amount of light received by the solution between  $\lambda_{i-1}$  and  $\lambda_{i-1} + \Delta\lambda$ ,  $A_{HS}^{\lambda_i}$  is the averaged absorbance of HS between  $\lambda_{i-1}$  and  $\lambda_{i-1} + \Delta\lambda$ , and  $\Delta\lambda$  is equal to 5 nm. The light intensities absorbed by CT alone,  $I_a^{CT}$ , and in the presence of HS,  $(I_a^{CT})_{HS}$ , were obtained using the relationships:

$$I_a^{CT} = \sum_{290}^{380} I_0^{\lambda_i} (1 - 10^{-A_{CT}^{\lambda_i}}) \quad (2)$$

$$(I_a^{CT})_{SH} = \sum_{290}^{380} I_0^{\lambda_i} \frac{A_{CT}^{\lambda_i}}{A_{HS}^{\lambda_i} + A_{CT}^{\lambda_i}} (1 - 10^{-(A_{HS}^{\lambda_i} + (A_{CT}^{\lambda_i}))}) \quad (3)$$

where  $A_{CT}^{\lambda_i}$  is the averaged absorbance of CT within the wavelength range of  $\lambda_{i-1}$  and  $\lambda_{i-1} + \Delta\lambda$  with  $\Delta\lambda = 5$  nm. The light screening effect of HSs on CT was taken into account by considering that the amount of light absorbed by CT was described by eq 2 in the absence of HSs and by eq 3 in the presence of HSs.

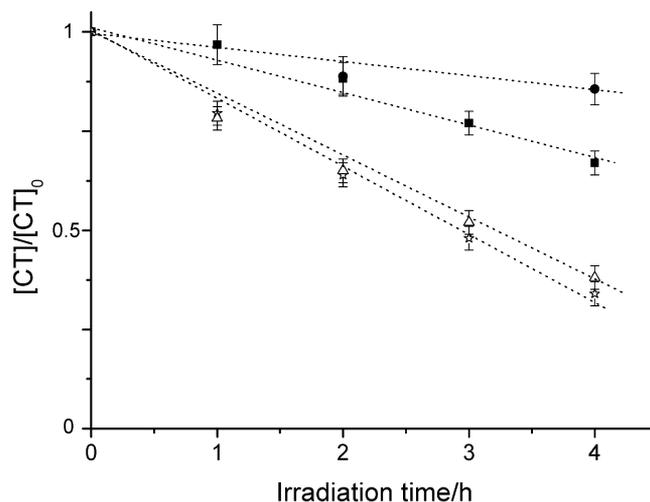
**Analytical Procedures.** UV-vis absorption spectra were recorded using a Cary 300 Varian spectrophotometer and quartz cells with a path length of 1 to 5 cm. The low-temperature (77 K) phosphorescence spectrum of CT was recorded using a Perkin Spectrometer LS 55 instrument, and the CT was dissolved in *n*-pentane. When CT and FFA were irradiated in the presence of HSs, the disappearances could be fitted by first-order kinetics and the rates of phototransformation were obtained by multiplying the apparent first-order rate constant by the initial concentration of the studied substrate (CT or FFA). The rate of CT photolysis in the absence of HSs could not be fitted by first-order kinetics due to a small accelerating effect of the photoproducts. Therefore, the rates of

phototransformation were measured for a conversion extent of 10%. Photoproducts identification is described in the SI.

## RESULTS AND DISCUSSION

### Enhancement Effect of HS on the CT Photodegradation in Air-Saturated Medium.

Figure 1 shows the CT

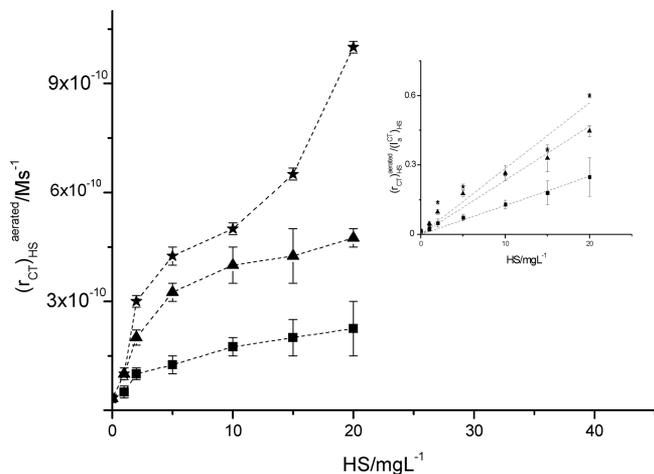


**Figure 1.** Photodegradation of CT ( $5 \times 10^{-6}$  M, pH 8) exposed to polychromatic light in the absence (circle), and in the presence of different HS ( $5 \text{ mg L}^{-1}$ ): FA<sub>E</sub> (star), HA<sub>E</sub> (square), and HA<sub>CM</sub> (triangle).

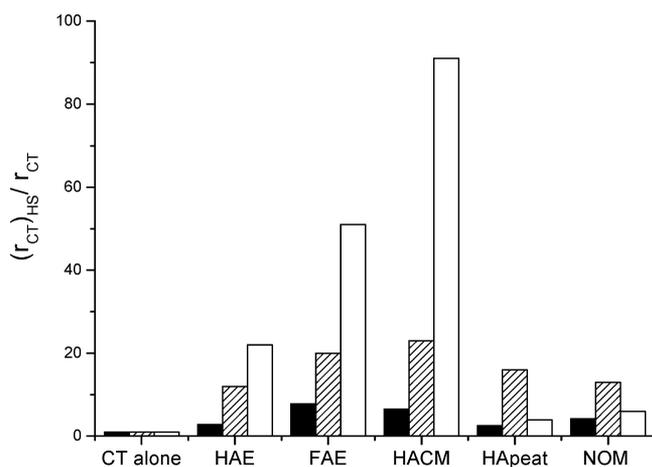
photodegradation profile measured upon irradiation with polychromatic light in the absence and presence of the different HSs. In the absence of HSs, CT disappears by 11% after 4 h, and the rate  $(r_{CT})^{\text{aerated}}$  is  $(4.0 \pm 0.5) \times 10^{-11} \text{ M s}^{-1}$ . Because  $I_a^{CT}$  is equal to  $(9.0 \pm 0.9) \times 10^{-8} \text{ M s}^{-1}$ , this result gives an apparent quantum yield of  $\sim 4 \times 10^{-4}$ , in agreement with previous reports.<sup>29,30,32,33</sup> This photolysis is due to the CT absorption above 290 nm (spectrum shown in SI Figure S2). Figure 1 also shows that the photodegradation of CT is significantly enhanced by the addition of HSs at  $5 \text{ mg L}^{-1}$ . The effect of various concentrations of HA<sub>CM</sub>, HA<sub>E</sub>, and FA<sub>E</sub> on the initial rate of CT photodegradation in aerated medium  $(r_{CT})_{HS}^{\text{aerated}}$  was also measured (Figure 2). The effect of HA<sub>CM</sub> and HA<sub>E</sub> at concentrations greater than  $10 \text{ mg L}^{-1}$  is less pronounced than at lower concentration. Values of  $(r_{CT})_{HS}^{\text{aerated}}$  are given in Table 1. The accelerating effect of HS in aerated medium is given by the ratio  $(r_{CT})_{HS}^{\text{aerated}} / (r_{CT})^{\text{aerated}}$ , which varies between 2.5 and 8 in the order FA<sub>E</sub>  $\sim$  HA<sub>CM</sub>  $>$  NOM  $>$  HA<sub>peat</sub>  $\sim$  HA<sub>E</sub> (Figure 3).

To suppress the direct CT photolysis pathway and excite the HSs selectively, monochromatic irradiations were conducted at 406 nm, where CT absorption is not detectable and  $(r_{CT})^{\text{aerated}}$  is barely measurable ( $< 10^{-12} \text{ M s}^{-1}$ ). In the presence of HA<sub>CM</sub>,  $(r_{CT})_{HS}^{\text{aerated}}$  is equal to  $(1.4 \pm 0.3) \times 10^{-11} \text{ M s}^{-1}$ , i.e., at least 14-fold greater than  $(r_{CT})^{\text{aerated}}$ .

**Effect of Oxygen on the Reaction.** The rate of CT photolysis in polychromatic light and in the absence of oxygen,  $(r_{CT})^{\text{argon}}$ , is significantly higher than the rate measured in aerated medium, and the ratio  $(r_{CT})^{\text{argon}} / (r_{CT})^{\text{aerated}}$  is equal to 20 (Table 1). This is in line with the involvement of  $^3\text{CT}^*$  in the reaction.<sup>32,33</sup> Solution deoxygenation also drastically increases the rate of CT phototransformation in the presence of HSs. The ratio  $(r_{CT})_{HS}^{\text{argon}} / (r_{CT})_{HS}^{\text{aerated}}$ , where  $(r_{CT})_{HS}^{\text{argon}}$  is the



**Figure 2.** Initial rates of CT phototransformation ( $5 \times 10^{-6}$  M, pH 8) when exposed to polychromatic light in the presence of  $\text{FA}_E$  (star),  $\text{HA}_E$  (square), and  $\text{HA}_{CM}$  (triangle). (inset) Plot of  $(r_{CT}/\text{HS})^{\text{aerated}}/(I_a^{\text{CT}})_{\text{HS}}$  against the HS concentration.



**Figure 3.** Accelerating effect of HS ( $5 \text{ mg L}^{-1}$ ) on the rate of CT photodegradation; see text: (black columns) upon irradiation in polychromatic light in air-saturated solutions; (gray columns) upon irradiation in polychromatic light in argon-saturated solutions; (white columns) upon irradiation at 406 nm in argon-saturated solutions.

rate of CT phototransformation in the presence of HS and in the absence of oxygen, is between 52 and 88 (Table 1). At 406 nm, deoxygenation has also a drastic effect on the rate of CT phototransformation in the presence of HSs. In the case of  $\text{HA}_{CM}$  ( $5 \text{ mg L}^{-1}$ ), the ratio  $(r_{CT}/\text{HS})^{\text{argon}}/(r_{CT}/\text{HS})^{\text{aerated}}$  is 71 (SI Table SI-1). The accelerating effect of HS in deoxygenated medium can be defined by the ratio  $(r_{CT}/\text{HS})^{\text{argon}}/(r_{CT})^{\text{argon}}$ . The ratio values are given in Figure 3 for polychromatic irradiation and for irradiation at 406 nm. The values are between 12 and 23 in the former case and the order of reactivity is  $\text{FA}_E \sim \text{HA}_{CM} > \text{HA}_{\text{peat}} > \text{NOM} \sim \text{HA}_E$ . At 406 nm, the values are between 4 and 91 with the following reactivity order:  $\text{HA}_{CM} > \text{FA}_E > \text{HA}_E > \text{NOM} \sim \text{HA}_{\text{peat}}$ . Thus, selective excitation of HSs significantly increases the accelerating factor, especially for  $\text{FA}_E$ ,  $\text{HA}_E$ , and  $\text{HA}_{CM}$ . Interestingly, the order of reactivity changes with the irradiation conditions. In particular,  $\text{HA}_E$ , which enhances the rate of CT phototransformation to a lesser extent than NOM and  $\text{HA}_{\text{peat}}$  in polychromatic light, has a more pronounced effect at 406 nm. Moreover,  $\text{HA}_{CM}$  has a greater effect than  $\text{FA}_E$  at 406 nm. These changes suggest mechanism modifications.

**Photoproducts.** Dechlorinated photoproducts, namely, chloro-1,3-dicyanobenzene ( $\text{CT}_{-3\text{Cl}}$ ), dichloro-1,3-dicyanobenzene ( $\text{CT}_{-2\text{Cl}}$ ), and trichloro-1,3-dicyanobenzene ( $\text{CT}_{-1\text{Cl}}$ ), were identified as the main photoproducts (see the SI) in accordance with the literature data.<sup>30,32,33</sup> In deoxygenated solutions, another photoproduct is observed. It shows the same  $m/z$  value in HPLC/MS but with a shorter HPLC retention time than 4-hydroxychorothalonil and is identified to 2-hydroxychorothalonil.<sup>33</sup> In polychromatic light, HSs reduces the rate of formation of this compound. At 406 nm, this compound is only detected in the irradiated solutions containing HSs.

**Reaction Mechanisms.** These results confirm the accelerating effect of HSs on the photolysis of CT under polychromatic excitation<sup>30,31</sup> and show that HSs sensitize or photoinduce the phototransformation of CT in irradiation conditions (406 nm) in which direct CT photolysis is practically absent or notably slow. Moreover, the results highlight the strong inhibiting effect of oxygen on these reactions. CT was previously shown to be unreactive toward singlet oxygen,<sup>32</sup> and therefore, this phototransformation pathway can be ruled out. The involvement of hydroxyl radicals can be also ruled out due to the presence of acetonitrile (5%). Alternatively, several other reaction pathways could take place, such as photoreduction by electrons produced by photoionization of HSs, reduction of  $^3\text{CT}^*$  by HSs via their hydrogen donating capacity (reaction 6 in which the H-donor is HS), and direct reaction of  $^3\text{HS}^*$  with CT.

**Reactive Species Involved.** Solvated electrons that are known to be generated from HSs via photoionization are potential candidates.<sup>37</sup> Interestingly, solvated electrons were demonstrated as being responsible for the photoreduction of mirex in irradiated humic acids solutions. In this particular case, the photoreduction is efficient because mirex is strongly bound to HA. Indeed, the DOC–water partition coefficient of mirex in the Aldrich HA solution is  $10^{6.26}$ ,<sup>19</sup> allowing 95% of mirex molecules to be bound to HA when they are used at a level of  $10 \text{ mg DOC L}^{-1}$ . This intrahumic location of mirex makes the reaction with solvated electrons possible. Compounds that are poorly bound to HA are much less subject to photoreduction because solvated electrons remain confined to the humic matrix.<sup>19</sup> For instance, CT has an octanol–water partition coefficient that is 3 orders of magnitude lower than that of mirex, and only 0.2% of CT is bound to HA ( $5 \text{ mg L}^{-1}$ ). The amount of solvated electrons that escape the intrahumic domain is small (quantum yield of  $\sim 5\text{--}8 \times 10^{-5}$ ). In polychromatic light, this level would produce an upper rate of electron formation of  $2 \times 10^{-10} \text{ M s}^{-1}$ , which is 50-fold smaller than  $(r_{CT}/\text{HS})^{\text{argon}}$ . Therefore, solvated electrons involvement can also be ruled out.

The two remaining possibilities, i.e. reduction of  $^3\text{CT}^*$  by HS and direct reaction of  $^3\text{HS}^*$  with CT will be studied by separate analysis of the results obtained in polychromatic light in which CT undergoes direct photolysis and those obtained at 406 nm in which HSs are selectively irradiated.

**Photoreduction of CT by HSs in Polychromatic Light and Aerated Solution.** In polychromatic light, CT undergoes direct photolysis, and the first mechanism to test is the one involving the reduction of  $^3\text{CT}^*$  by HS via reaction 6. CT disappears via reactions 1–5 and  $(r_{CT})^{\text{aerated}}$  can be written as follows:

$$(r_{CT})^{\text{aerated}} = r_4 = k_4[{}^3\text{CT}^*] \quad (4)$$

An accelerating effect is observed in the course of the reaction due to photoproduct accumulation.<sup>33</sup> However, this effect is small at 10% conversion, and for simplification, we neglect it. From the relationship:

$$r_2 = r_3 + r_4 + r_5 \quad (5)$$

the stationary concentration of  $^3\text{CT}^*$  is calculated as

$$[^3\text{CT}^*] = I_a^{\text{CT}} \Phi_T^{\text{CT}} \frac{1}{k_3 + k_4 + k_5[\text{O}_2]} \quad (6)$$

giving

$$(r_{\text{CT}})^{\text{aerated}} = I_a^{\text{CT}} \Phi_T^{\text{CT}} \frac{k_4}{k_3 + k_4 + k_5[\text{O}_2]} \quad (7)$$

with  $\Phi_T^{\text{CT}}$  indicating the quantum yield of  $^3\text{CT}^*$  formation.

We shall first consider that the rate enhancement by HSs is due to reaction 6 in which the H-donor represents HS.  $(r_{\text{CT}})_{\text{HS}}^{\text{aerated}}$  is equal to

$$(r_{\text{CT}})_{\text{HS}}^{\text{aerated}} = r_4 + \alpha r_6 = [^3\text{CT}^*](k_4 + \alpha k_6[\text{HS}]) \quad (8)$$

The  $\text{CTH}^\bullet$  radicals produced in reaction 6 are likely oxidized by oxygen to regenerate CT and the hydroperoxyl radical. The factor  $\alpha$  in eq 8 corresponds to the fraction of  $\text{CTH}^\bullet$  radicals that leads to photoproducts. The fraction of  $\text{CTH}^\bullet$  radicals that regenerate CT is  $1 - \alpha$ . The quasi-stationary state hypothesis on  $^3\text{CT}^*$  leads to the equality

$$r_2 = r_3 + r_4 + r_5 + r_6 \quad (9)$$

and to

$$[^3\text{CT}^*] = (I_a^{\text{CT}})_{\text{SH}} \Phi_T^{\text{CT}} \frac{1}{k_3 + k_4 + k_6[\text{HS}] + k_5[\text{O}_2]} \quad (10)$$

One finally gets:

$$(r_{\text{CT}})_{\text{HS}}^{\text{aerated}} = (I_a^{\text{CT}})_{\text{SH}} \Phi_T^{\text{CT}} \frac{k_4 + \alpha k_6[\text{HS}]}{k_3 + k_4 + k_6[\text{HS}] + k_5[\text{O}_2]} \quad (11)$$

To rationalize the curvatures observed for the data of Figure 2 in the case of  $\text{FA}_E$ ,  $\text{HA}_E$ , and  $\text{HA}_{\text{CM}}$ , we divided  $(r_{\text{CT}})_{\text{HS}}^{\text{aerated}}$  by  $(I_a^{\text{CT}})_{\text{SH}}$  and plotted this ratio against  $[\text{HS}]$  (Figure 2, inset). The plots are satisfactorily linear in good agreement with eq 11, in the case the inequality  $k_6[\text{HS}] < k_3 + k_4 + k_5[\text{O}_2]$  is postulated. Actually, this inequality is confirmed by the strong inhibiting effect of oxygen on CT phototransformation which shows that the triplet decay is governed by its reactivity with oxygen. The slopes are equal to  $\Phi_T^{\text{CT}} \alpha k_6 / (k_3 + k_4 + k_5[\text{O}_2])$  and only differ by  $k_6$ , which is approximately two times higher for  $\text{FA}_E$  and  $\text{HA}_{\text{CM}}$  than for  $\text{HA}_E$ .

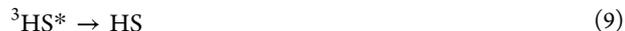
The data on the accelerating effect of HSs on CT phototransformation can also be exploited. The accelerating effect of HSs shown in Figure 3 corresponds to the relationship obtained by dividing eq 11 by eq 7. After simplifications, the ratio can be written as follows:

$$(r_{\text{CT}})_{\text{HS}}^{\text{aerated}} / (r_{\text{CT}})^{\text{aerated}} = (1 + \alpha k_6[\text{HS}] / k_4) (I_a^{\text{CT}})_{\text{HS}} / I_a^{\text{CT}} \quad (12)$$

After correction for the ratio  $(I_a^{\text{CT}})_{\text{HS}} / I_a^{\text{CT}}$ , we obtain the term  $\alpha k_6[\text{HS}] / k_4$ , the value of which falls between 2 and 8 and varies in the order  $\text{FA}_E \sim \text{HA}_{\text{CM}} > \text{NOM} > \text{HA}_{\text{peat}} \sim \text{HA}_E$ , indicating that the less humified HSs as well as carboneous  $\text{HA}_{\text{CM}}$  are better electron or H-donors than the other HSs. For comparison, we measured the effect of 2-propanol added into

the CT solutions at a concentration of 0.085 M. Under these conditions, we measured an accelerating effect close to that of  $\text{FA}_E$  (see Table 1). Considering that  $\text{FA}_E$  shows the same reducing effect as 2-propanol but at a concentration near 1000-fold lower in total organic carbon, this means that  $\text{FA}_E$  reacts via constituents, showing high reducing properties such as phenolic-antioxidant-type molecules as previously suggested.<sup>23,27</sup>

The second possible mechanism involves the reaction of CT with  $^3\text{HS}^*$  and implies the following reactions:



In this case, one finds

$$(r_{\text{CT}})_{\text{HS}}^{\text{aerated}} = r_4 + r_{10} + r_{11} + r_{12} \quad (13)$$

$$(r_{\text{CT}})_{\text{HS}}^{\text{aerated}} = (I_a^{\text{CT}})_{\text{SH}} \Phi_T^{\text{CT}} \frac{k_4}{k_3 + k_4 + k_5[\text{O}_2]} + I_a^{\text{HS}} \Phi_T^{\text{HS}} \frac{(k_{10} + k_{11} + k_{12})[\text{CT}]}{(k_{10} + k_{11} + k_{12})[\text{CT}] + k_9 + k_{13}[\text{O}_2]} \quad (14)$$

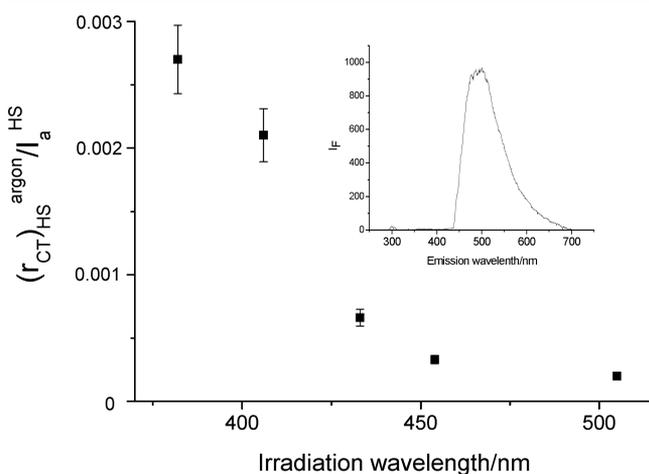
where  $\Phi_T^{\text{HS}}$  is the quantum yield of  $^3\text{HS}^*$  formation. In this expression, the first term decreases when  $[\text{HS}]$  increases because of the light screening effect of HS on CT absorption; whereas, the second one increases with  $[\text{HS}]$  via  $I_a^{\text{HS}}$ . In general, the enhancement effect of HS is significant, indicating that  $(r_{\text{CT}})_{\text{HS}}^{\text{aerated}}$  is dominated by the second term and should increase as  $I_a^{\text{HS}}$ . Figure 2 yet shows that the variation of  $(r_{\text{CT}})_{\text{HS}}^{\text{aerated}}$  with  $[\text{HS}]$  is autoinhibited in the case of  $\text{HA}_{\text{CM}}$ . For instance, for  $\text{HA}_{\text{CM}}$ , the rate increases by a factor of 1.5 when  $I_a^{\text{HS}}$  is increased by 2.1, and for  $\text{HA}_E$ , the rate increases by a factor of 1.6 when  $I_a^{\text{HS}}$  is increased by 2.5. Thus, eq 14 does not model experimental data. We conclude that the enhancement effect of HSs in aerated media and polychromatic light is primarily due to the H-donating effect of HSs.

**Energy Transfer from  $^3\text{HS}^*$  to CT in Deoxygenated Medium at  $\lambda \geq 406$  nm.** At 406 nm and in the absence of oxygen, CT direct photolysis is notably slow. The important enhancing effect of  $\text{FA}_E$ ,  $\text{HA}_{\text{CM}}$ , and  $\text{HA}_E$  (factor between 20 and 90) suggests that the transformation of CT involves  $^3\text{HS}^*$ . An energy transfer process (reaction 10) or a photoredox process (hydrogen atom or electron transfer) (reactions 11 and 12), all originating from  $^3\text{HS}^*$  are the most relevant. Considering that CT contains strong electro-acceptor substituents and is a strong electro-acceptor compound, reaction 11 can be ruled out, and only reactions 10 and 12 must be taken into account. To delineate which reaction is operating, we consider the following points and additional experiments.

(i) The effect of the well-known  $^3\text{HS}^*$  scavenger 2,4,6-trimethylphenol (TMP) on the reaction was investigated<sup>4,6</sup> in which TMP is a chemical susceptible to be oxidized by  $^3\text{HS}^*$

and should thus react with oxidant  $^3\text{HS}^*$ . In contrast, CT is expected to be reduced by  $^3\text{HS}^*$  and should react with the reductant  $^3\text{HS}^*$ . In addition, both oxidant and reductant  $^3\text{HS}^*$  could potentially transfer their energy to acceptors on the condition that the electronic excitation energy available to  $^3\text{HS}^*$  is sufficient to promote the acceptor to its triplet excited state. The absence of any TMP effect on the CT-sensitized phototransformation would indicate that TMP and CT are not competitors and therefore react with different  $^3\text{HS}^*$  types. In contrast, any inhibiting effect of TMP on  $r_{\text{CT}}^{\text{argon}}$  would evidence the existence of a competition. This competition is only possible if it involves energy transfer, i.e., a common property of all the  $^3\text{HS}^*$  regardless of their photoredox reactivity. The experiment was carried out using  $\text{HA}_{\text{CM}}$  ( $5 \text{ mg L}^{-1}$ ) and TMP at  $10^{-4} \text{ M}$ .  $(r_{\text{CT}})_{\text{HS}}^{\text{argon}}$  at 406 nm was  $(1.02 \pm 0.1) \times 10^{-9} \text{ M s}^{-1}$  in the absence of TMP, but  $7.8 \times 10^{-10} \text{ M s}^{-1}$  in its presence. Thus, an inhibiting effect of TMP was observed in favor of the energy transfer reaction hypothesis.

(ii) The conditions for the energy transfer were studied more deeply. First, the sensitized phototransformation of CT by  $\text{HA}_{\text{CM}}$  ( $5 \text{ mg L}^{-1}$ ) was measured at several irradiation wavelengths between 382 and 505 nm. The objective was to determine up to which wavelengths the reaction takes place. For each irradiation wavelength,  $(r_{\text{CT}})_{\text{HS}}^{\text{argon}}$  was divided by  $I_{\text{a}}^{\text{HS}}$  to obtain the quantum yield of sensitized CT phototransformation. Figure 4 shows that the quantum yield is the



**Figure 4.** Wavelength dependence of the quantum yield of sensitized CT photolysis upon irradiation in the presence of  $\text{HA}_{\text{CM}}$  ( $5 \text{ mg L}^{-1}$ ) and argon-saturated medium. (inset) Phosphorescence spectrum of CT in pentane at 77 K.

highest between 382 and 406 nm, decreases sharply for longer wavelengths and becomes quite small above 450 nm. Second, the phosphorescence spectrum of CT could be successfully recorded at 77 K in pentane (Figure 4, inset) allowing the determination of the 0–0 level of the  $T_1-S_0$  transition at  $435 \pm 5 \text{ nm}$ . This value is in line with the data of Figure 4. Indeed, the energy transfer becomes notably small above 450 nm, i.e., if  $\text{HA}_{\text{CM}}$  is excited with radiation whose energy ( $265 \text{ kJ mol}^{-1}$ ) is lower than the energy needed to generate  $^3\text{CT}^*$  ( $275 \text{ kJ mol}^{-1}$ ). This observation is in favor of an energy transfer case from  $^3\text{HS}^*$  to ground state CT.

(iii) The ability of HSs to generate singlet oxygen upon excitation with polychromatic light was measured. Details of the measurement are described in the SI. The quantum yields of

singlet oxygen production are listed in Table 1. The three HSs that exhibit the highest sensitizing effect on CT ( $\text{HA}_{\text{CM}}$ ,  $\text{FA}_{\text{E}}$ , and  $\text{HA}_{\text{E}}$ ) are those that show the highest quantum yields of singlet oxygen production.

(iv) When  $^3\text{CT}^*$  is produced by energy transfer from  $^3\text{HS}^*$ ,  $(r_{\text{CT}})_{\text{HS}}^{\text{argon}}$  is again given by eq 4. We postulate  $\alpha = 1$  because the oxygen concentration in the medium has been notably reduced. The quasi-stationary state hypotheses on  $^3\text{HS}^*$  and of  $^3\text{CT}^*$  lead to the equalities:

$$r_8 = r_9 + r_{10} \quad (15)$$

$$r_{10} = r_3 + r_4 + r_6 \quad (16)$$

This gives

$$[^3\text{HS}^*] = (I_{\text{a}}^{\text{HS}}) \Phi_{\text{T}}^{\text{HS}} \frac{1}{k_{10}[\text{CT}] + k_9} \quad (17)$$

$$[^3\text{CT}^*] = [^3\text{HS}^*] \frac{k_{10}[\text{CT}]}{k_3 + k_4 + k_6[\text{HS}]} \quad (18)$$

and

$$(r_{\text{CT}})_{\text{HS}}^{\text{argon}} = I_{\text{a}}^{\text{HS}} \Phi_{\text{T}}^{\text{HS}} \frac{k_{10}[\text{CT}]}{k_{10}[\text{CT}] + k_9} \frac{k_4 + k_6[\text{HS}]}{k_3 + k_4 + k_6[\text{HS}]} \quad (19)$$

This kinetic law means that HSs have two effects: they sensitize the production of  $^3\text{CT}^*$  through energy transfer and react with  $^3\text{CT}^*$  through reduction. In the case of  $\text{HA}_{\text{CM}}$ ,  $(r_{\text{CT}})_{\text{HS}}^{\text{argon}}$  was measured for several CT concentrations. In SI Figure S4, it appears that  $(r_{\text{CT}})_{\text{HS}}^{\text{argon}}$  increases with  $[\text{CT}]$  and reaches a plateau for  $[\text{CT}] \sim 1.5 \times 10^{-5} \text{ M}$ . Therefore, at this concentration, we obtain the inequality:  $k_{10}[\text{CT}] \gg k_9$ . On the basis of a maximum value of  $10^9 \text{ M}^{-1} \text{ s}^{-1}$  for  $k_{10}$ , this means that  $k_9$  is well below  $10^4 \text{ s}^{-1}$ , a value that is in line with the lifetime of  $2 \mu\text{s}$  estimated for  $^3\text{HS}^*$  in aerated medium.<sup>6</sup>

For all HSs, we calculated the quantum yield of sensitized CT photolysis at 406 nm by dividing  $(r_{\text{CT}})_{\text{HS}}^{\text{argon}}$  by  $I_{\text{a}}^{\text{HS}}$  (see SI Table S1). We found values of  $10^{-4}$  for  $\text{HA}_{\text{peat}}$ ,  $3.1 \times 10^{-4}$  for  $\text{HA}_{\text{E}}$ ,  $3.8 \times 10^{-4}$  for NOM,  $2.1 \times 10^{-3}$  for  $\text{HA}_{\text{CM}}$ , and  $3.5 \times 10^{-3}$  for  $\text{FA}_{\text{E}}$ . These yields correspond to the overall effect (sensitizing and H-donor), and it is not possible to assess the quantum yield of sensitization alone. Considering that  $\text{FA}_{\text{E}}$  and  $\text{HA}_{\text{CM}}$  give quantum yields that are 10- to 6-fold higher than the other HSs, one can estimate that they are better energy donors as well. The  $\text{HA}_{\text{E}}$  is an intermediary case;  $\text{HA}_{\text{E}}$  is the worst H-donor HS in the tested series, and therefore, given that its quantum yield of sensitized CT photolysis is equal and 3-fold higher than those of NOM and  $\text{HA}_{\text{peat}}$ , respectively, one could deduce that it is a better energy donor than these materials. Moreover, the high absorbance properties of  $\text{HA}_{\text{E}}$  above 350 nm compared with those of the other HSs counterbalances the moderate quantum yield of sensitized CT photolysis and makes  $(r_{\text{CT}})_{\text{HS}}^{\text{argon}}$  much higher for  $\text{HA}_{\text{E}}$  than for  $\text{HA}_{\text{peat}}$  and NOM.

(v) The same photoproducts are observed when CT is irradiated in the absence and in the presence of HSs, i.e., dechlorinated products and hydroxylated CT. This latter may be produced by photohydrolysis, which is a typical reaction of an excited chlorinated compound with water.<sup>38</sup> The hydroxylated photoproduct likely occurs from  $^3\text{CT}^*$  based on the inhibiting effect of TMP and HSs on its formation; thus, its

detection upon irradiation of CT at 406 nm in the presence of HSs is in agreement with energy transfer.

**Photoreduction vs Energy Transfer in Deoxygenated Medium and Polychromatic Light.** When CT is irradiated in polychromatic light and in the absence of oxygen, both direct photolysis of CT and a sensitized reaction are expected to take place. The greater accelerating effect in a deoxygenated medium than in air-saturated solution (Figure 3) supports this hypothesis. Therefore,  $(r_{CT})_{HS}^{argon}$  is given by eq 20:

$$(r_{CT})_{HS}^{argon} = (I_a^{CT})_{SH} \Phi_T^{CT} \frac{k_4 + k_6[HS]}{k_3 + k_4 + k_6[HS]} + I_a^{HS} \Phi_T^{HS} \frac{k_{10}[CT]}{k_{10}[CT] + k_9} \frac{k_4 + k_6[HS]}{k_3 + k_4 + k_6[HS]} \quad (20)$$

The first term corresponds to the direct photolysis of CT in the presence of HS, and the second term corresponds to the humic sensitized reaction. To evaluate the rates of the sensitized reactions in polychromatic light, we used data obtained at 406 nm and postulated that the rates only differ by the amount of photons absorbed. Calculations were carried out for HA<sub>CM</sub>, FA<sub>E</sub>, and HA<sub>E</sub>, i.e., for the three HSs for which the accelerating effect is important and direct photolysis is negligible at 406 nm. This observation finally gives a contribution for the sensitized reaction equal to 14%, 20%, and 30% for HA<sub>E</sub>, FA<sub>E</sub>, and HA<sub>CM</sub> respectively.

## 5. ENVIRONMENTAL SIGNIFICANCE

The phototransformation of CT in pure water is a slow reaction, but the presence of HS significantly enhances this reaction. Therefore, CT is expected to be photolyzed faster in surface waters than in pure water, especially in surface waters enriched in natural organic matter and terrestrial inputs. This observation is confirmed by selected literature data.<sup>31</sup> On the basis of the findings of this work, this enhancement is due to the H-donor and sensitizing properties of HS. The reduction of the triplet excited state of CT by HS significantly increases the CT degradation regardless of the mechanism of triplet CT formation (direct or sensitized). The consequence of this reduction is the formation of dechlorinated photoproducts. The CT photolysis in the presence of HS is affected by several parameters. The irradiation wavelength range will impact the relative contribution direct/sensitized reactions, and direct photolysis is favored at short wavelengths. Oxygen is an important parameter. In well-oxygenated water bodies, sensitized reactions will be unfavorable.

This work also stresses the importance of the nature of HS on both its reducing and sensitizing properties. Fulvic acids from Elliott as well as humic acids extracted from natural carbonaceous material are better H-donors than Nordic NOM, Elliott, and Pahokee peat humic acids. This observation may be linked to their phenolic content.<sup>23,27</sup> Energy transfer could be evidenced upon selective excitation of HS. However, the H-donor process also contributes to the overall reaction, making it difficult to assess the contribution of energy transfer. Comparing all the data, the triplet excited states of Elliott fulvic acids and humic acids from natural carbonaceous material seem more capable of transferring their energy to CT than NOM and Pahokee peat humic acids. The sensitization effect of HA<sub>E</sub> is significant due to its high absorbance compared with that of the other HSs.

## ■ ASSOCIATED CONTENT

### Supporting Information

Four figures, three tables, and detailed descriptions of singlet oxygen measurement and products analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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