

Multiple Roles of Dissolved Organic Matter in Advanced Oxidation Processes

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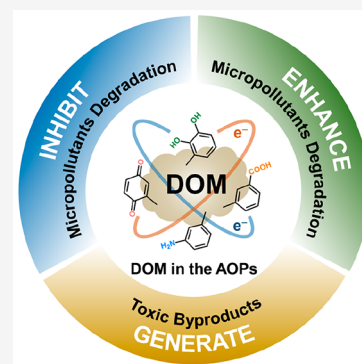
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ABSTRACT: Advanced oxidation processes (AOPs) can degrade a wide range of trace organic contaminants (TrOCs) to improve the quality of potable water or discharged wastewater effluents. Their effectiveness is impacted, however, by the dissolved organic matter (DOM) that is ubiquitous in all water sources. During the application of an AOP, DOM can scavenge radicals and/or block light penetration, therefore impacting their effectiveness toward contaminant transformation. The multiple ways in which different types or sources of DOM can impact oxidative water purification processes are critically reviewed. DOM can inhibit the degradation of TrOCs, but it can also enhance the formation and reactivity of useful radicals for contaminants elimination and alter the transformation pathways of contaminants. An in-depth analysis highlights the inhibitory effect of DOM on the degradation efficiency of TrOCs based on DOM's structure and optical properties and its reactivity toward oxidants as well as the synergistic contribution of DOM to the transformation of TrOCs from the analysis of DOM's redox properties and DOM's transient intermediates. AOPs can alter DOM structure properties as well as and influence types, mechanisms, and extent of oxidation byproducts formation. Research needs are proposed to advance practical understanding of how DOM can be exploited to improve oxidative water purification.

KEYWORDS: complex water matrices, radicals, trace organic contaminants, advanced oxidation, water and wastewater treatment



1. INTRODUCTION

Advanced oxidation processes (AOPs) include a range of technologies applied in water and wastewater treatment to degrade a wide range of trace organic contaminants (TrOCs), including pharmaceuticals, personal care products, endocrine-disrupting compounds, pesticides and algal toxins, and other pathogens.^{1–9} AOPs produce radical species (RS) that react to degrade TrOCs. AOPs that produce hydroxyl radicals ($\bullet\text{OH}$) or sulfate radicals ($\text{SO}_4^{\bullet-}$) are widely studied because of those radicals' high redox potentials (1.90–2.70 V and 2.60–3.10 V, respectively).^{3,10–13} The superoxide ion ($\text{O}_2^{\bullet-}$) and singlet oxygen ($^1\text{O}_2$) are also often involved but are not as frequently studied.^{14–17} These reactive oxygen species are generated *in situ* by activating precursors such as hydrogen peroxide (H_2O_2), peroxymonosulfate (PMS) or peroxydisulfate (PDS) with ultraviolet (UV) or solar light, ozone, metal ions, or carbon- or metal-derived materials, perhaps in nanoscale particles.^{1,3,18–26} Additionally, high-energy ionizing radiation (HEIR) can be used, which uses γ -rays or electron beams to simultaneously generate reactive H atoms, hydrated electrons, and $\bullet\text{OH}$.²⁷ Other AOPs relying instead on reactive chlorine atoms (Cl^\bullet , $E^0(\text{Cl}^\bullet/\text{Cl}^-) = 2.55 \text{ V}$) have also received attention in recent years.^{28–31} Specifically, chloramines used to control membrane biofouling pass through the micro-filtration and reverse osmosis membranes in wastewater reuse treatment and carry over to the downstream AOP to form a

mixed UV/ H_2O_2 and UV/chloramine AOP.^{8,19,32–36} The collective universe of reactive species produced in different AOPs is summarized in Table S1. Research indicates synergistic benefits in TrOC degradation when combinations of radical species are employed.³⁷

Dissolved organic matter (DOM) and inorganic ions (e.g., chloride, bromide, and bicarbonate ions) present in all natural water sources influence the type, formation rate, and reactivity toward TrOCs by RS produced during AOPs, so the composition of the feed water influences process effectiveness in removing TrOCs. Secondary radicals, including carbonate radicals ($\text{CO}_3^{\bullet-}$), chlorine radicals ($\text{Cl}^\bullet/\text{Cl}_2^{\bullet-}$), and bromine radicals ($\text{Br}^\bullet/\text{Br}_2^{\bullet-}$), can be produced through reactions between $\bullet\text{OH}$ or $\text{SO}_4^{\bullet-}$ and dissolved salts. The secondary radicals may themselves degrade some TrOCs, acting synergistically with the process's primary RS, or they can act antagonistically by scavenging $\bullet\text{OH}$ or $\text{SO}_4^{\bullet-}$ from the solution before the primary RS reacts with TrOCs. The key to understanding the relative significance of primary and

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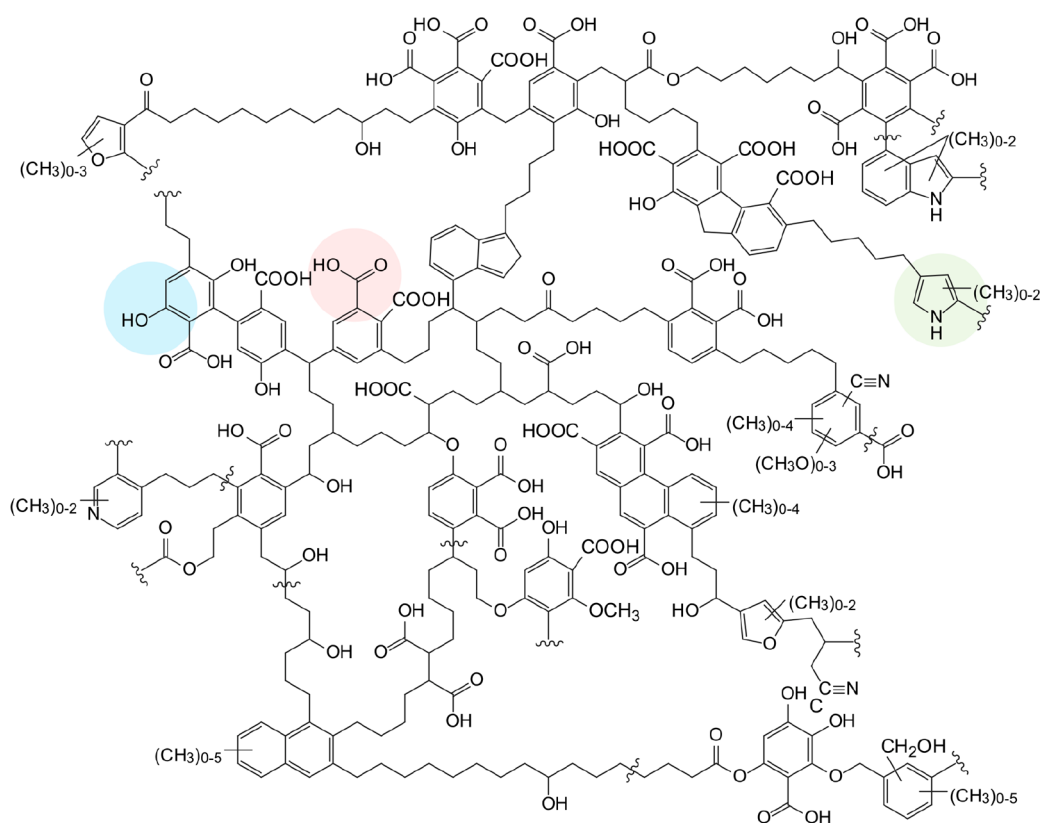


Figure 1. Representative structure and active moieties of DOM involving various oxidative reactions in AOPs.⁵⁷ The ovals represent key moieties: red for carboxylic groups, blue for phenolic groups, green for nitrogen heterocycles. Reproduced with permission from ref 57. Copyright 1996 Elsevier.

secondary RS involves having quantitative information about their aqueous concentrations and rate constants. These have been the subject of research over several decades.^{38–41} TrOCs bearing strong electron-donating substituents (e.g., $-\text{OH}$, $-\text{NH}_2$, and $-\text{OCH}_3$) generally react rapidly with radical oxidants, as do amines, organic sulfur, and olefinic functional groups.^{12,13} However, compared to ample quantitative data on the role of inorganic dissolved salts in AOPs, there is less of a well-integrated and consistent framework for describing the roles of DOM.

DOM is ubiquitous in surface or ground water at concentrations of $1\text{--}10\text{ mg}_C\text{ L}^{-1}$, and in most treated wastewater at $5\text{--}30\text{ mg}_C\text{ L}^{-1}$.^{42,43} DOM is a complicated and heterogeneous mixture of macromolecules including phenols, quinones, olefins, amines, sulfides, and heterocyclic moieties (Figure 1). The structure of DOM is postulated to be dominated by aggregates formed via hydrogen and/or metal interactions.^{44–48} The composition of DOM varies widely depending on its origin and the biogeochemical processes it has undergone.^{49–51} For example, waters dominated by allochthonous DOM inputs are more hydrophobic, richer in aromatic content, and have relatively high specific UV- and visible-light absorption.^{44,52} Effluent organic matter (EfOM) discharged from wastewater processing is dominated by more hydrophilic bacterial DOM sources and enriched in organic nitrogen.^{45,53–55} DOM with different hydrophilic or hydrophobic fractions can show different reactivities toward oxidants.^{51,56}

During ozonation, DOM can initiate or promote ozone decomposition and form reactive byproducts that lead to high $\bullet\text{OH}$ yields for a very short period.^{58,59} Because DOM also

scavenges $\bullet\text{OH}$, the net effect is generally lower $\bullet\text{OH}$ exposure ($\bullet\text{OH}$ concentration multiplied by the lifetime of the oxidant) at higher ozone dosages.^{60–64} Waters where AOPs are applied can have DOM concentrations orders of magnitude higher than those of the TrOCs, so the DOM can outcompete the TrOCs for $\bullet\text{OH}$.^{11,29,65} Consequently, the presence of DOM is generally viewed as decreasing the effectiveness of AOPs toward TrOC degradation. For example, DOM can quench RS (e.g., $\bullet\text{OH}$ and hydrated electrons) formed in the high-energy ionizing radiation-based AOPs, thus inhibiting the removal efficiency of contaminants.⁶⁶

Treatment processes such as adsorption, membrane separation, and pre-oxidation are often considered necessary to remove DOM or decrease DOM reactivity prior to the AOP. Less well acknowledged is how DOM can also promote TrOC degradation through forming reactive intermediates such as triplet excited states ($^3\text{DOM}^*$), $^1\text{O}_2$, phenoxy radicals, and peroxy radicals.^{67–73} The contribution of the transient species within DOM, especially $^3\text{DOM}^*$, to the degradation of TrOCs, is most widely studied not in AOPs but in the context of pollutant degradation in surface waters under solar irradiation.^{74–76} However, the accurate prediction of TrOC degradation in natural waters and in AOPs remains far from satisfactory.^{11,65,77–79}

Beyond affecting the degradation kinetics of TrOCs, radical reactions involving DOM may form toxic byproducts (e.g., chlorinated byproducts with $\text{Cl}\bullet/\text{Cl}_2^{\bullet-}$, dicarbonyls with $\bullet\text{OH}$) or change the extent or mechanisms of byproduct formation (e.g., bromate and chlorate in UV/PDS AOPs).^{56,80–83} DOM is a key precursor of disinfection byproducts when using chlorine, chloramines or ozone as a disinfectant.^{1,84–86}

Likewise, oxygenated and halogenated byproducts from UV/chlor(am)ine, UV/ozone and ozone/H₂O₂ AOPs are inevitable.^{19,33,62,87–90}

This critical review aims at providing a comprehensive understanding of the multiple roles of DOM in the application of AOPs. We conducted in-depth analysis of the inhibitory effect of DOM on the degradation efficiency of TrOCs based on DOM's structure and optical properties and its reactivity toward oxidants (Section 2), followed by the synergistic contribution of DOM on the transformation of TrOCs from the analysis of DOM's redox properties and DOM's transient intermediates (Section 3). Furthermore, DOM's changes in structure and property during various AOPs and related oxidation byproducts formation are briefly discussed (Section 4). Finally, the challenges and opportunities for AOPs treatment in real applications are defined (Section 5).

2. ANTAGONISTIC INFLUENCE OF DOM ON TROC REMOVAL IN AOPS

2.1. DOM Inhibits the Generation of Reactive Species. It is well-known that the presence of DOM can reduce the steady-state concentration of reactive species ([RS]_{ss}). It can inhibit their generation rates (r_{RS}^f) and increase their consumption rates (k_{RS}^d) (eq 1 and Figure 2).

$$[RS]_{ss} = \frac{r_{RS}^f}{\sum k_i S_i} \quad (1)$$

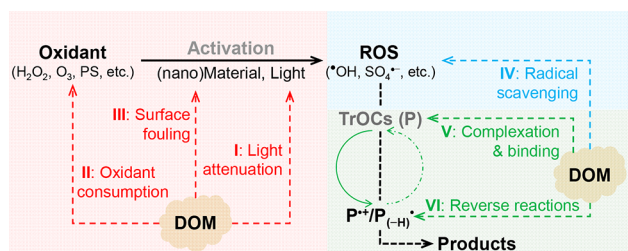


Figure 2. Reaction types and pathways involved in DOM's inhibition of TrOC transformation in AOPs. Red area: DOM inhibits the generation of reactive species via light attenuation (I), oxidant consumption (II), and surface fouling (III). Blue area: DOM quenches reactive species (IV). Green area: DOM interferes with TrOC degradation kinetics via complexation and binding with TrOC (V) and reverse reactions in which antioxidants in DOM reduce the intermediate radicals back to the parent compounds (VI).

where r_{RS}^f represents the generation rates of RS in a specific AOP. $\sum k_i S_i$ represents the sum of reactions between RS and water matrix components (e.g., inorganic anions, DOM, and the activating chemicals for RS generation).

2.1.1. DOM Absorbs UV/Solar Light. Chromophores in DOM absorb light across the ultraviolet and visible spectra. There is an exponential decrease in the molar absorbance coefficient at longer wavelengths (Figure 3a).^{91–95} Decreased transmittance of light limits direct photolysis of some TrOCs and influences the activation of some AOP chemicals (e.g., H₂O₂, PMS, PDS). That reduces radicals' generation and their reactions with TrOCs.^{96,97} Consider low pressure UV-light-driven AOPs as an example. The specific UV absorbance (SUVA₂₅₄) is calculated by dividing measured absorbance at 254 nm (UV₂₅₄) by DOM concentrations (mg_C L⁻¹). SUVA₂₅₄ serves as an indicator for aromaticity of DOM, and the common values range from ~1 to ~7 L m⁻¹ mg_C⁻¹, from less

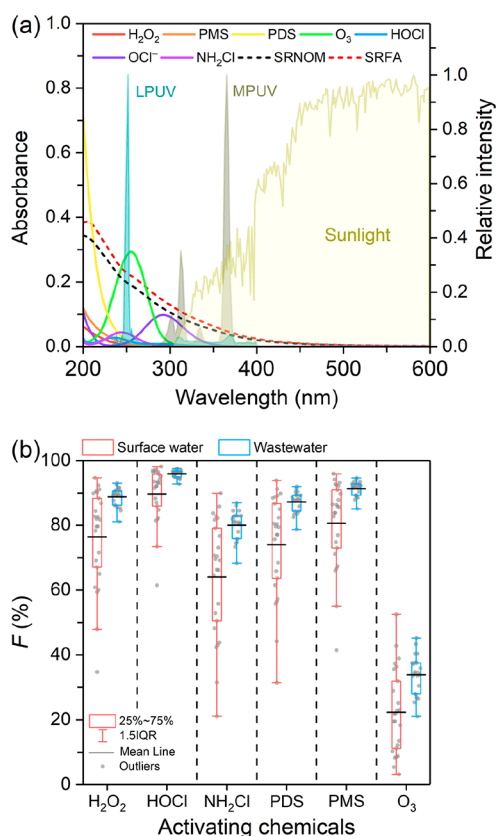


Figure 3. (a) UV–vis absorbance spectra of the activating chemicals and two DOM isolates with low pressure UV (LPUV), medium pressure UV (MPUV), and sunlight (H₂O₂, PMS, and PDS at a concentration of 1 mM, O₃, HOCl, NH₂Cl, and OCl⁻ at 0.1 mM, [SRNOM] and [SRFA] at 5 mg_C L⁻¹). (b) Screening fractions (*F*) with different activating chemicals under LPUV irradiation (eq 2). The SUVA and DOC concentrations are averaged from the data of 26 source water samples and 22 wastewater treatment plant effluents (Table S2). IQR: interquartile range.

to more aromatic in nature.^{44,54,56} Besides DOM, inorganic compounds in water also absorb light at 254 nm. For example, the molar absorptivity value at 254 nm (ϵ_{254}) for H₂O₂ is 18.6 M⁻¹ cm⁻¹, whereas those of HOCl and OCl⁻ are 62 and 60 M⁻¹ cm⁻¹, respectively. The molar absorptivity at 254 nm for NH₂Cl is 371 M⁻¹ cm⁻¹, whereas for PMS and PDS the values are 14 and 21.6 M⁻¹ cm⁻¹, respectively. O₃ exhibits the highest ϵ_{254} of 3000 M⁻¹ cm⁻¹ (Figure 3a).^{8,98–101} In environmentally relevant conditions (e.g., pH 6–9), there is little variation in the speciation and corresponding absorbance properties of H₂O₂ (pK_a = 11.8), PMS (pK_a = 9.3), and PDS (pK_a = -3.5). Though HOCl has a pK_a value of 7.5, the ϵ_{254} value of HOCl is very close to that of OCl⁻, resulting in negligible absorbance changes in aqueous chlorine species between pH 6 and 9. The attenuation of light absorption by activating chemicals (AC) because of DOM competition for photons (*F*) can be calculated as

$$F(\%) = \frac{\text{SUVA}_{254} \times [\text{DOM}]}{\text{SUVA}_{254} \times [\text{DOM}] + \epsilon_{254}[\text{AC}]} \times 100\% \quad (2)$$

where the brackets indicate chemical concentrations.

Data for 26 source water samples from different regions including the United States, Europe, Australia, and China has been collected, and the results are summarized in Table S2,

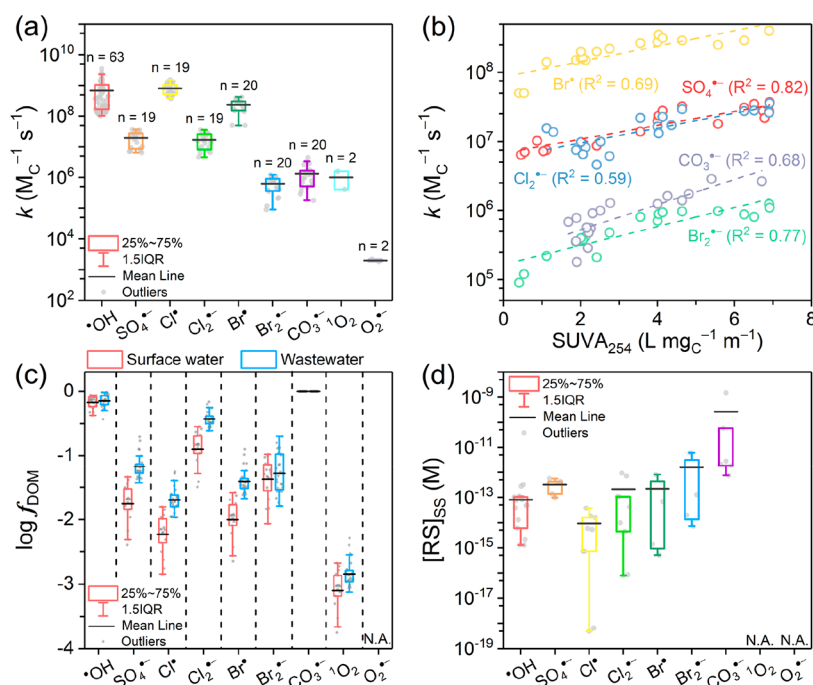


Figure 4. (a) Second-order reaction rate constants of reactive species with DOM. (b) Correlation of the second-order reaction rate constants with the DOM's $SUVA_{254}$. (c) Radical scavenging fraction by DOM in real waters. The data are the average of 20 surface water samples and 27 wastewater effluent samples. (d) Steady-state concentrations of $\cdot\text{OH}$, $\text{CO}_3^{\cdot-}$, $\text{Cl}_2^{\cdot-}$, Br^{\cdot} , $\text{Br}_2^{\cdot-}$, and $\text{SO}_4^{\cdot-}$ in typical AOPs.^{8,11,41,65,133,137,138}

which was used to make quantitative calculation of the impacts of DOM on AOP effectiveness. The $SUVA_{254}$ values varied from 0.9 to 3.8 $\text{L m}^{-1} \text{mgC}^{-1}$ with DOM concentrations ranging from 0.9 to 10.7 mgC L^{-1} . With a typical dose of activating chemicals (e.g., 1 mM H_2O_2 , PMS or PDS, 0.1 mM HOCl, O_3 or NH_2Cl), DOM screening can be expected to reduce the absorption between 3.2 and 98% (Figure 3b). In comparison, the light screening fraction (F) by DOM in typical wastewater effluents ($SUVA_{254} = 1.6\text{--}5.5 \text{ L m}^{-1} \text{mgC}^{-1}$ and $[\text{DOC}] = 3.8\text{--}10.6 \text{ mgC}^{-1}$ based on data from 22 wastewater treatment plants) ranged between 21 and 97% (Figure 3b). At those doses, DOM attenuates HOCl's absorption of 254 nm UV light the most, followed by $\text{H}_2\text{O}_2/\text{PDS}/\text{PMS}/\text{NH}_2\text{Cl}$ and then O_3 . Therefore, DOM generally inhibits UV-based AOPs.

Some AOPs use visible light ($>400 \text{ nm}$) to minimize DOM's screening effects. At environmentally relevant DOM concentrations, less than 1% of the incident light at 400–470 nm is screened out in chlorine- C_3N_4 ,^{20,102} MCNT- TiO_2 ,¹⁰³ or BiFe-ZnO¹⁰⁴ AOPs (Figure S1). Future research might usefully emphasize artificial rather than solar light to decrease the size requirements and diurnal variation limitations of natural sunlight-driven AOPs.

2.1.2. DOM Consumes Activating Chemicals Used in AOPs. H_2O_2 , PMS, and PDS are rather stable in the presence of typical DOM concentrations.^{105–109} However, DOM is rapidly transformed in the presence of stronger oxidants such as ozone, free chlorine, or chloramines.^{110,111} Ozone selectively reacts with olefins, amines, and activated aromatic moieties within DOM.⁶³ When bromide is present, free bromine is formed. Free chlorine and bromine are particularly reactive toward phenolic groups, amines, and reduce sulfur moieties in DOM,^{112,113} but free bromine reacts about ten times faster with DOM than free chlorine.¹¹¹ Monochloramine (NH_2Cl) and dichloramine (NHCl_2) formed from the reaction of free chlorine with ammonia have smaller reaction rate constants

with DOM.^{114,115} The decomposition of O_3 , free chlorine, and free bromine in the presence of DOM follows a two-stage kinetics with a rapid initial stage (lasting less than about 20 s) and a slower consumption stage.^{64,111,116} Notably, relatively high yields of $\cdot\text{OH}$ are formed in the rapid initial stage of ozone reactions with DOM. That helps to reduce ozone-resistant TrOCs.^{64,116} Depending on the types and concentrations of DOM, the decomposition rates of these chemical oxidants vary and the generation of radicals is inhibited in the presence of DOM, except in O_3 -based processes.

2.1.3. DOM Blocks the Active Sites of Solid-Phase Catalysts. AOPs based on heterogeneous catalysis generate surface-bound or solution-released RS that degrade TrOCs. In some cases the TrOCs are adsorbed on the catalyst's surface (Figure 2).^{22,117–121} DOM adsorbed on the catalyst's surface hinders performance to degrade TrOCs that occur at much lower concentrations (from ng/L to $\mu\text{g/L}$) compared with DOM concentrations (mg/L).^{122–126} Adsorbed DOM may also block pores reducing the catalyst's available intraparticle surface area.¹⁰³ This impairment has been demonstrated in Fenton-like systems.¹²⁴ DOM adsorption on catalyst surfaces has been shown to reduce persulfate activation by the catalyst, inhibiting the generation of reactive species.^{127–129} To our knowledge there are no clear examples of DOM improving TrOC removal in a heterogeneous catalysis-based AOP.

2.2. DOM Quenches Reactive Species. Reactions between radicals and DOM commonly follow second-order reaction kinetics with respect to both the concentrations of radicals and DOM (eq 3), and are therefore similar to bimolecular reactions between radicals and organic/inorganic compounds:^{12,13}

$$\frac{d[\text{RS}]}{dt} = -k[\text{RS}][\text{DOM}] \quad (3)$$

The second-order rate constants for the reactions of reactive species with DOM were collected from literature, and the results are represented several ways within Figure 4. Figure 4a summarizes the rate constant ranges between DOM and common RS. As the figure shows, $k_{\bullet\text{OH},\text{DOM}} \approx k_{\text{Cl}\bullet,\text{DOM}}$ ($10^8\text{--}10^9 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$) $> k_{\text{Br}\bullet,\text{DOM}}$ ($10^7\text{--}10^8 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$) $> k_{\text{SO}_4\bullet-,\text{DOM}}$ ($10^7\text{--}10^8 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$) $> k_{\text{Cl}_2\bullet-,\text{DOM}}$ ($10^6\text{--}10^7 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$) $> k_{\text{Br}_2\bullet-,\text{DOM}}$ ($10^5\text{--}10^6 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$) $\approx k_{\text{CO}_3\bullet-,\text{DOM}}$ ($10^5\text{--}10^6 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$).^{44,51,55,56,130–135} For example, the second-order reaction rate constant for Suwannee River fulvic acid (SRFA) reacting with $\bullet\text{OH}$ is $(1.86 \pm 0.25) \times 10^8 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$.¹³⁶ With $\text{Cl}\bullet$ it is $(4.12 \pm 0.32) \times 10^8 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$,⁵⁶ with $\text{Br}\bullet$ $(3.0 \pm 0.3) \times 10^8$,¹³⁵ with $\text{SO}_4\bullet-$ $(2.28 \pm 0.07) \times 10^7$,¹³² with $\text{Cl}_2\bullet-$ $(1.64 \pm 0.35) \times 10^7$,⁵⁶ with $\text{CO}_3\bullet-$ $(1.74 \pm 0.06) \times 10^6$,¹³¹ and with $\text{Br}_2\bullet-$ $(9.4 \pm 1.3) \times 10^5 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$.¹³⁵ The reaction kinetics between DOM and $\bullet\text{OH}$ have been the most extensively studied, with far fewer studies reporting reaction rate constants of DOM with $\text{Cl}\bullet$, $\text{Cl}_2\bullet-$, $\text{Br}\bullet$, $\text{Br}_2\bullet-$, $\text{SO}_4\bullet-$, or $\text{CO}_3\bullet-$. Tables S3 and S4 summarize what is known about the second-order rate constants of reactions between DOM and oxidants used in AOPs.

Noteworthy in Table S3 is that only two rate constant values are reported for DOM's reactions with $^1\text{O}_2$ or $\text{O}_2\bullet-$. DOM reportedly quenches $^1\text{O}_2$ with an overall reaction rate constant of $(0.41\text{--}1.6) \times 10^6 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$. Phenols and aromatic amines are the dominant DOM constituents involved.^{139,140} A recent study using a flow injection analysis system determined an apparent rate constant for SRFA with $\text{O}_2\bullet-$ of approximately $(1.8\text{--}2.2) \times 10^3 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$.¹⁴¹ $\text{O}_2\bullet-$ is a weak oxidant that can be reduced to H_2O_2 ($E^0(\text{O}_2\bullet-/\text{H}_2\text{O}_2) = 0.91 \text{ V}$ vs. the normal hydrogen electrode (NHE)) or itself serve as a moderately strong reducing agent ($E^0(\text{O}_2\bullet-/\text{O}_2) = -0.33 \text{ V}$ vs. NHE).¹⁴² $\text{O}_2\bullet-$ has relatively high reaction rate constants with cations and quinones,¹⁴³ but such compounds may mainly play a catalytic role during the formation of H_2O_2 from $\text{O}_2\bullet-$.¹⁴⁴ Overall, more studies focusing on the kinetics of the reactive species' reactions with DOM are needed to understand the sensitivity of different structures and the influence of the DOM's composition.

DOM from different sources shows distinct reactivity patterns. For example, the $k_{\bullet\text{OH},\text{DOM}}$ and $k_{\text{Cl}\bullet,\text{DOM}}$ values for EfOM isolates are higher than those of natural organic matter (NOM) isolates; however, $k_{\text{CO}_3\bullet-,\text{DOM}}$ values are lower for EfOM isolates.¹³¹ Humic acids (HAs) have higher $k_{\text{Cl}\bullet,\text{DOM}}$ values than more hydrophilic and less aromatic fulvic acids (FAs), but no significant difference in $k_{\text{Cl}_2\bullet-,\text{DOM}}$ is observed between HA and FA.⁵⁶ $k_{\text{SO}_4\bullet-,\text{DOM}}$, $k_{\text{Cl}_2\bullet-,\text{DOM}}$, and $k_{\text{CO}_3\bullet-,\text{DOM}}$ all correlate negatively with E2/E3 (the absorbance at 254 nm divided by the absorbance at 365 nm) (Figure S2). However, they and $k_{\text{Br}\bullet,\text{DOM}}$ and $k_{\text{Br}_2\bullet-,\text{DOM}}$ have a positive correlation with the DOM's phenolic content and aromaticity as expressed by its SUVA₂₅₄ (Figure 4b).^{56,131} $k_{\text{Cl}\bullet,\text{DOM}}$ and $k_{\bullet\text{OH},\text{DOM}}$ however, are not similarly correlated. $k_{\text{Cl}\bullet,\text{DOM}}$ correlates negatively with the DOM's average molecular weight because of diffusion controlled reactions.⁵⁶ Different studies have reported contradictory trends with molecular weight.^{44,52,56} Both $\bullet\text{OH}$ and $\text{Cl}\bullet$ are highly reactive toward organics with rate constants (e.g., $k_{\bullet\text{OH},\text{phenol}} = 0.7\text{--}1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{Cl}\bullet,\text{phenol}} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) often approaching the diffusion-controlled limits ($\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, i.e., $\sim 10^9 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$ based on the Smoluchowski equation).^{41,145} The $k_{\text{Cl}\bullet,\text{DOM}}$ and $k_{\bullet\text{OH},\text{DOM}}$ values often reach the diffusion-controlled limits ($\sim 10^9 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$) as shown in Figure 4a, suggesting the reactions are more diffusion-controlled rather than activation-controlled, thus the rates were more affected by the molecular size.^{51,56,146} Whereas $\text{SO}_4\bullet-$, $\text{Cl}_2\bullet-$, $\text{Br}\bullet$, $\text{Br}_2\bullet-$, and $\text{CO}_3\bullet-$ are more selective and reactive with the electron-donating groups in DOM.

As has been mentioned, inorganic ions such as HCO_3^- , CO_3^{2-} , Cl^- , Br^- , etc. in the water matrix also scavenge radicals.¹⁴⁷ The second-order rate constants of those reactions are also summarized in Table S4. Analysis of the competitive kinetics can give some quantitative understanding of the relative importance of radical scavenging by inorganic ions versus scavenging by DOM. DOM's relative contribution to radical scavenging (f_{DOM}) can be estimated using eq 4.

$$f_{\text{DOM}}(\%) = \frac{k_{\text{DOM}} \times [\text{DOM}]}{k_{\text{DOM}} \times [\text{DOM}] + k_{\text{HCO}_3^-} \times [\text{HCO}_3^-] + k_{\text{NO}_2^-} \times [\text{NO}_2^-] + k_{\text{Cl}^-} \times [\text{Cl}^-] + k_d} \times 100\% \quad (4)$$

The term k_d is the first-order natural decay rate constants for these transients (e.g., $^1\text{O}_2$ is quickly relaxed to ground state triplet oxygen in water). The k_d values are $2.4 \times 10^5 \text{ s}^{-1}$ for $^1\text{O}_2$, $2.5 \times 10^5 \text{ s}^{-1}$ for $\text{Cl}\bullet$, 1300 s^{-1} for $\text{Cl}_2\bullet-$, 1.4 s^{-1} for $\text{Br}\bullet$, and 660 s^{-1} for $\text{SO}_4\bullet-$; they are not available for others.^{148,149} It should also be noted that the reactions of Cl^- with $\bullet\text{OH}$ generate $\text{ClOH}\bullet-$ as the intermediate ($4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), which quickly reverses back to regenerate $\bullet\text{OH}$ ($6.0 \times 10^9 \text{ s}^{-1}$). Thus, Cl^- does not significantly impact the $\bullet\text{OH}$ concentrations at the typical concentrations in water and some wastewater and is thus not included in calculating the f_{DOM} for $\bullet\text{OH}$.

To illustrate the importance of commonly occurring compounds in water, 20 surface waters and 27 wastewater treatment effluents reported in the literature (Table S5) were evaluated, which have DOM concentrations ranging from 6.1 to 8.2 mg_C/L. These waters had concentrations of HCO_3^-

from 2.23 to 2.74 mM, 1.96 to 6.31 μM for nitrate, and 0.27 to 2.08 mM for Cl^- . At the typical pH range of 6.5–8 in surface water and wastewater effluents, bicarbonate is the dominant species (i.e., H_2CO_3 and CO_3^{2-} are not considered as significant). Equation 4 was used to calculate the f_{DOM} values for different RS. As Figure 4c shows, DOM acts as the major sink for $\text{CO}_3\bullet-$ ($f_{\text{DOM}} \sim 100\%$) and $\bullet\text{OH}$ (f_{DOM} values range from 37 to 96% depending on the source and composition of the DOM). In contrast, f_{DOM} values decrease to 0.4–20% for $\text{SO}_4\bullet-$, to 0.14–6% for $\text{Cl}\bullet$, to 5–68% for $\text{Br}\bullet$, to 0.2–12% for $\text{Br}_2\bullet-$, and to 0.9–20% for $\text{Cl}_2\bullet-$ because of the significant competition from HCO_3^- and Cl^- in real waters. $^1\text{O}_2$ exhibits little DOM scavenging ($f_{\text{DOM}} < 0.5\%$) because most of it could naturally relax to the ground state triplet oxygen in water.¹⁵⁰ Although $\text{Cl}_2\bullet-$ and $\text{CO}_3\bullet-$ are less reactive with DOM than $\bullet\text{OH}$ and $\text{SO}_4\bullet-$ (Figure 4a), their aqueous concentrations could be up to 4 orders of magnitude higher in some AOPs

(Figure 4d), resulting in comparable overall radical species exposures ($\int [RS]_{ss} dt$).^{11,151}

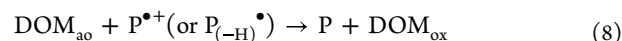
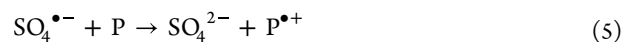
2.3. DOM Interferes with TrOC Degradation. In addition to affecting the formation and consumption of reactive species, DOM associates with TrOCs and/or alters the transformation pathways of TrOCs, thus inhibiting overall degradation.

2.3.1. DOM Associates with TrOCs. A few studies have found that DOM can enmesh TrOCs within its macromolecular structure in ways that reduce TrOCs' susceptibility to reactive species in solution. The current view is that DOM can be represented as a supra-molecular assembly held together by van der Waals interactions, and that TrOCs can interact with that structure via electrostatic interaction,^{152,153} hydrogen bonding,^{11,154} or hydrophobic interaction.^{155,156} DOM components are amphiphilic, containing both non-polar domains (e.g., aliphatic and aromatic hydrocarbons) and polar domains (e.g., oxygen-, nitrogen-, and sulfur-bearing moieties). That results in its three-dimensional structure and charge density depending on the solution's pH and ionic strength.^{156,157} At a circumneutral pH, DOM is negatively charged because of deprotonation of its carboxylic and phenolic moieties.¹⁵³ Positive-charged TrOCs such as aminoglycoside antibiotics can therefore absorb into DOM via electrostatic interaction.¹⁴⁶ Phototransformation of aminoglycosides and histidine is reportedly enhanced through such absorption because of the much higher concentrations of RS (e.g., 1O_2 and $^{\bullet}OH$) in the DOM's microenvironment than in the bulk water.^{152,153} However, this has not been well documented in an AOP. The hydrophobic interaction between DOM and hydrophobic organic compounds (e.g., PAHs and polychlorinated biphenyl) is related to their hydrophobicity.^{158,159} Hydrogen bonds were reported to form between DOM and TrOCs.¹¹ For instance, the imidazole ring of nitroimidazole antibiotics forms hydrogen bonds with phenolics and quinones in DOM.^{160,161} That facilitates hydrogen-atom transfer in RS generation.¹⁶²

Enhanced degradation of pollutants in the presence of DOM has also been reported. For instance, DOM is reported to enhance the degradation of perfluoro-octanesulfonate (PFAS) in UV/iodide treatment. One reason is because confinement by an iodide-DOM-PFAS adduct constrains the generation of e_{aq}^- and the local decomposition of PFAS.^{163,164} Because of the complicated interactions among pollutant, DOM, and RS, the reaction kinetics and mechanisms in such confined volume reactions are not yet well understood, nor is the fate of TrOCs absorbed into DOM.

2.3.2. DOM Reduces Organic Radical Intermediates. Various functional groups in DOM can interfere with TrOC degradation in different ways. For example, antioxidant groups found in DOM, such as phenols, can interfere in the redox reactions of TrOCs in AOPs.^{110,165–168} Single electron transfer, H-abstraction, and radical addition are three well-known pathways for reactions involving radicals.^{3,12,13,41} During radicals' reactions with a TrOC (e.g., P), single electron transfer generates a radical cation ($P^{\bullet+}$) and H-abstraction generates a neutral radical ($P_{(-H)}^{\bullet}$) (eq 5). $P^{\bullet+}$ can also deprotonate to $P_{(-H)}^{\bullet}$ depending on the pH (eq 6).^{169,170} In the absence of DOM, $P^{\bullet+}$ and $P_{(-H)}^{\bullet}$ will decompose to generate oxidized P_{ox} (eq 7). In the presence of DOM, however, $P^{\bullet+}$ and $P_{(-H)}^{\bullet}$ may be quenched by antioxidants in the DOM (DOM_{ao}) and revert back to the parent compound (eq 8). This is thought to explain DOM's inhibition of the

photosensitized transformation of certain TrOCs under solar irradiation.^{165,171,172} Recently, the inhibitory effect of DOM on anilines and sulfonamide antibiotics in a $SO_4^{\bullet-}$ -based AOP has been reported. It is thought to be mainly caused by reduction of intermediate radicals by phenolic groups in the DOM.¹⁶⁶ However, the antioxidant capacity of DOM does not follow the same pattern as its inhibitory effects. That is, the DOM with the greatest antioxidant capacity does not deliver the strongest inhibition. The reason remains unknown.



Quantitative examination of the quenching of $P^{\bullet+}/P_{(-H)}^{\bullet}$ by antioxidants in DOM has so far been quite limited. Three recent studies tracked the transient spectra of the intermediate radicals and obtained the quenching kinetics for tryptophan radical cation ($Trp^{\bullet+}$), 4-(dimethylamino) benzonitrile radical cation ($DMABN^{\bullet+}$), and neutral adenine radical ($ADN_{(-H)}^{\bullet}$). The rate constants for their quenching reactions varied from 10^7 to $10^9 \text{ M}^{-1} \text{ s}^{-1}$ with the phenolic model compounds studied and from 10^7 to $10^8 \text{ M}^{-1} \text{ s}^{-1}$ with Suwannee River DOM isolates.^{167–169} Only 37% of the $SO_4^{\bullet-}$ was quenched in the presence of 1 mgC L^{-1} of Suwannee River NOM (SRNOM), but the first-order degradation rate constant of ADN decreased by 88% compared with that in the absence of SRNOM. That has been attributed to the reversing of $ADN_{(-H)}^{\bullet}$'s reactions by the phenolic moieties within DOM.¹⁷³ In consideration of the higher concentrations of DOM (mgC L^{-1}) found in natural waters, the reverse reactions may significantly affect the degradation of TrOCs in AOPs, especially those with high reaction rate constants (eq 8).¹⁷⁴

Not all contaminant radicals can be quenched by the antioxidants in DOM. The three intermediate radicals discussed above all have relatively high reduction potentials. For $Trp^{\bullet+}$ it is 1.0 V vs. standard hydrogen electrode (SHE) (at pH 7.0). For $DMABN^{\bullet+}$ it is 1.3 V and for $ADN_{(-H)}^{\bullet}$ it is 1.32 V vs. SHE.^{167–169} The reduction potential for aniline radical cations is also high at about 1.0 V vs. SHE.¹⁷⁵ Regarding the antioxidants in DOM, taking the phenolic compounds as examples, their oxidation potentials are in the range from -0.79 to -0.4 V for their deprotonated forms.¹⁷⁶ As such, most phenols are susceptible to oxidation by these $P^{\bullet+}$ or $P_{(-H)}^{\bullet}$ via single electron transfer. However, the reduction potential difference is not the only factor controlling the reaction between $P^{\bullet+}$ or $P_{(-H)}^{\bullet}$ and antioxidants. Some phenolic and thiol-containing compounds can undergo proton-coupled electron transfer with $P^{\bullet+}$ or $P_{(-H)}^{\bullet}$.^{177,178} Previous studies also indicate that the reaction rate constants between $P^{\bullet+}$ or $P_{(-H)}^{\bullet}$ and antioxidants are not exactly in line with the reduction potentials. That suggests that both proton-coupled electron transfer and single electron transfer might be involved in the reactions.¹⁶⁷

3. SYNERGISTIC CONTRIBUTION OF DOM TOWARD TROC TRANSFORMATION

Often overlooked and rarely intentionally integrated into AOP design or operation is the potential for DOM to synergistically

enhance TrOC removal. Figure 5 illustrates some synergistic mechanisms and their potential relevance.

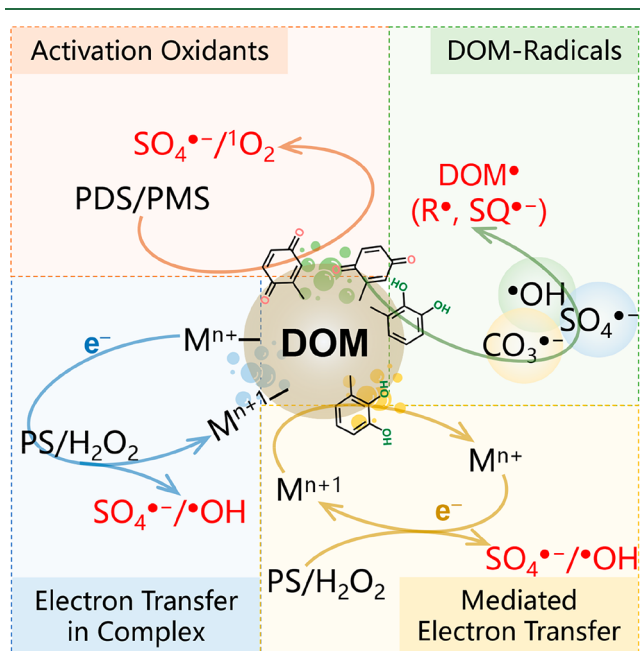
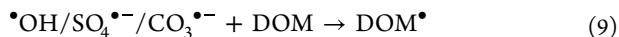


Figure 5. Synergistic mechanisms involving generation of reactive species from DOM that potentially accelerate the transformation of TrOCs in an AOP. PS means inclusion both of PDS and PMS.

3.1. Formation and Reactivity of Transient Species within DOM. The reactions of inorganic radicals with DOM can generate DOM radicals (DOM[•]), which may also contribute to the degradation of TrOCs in an AOP (eqs 9 and 10) (Table S6).



The absorption spectra of DOM[•] appear during [•]OH reactions with DOM isolates. The peak absorbance is at 325–400 nm.⁵¹ DOM[•]'s absorbance at 400 nm because of [•]OH oxidation of SRFA decays exponentially within milliseconds. In SO₄^{•-} oxidation of DOM the transient absorbance at 450 nm may be attributed to phenoxyl radicals resulting from one-electron oxidation of phenolic moieties in the DOM.¹³² The current understanding of transient species within DOM is still quite limited, but it seems to be present as longer and shorter lived species that can also be important in engineered AOP systems. The millisecond time scale of DOM[•]'s existence is sufficient for it to be involved in reactions with other radicals.

DOM[•] species including phenoxyl (PhO[•]), alkoxyl (RO[•]), peroxy (ROO[•]), and percarboxyl radicals (RC(O)OO[•]) have half-lives ranging from microseconds or milliseconds for PhO[•] and RO[•] to a few seconds for ROO[•].^{179,180} The reduction potential for the unsubstituted phenoxyl radical (PhO[•]) is 0.79 V (vs. NHE).¹⁷⁶ Those of substituted phenoxyl radicals vary from near zero for electron-rich substituents (e.g., 4-O⁻-PhO[•]) to 1.22 V (vs. NHE) for electron-poor substituents (e.g., 4-NO₂-PhO[•]).¹⁷⁶ The reduction potentials are 1.23–1.47 V (vs. NHE) for RO[•], 1.05–1.19 V (vs. NHE) for ROO[•], and 0.71–0.83 V (vs. NHE) for RC(O)OO[•].^{181,182} Consequently, organic radicals are potentially as capable as inorganic radicals of transforming TrOCs. The oxidation potential of TrOCs can

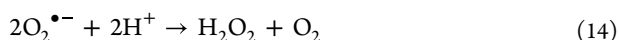
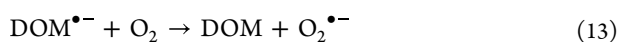
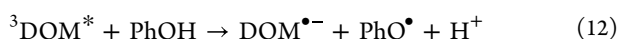
vary widely, for example from –1.22 to –0.54 V for phenols or –1.32 to –0.59 V for anilines.^{10,67,73} Thus, their oxidation by transient species within DOM is thermodynamically feasible. Note that other transient species formed from amino acids present in DOM (amine radical cations for example) may be reactive because of their relatively high reduction potential (~1.0 V vs. SHE),^{175,176} but their impact is minor because of their much lower concentrations relative to phenolic moieties within DOM.¹⁸³

Second-order reaction rate constants between organic radicals (e.g., RO[•] and ROO[•]) and common moieties and classes of pollutant (e.g., phenols, aromatic amines, and hydrocarbons) are listed in Table S7. Among the long-lived transient species within DOM, phenoxyl radicals may be the most important because of the prevalence of phenolics in DOM (at mM gC⁻¹ levels).^{183,184} Phenoxyl radicals are very selective and reactive toward electron-rich organic compounds such as phenolates and amines via single electron transfer reactions.¹⁸⁵ For example, the second-order rate constants for reactions between phenoxyl radicals and dissociated catechol, hydroquinone, and thiols approach diffusion-controlled rate limits (~10⁹ M⁻¹ s⁻¹).¹⁸⁵ However, the rate constants for reactions with electron-poor moieties (e.g., olefins and fatty acid esters) are very low (from ~10⁻⁵ to 10 M⁻¹ s⁻¹).¹⁸⁵ The oxidation of some TrOCs such as anilines and sulfonamide antibiotics in SO₄^{•-}-based AOPs has been attributed to phenoxyl radicals generated from electron-poor moieties within DOM (roughly 1.0 to 1.3 V vs. NHE).¹⁶⁶ Despite the evidence of a role for phenoxyl radicals, little is known about their structures, levels, and distribution within the DOM ensemble. Additionally, *tert*-butoxyl radicals are also reactive toward electron-rich moieties, such as the unsaturated fatty acids and some nucleosides and their reaction rate constants reach ~10⁸ M⁻¹ s⁻¹.¹⁸⁶ Phenylperoxyl radicals can react with 4-methoxyphenolate and chlorpromazine at ~10⁸ M⁻¹ s⁻¹ via the electron-transfer reaction pathway.¹⁸⁷ The transient species within DOM can be versatile because of the diverse function groups of DOM. Many factors, including self-reactions or steric hindrance, can affect their reactivity. Though the reaction rate constants of DOM[•] with TrOCs have not been well studied so far, related literature results imply that they may play important roles in degrading some TrOCs, especially those with electron-rich moieties.

Besides redox reactions, nucleophilic addition reactions to quinones or semiquinone radicals have also been reported. The aniline nitrogen in sulfonamide antibiotics and the thiol-sulfur in captopril undergo addition reactions at the DOM's electron-poor sites.^{70–72} Besides the 1,2-nucleophilic and 1,4-nucleophilic addition reactions of aniline with quinones in DOM, radical reactions involving anilino and semiquinone radicals are also possible.^{70–72} This could constitute an additional TrOC degradation pathway in the presence of DOM.

In addition to the long-lived DOM[•], DOM also produces other short-lived reactive species such as O₂^{•-} and [•]OH. Previous studies have indicated that redox-active moieties such as phenolic and quinone-like groups present in DOM may be responsible for the formation of O₂^{•-} in AOPs.^{144,188–190} Upon photoexcitation and/or oxidation by SO₄^{•-}, electron-donating phenolic groups in DOM may transfer electrons to quinone-like groups with electron-accepting capacity yielding one-electron reducing intermediates (DOM^{•-}) (eqs 11 and 12). The DOM^{•-} can be further oxidized by oxygen

generate $O_2^{\bullet-}$ (eq 13). Furthermore, the formation of H_2O_2 is dominated by catalyzed and uncatalyzed $O_2^{\bullet-}$ dismutation processes (eq 14).¹⁹¹ H_2O_2 can also produce $\bullet OH$ via further photolysis or through the Fenton-type reactions (eq 15).^{192–194} $\bullet OH$ can also be formed from O_3 oxidation of DOM (eq 16). DOM moieties such as phenols, amines, and amino acids generate $\bullet OH$ upon O_3 oxidation.^{64,116} Electron-rich moieties in DOM, such as phenols, anilines, olefins can act as radical initiator and initiate the transformation of O_3 to $\bullet OH$.⁶⁴ Carboxylic acid, hydroxyl, and aryl groups in DOM react with $\bullet OH$ and can act as radical promoters, through which organic radicals can form and then propagate the radical chain reactions to eventually produce another $\bullet OH$.^{44,54,63,195} Alkyl groups in DOM act as inhibitors to interrupt radical chain reactions by rapidly scavenging $\bullet OH$. Depending on DOM properties, both inhibitory and promoting effects on pollutants removal have been observed in ozonation and ozone-based AOPs.^{196,197}



The synergistic impact of transient species within DOM on TrOC degradation should be considered relative to its impact on the inorganic reactive species for which most AOPs are designed. Long-lived DOM^{\bullet} forms because it has relatively low reactivity with other compounds in the water compared to other radical species. That may leave higher DOM^{\bullet} concentrations in the water to react with TrOCs in competition with inorganic radicals. There are, however, few reports of DOM^{\bullet} 's concentrations measured during AOPs. That is an area where future research is likely to be fruitful.

Consider the potential importance of transient species within DOM. For TrOCs having relatively high reaction rate constants with DOM^{\bullet} (say, 10^6 – 10^9 $M^{-1} s^{-1}$), the contribution of transient species within DOM to their degradation may not be negligible. A recent study has demonstrated that semiquinone radicals ($SQ^{\bullet-}$) can make a significant contribution to the degradation of nitroimidazoles in $SO_4^{\bullet-}$ -based oxidation process with DOM present.⁷³ The $SQ^{\bullet-}$ is formed via the $SO_4^{\bullet-}$ -induced oxidation of the DOM's quinone- and hydroquinone-like moieties. The second-order rate constant for tinidazole's reaction with $SQ^{\bullet-}$ has been determined to be $(5.69 \pm 0.59) \times 10^6$ $M^{-1} s^{-1}$.⁷³ Although $SQ^{\bullet-}$ reacts with tinidazole with a much lower rate constant than that of $SO_4^{\bullet-}$ ($(2.70 \pm 0.06) \times 10^9$ $M^{-1} s^{-1}$), the concentration of $SQ^{\bullet-}$ is typically about 3 orders of magnitude higher than that of $SO_4^{\bullet-}$, resulting in $SQ^{\bullet-}$ making a comparable contribution to tinidazole elimination.⁷³ Deprotonated phenolic and thio-containing TrOCs may be affected by the generation of transient species within DOM in AOPs because of their high reactivity with DOM^{\bullet} .¹⁸⁵

The importance of reactive species from DOM is dependent on their concentrations and reaction rate constants. Production of ${}^3DOM^*$, 1O_2 , and H_2O_2 that occurs during UV irradiation treatment of water containing DOM and ${}^3DOM^*$ was

concluded to impact TrOCs' removal only at very high UV doses (e.g., 2000 mJ/cm^2).⁹⁵ In $\bullet OH$ -based AOPs for surface water and wastewater treatment, such as O_3/H_2O_2 and UV/ H_2O_2 AOPs, models to predict TrOCs' degradation currently not only account for the scavenging impacts of DOM but also show acceptable predictive performance.^{79,198,199} These findings suggest the minimal impacts of transient species within DOM in $\bullet OH$ -based AOPs, whereas such DOM impacts may be more significant in $SO_4^{\bullet-}$ -based AOPs. The difference between $\bullet OH$ - and $SO_4^{\bullet-}$ -based AOPs relates to the reaction mechanisms of $\bullet OH$ and $SO_4^{\bullet-}$ radicals with DOM and the different types of transient DOM species produced. For example, $\bullet OH$ is prone to react with DOM via unsaturated bond addition to produce $\bullet OH$ -adducts, which react rapidly with oxygen (10^8 – 10^9 $M^{-1} s^{-1}$).²⁰⁰ In contrast, $SO_4^{\bullet-}$ serves as a one-electron oxidant, and produced $DOM^{\bullet+}$ or $DOM_{(-H)}^{\bullet}$ may participate in the redox reactions of TrOCs. Additionally, the concentrations of DOM^{\bullet} generated in $\bullet OH$ - and $SO_4^{\bullet-}$ -based AOPs may also be quite different and exert different impacts in TrOC transformation (Figure 4). The information on DOM^{\bullet} in different AOPs needs more exploration.

Transient DOM species' influence on TrOC degradation may be advanced by improved quantitative detection and tracking their concentrations. Application of time-resolved spectroscopy, electron paramagnetic resonance spectroscopy, and electrochemical analysis can provide some information about the optical and redox properties of DOM^{\bullet} . The reactivity of a specific radical can be explored by using laser flash photolysis or pulse radiolysis techniques. We postulate the difficulty lies in the quantification of $[DOM^{\bullet}]_{ss}$ because of the heterogeneous structures that comprise DOM, the coexistence of multiple organic radicals, and the lack of specific probe for the organic radicals. Novel chemical probes that detect these intermediates would be highly beneficial and are urgently needed. In consideration of the large quantity of phenolic and quinoid moieties in DOM ($\mu M/mgC$),^{73,183,184} research on phenoxyl radicals and semiquinone radicals may be a good starting place for future research.

3.2. DOM Involved Pathways to Generate Reactive Species. Phenolic and quinone moieties seem to play the most important roles in the radical formation in AOPs (Figure 5). Quinones can activate PDS or PMS to generate reactive species.^{201–204} For example, 1,4-benzoquinone (BQ) can activate PDS to generate $SO_4^{\bullet-}$ through forming a semiquinone radical,²⁰¹ or it can react with PMS to form a dioxirane intermediate, which subsequently decomposes to produce singlet oxygen (1O_2).²⁰² However, in studies of the activation of PMS or PDS the relative importance of DOM has not been significant. This is probably because of the low concentrations of quinone compounds in natural waters and wastewater.¹⁰⁹

Phenolic and quinone moieties are involved in the redox transformation of Fe(III) to Fe(II) ($E^0 = 0.77$ V vs. NHE).²⁰⁵ Fe(II) can activate H_2O_2 , PMS, or PDS to generate $\bullet OH$ or $SO_4^{\bullet-}$. The slow transformation from Fe(III) back to Fe(II) is known to be the rate-limiting step in Fe(II)-mediated AOPs, so the presence of DOM can enhance the working of Fenton and Fenton-like processes because hydroquinone- and/or semiquinone-type species in DOM can promote Fe(III)/Fe(II) redox cycling.^{188,206} The enhancement of course depends on the types and concentrations of the reducing moieties, as DOM also consumes radicals. Additionally, DOM complexes with iron species. The complexation changes the

reduction potential of iron and can accelerate the rate of Fe(II)'s oxidation by the oxidants such as H₂O₂, PMS, or PDS. That would enhance radical formation.^{207,208} That is why the presence of DOM has been found to enhance the degradation rates of certain TrOCs in the Fe(II)/H₂O₂, Fe(III)/H₂O₂, Fe(II)/PDS, and PMS-amended iron coagulation processes using ferric salts.^{109,208–211} Similarly, the redox-active moieties in DOM can also mediate the redox cycling of Cu(II)/Cu(I) and vanadium(V)/vanadium(IV), and that can also enhance the activation of PDS or PMS.^{212,213} Moreover, in a PMS system activated by visible-light-excited humic acid, quinone moieties are photo-induced and act as electron shuttles to accelerate electron transfer between the humic acid and the PMS. That can activate PMS to form reactive species for the degradation of bisphenol-A.²¹⁴ Future experiments may better elucidate the role of DOM by examining the net effects of bisphenol-A degradation by light-activated PMS across a range of concentrations of DOM from different sources.

3.3. Engineering Systems Containing DOM to Generate More Reactive Species. Phenolic, quinone, and quinone-like moieties in DOM are the redox-active moieties, and they can complex with metals, induce and mediate electron transfer with transition metals, and activate oxidants to generate reactive species.^{201,205,215–217} Tailoring technologies to utilize DOM in water to enhance the generation of reactive species for the degradation of TrOCs is an emerging opportunity. It may constitute an attractive alternative to removing DOM prior to advanced oxidation treatment. For example, an organic Fenton-like catalyst was developed recently by exploiting quinone-like compounds as H₂O₂ activators to generate reactive [•]OH and ¹O₂. This results in improving pollutant reduction while refreshing electrochemically the working electrodes.¹⁹⁴ Another example is a PMS-amended iron coagulation process that achieves both coagulation and advanced oxidation mainly by relying on DOM's ability to complex with Fe and promoting its redox cycling. The result is enhanced generation of [•]OH and SO₄^{•-}.^{109,213} The degradation of bisphenol-A has been shown to be enhanced in a process in which PMS is activated by an FeAl layered double hydroxide compounded with DOM.²¹⁸

To improve our fundamental understanding of these systems, we must improve the quantitative characterization of specific functional groups present in DOM that are involved in the pathways to generate reactive species (e.g., electron shuttles and/or direct electron transfer). Specifically, quantification of reactive species formation efficiency based on the number of electrons transfer between DOM and activating chemical/materials are required. These insights will then allow new and novel engineered designs that enhance electron transfer efficiency to improve the positive effect of DOM.

4. DOM TRANSFORMATION AND BYPRODUCT FORMATION

Reactions with radical oxidants and activating agents (e.g., UV light) inevitably alter DOM's composition and may result in byproducts formation. Figure 6 illustrates representative transformations in DOM structure and byproduct formation during AOP treatment.

4.1. Alteration of DOM Compositions. Quantifying the alterations of DOM in AOPs has involved techniques such as monitoring changes in optical properties using UV–vis absorption and fluorescence spectroscopy.^{44,52,219} Changes in redox properties can be monitored using electrochemical

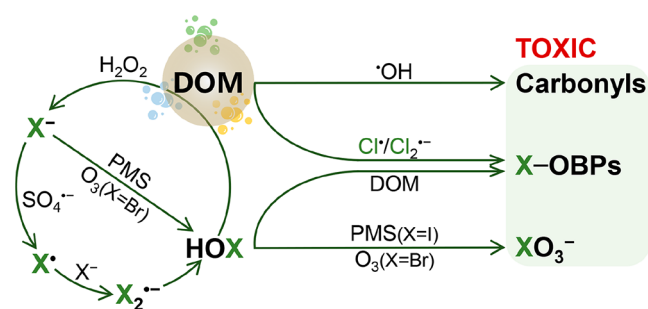


Figure 6. Formation of byproducts from DOM transformation in an AOP.

detection and titration methods,^{110,183,220–222} and changes in chemical composition are apparent through size exclusion chromatography, nuclear magnetic resonance (NMR) spectroscopy, and mass spectrometry.^{44,45,52,80,111,146,223–225}

DOM's aromatic content commonly decreases during an AOP and is reflected in a reduction in its SUVA.^{89,92,105,219–222} DOM's aromatics are responsible for UV absorbance around 254 nm, and their selective attack during AOP treatment is logical given the positive relationship between radical reactivity and DOM's SUVA (Figure 4b). The transformation of high molecular weight DOM fractions into lower molecular weight ones is observed both in [•]OH-based AOPs and in UV/chlorine treatment.^{226,227} In SO₄^{•-}-based oxidation, there is often simultaneous removal of higher molecular weight chromophores and mineralization.²²⁵ The incorporation of nitrite-sourced nitrogen into DOM molecules has been confirmed by ¹⁵N NMR analysis in a heat/PDS system.²²⁸

DOM transformation at the molecular level has been increasingly investigated by using high-resolution mass spectrometry methods, such as Fourier transform ion cyclotron resonance (FT-ICR) and Orbitrap mass spectrometry (MS).^{80,224,229,230} A reduction in aromaticity and in double-bond equivalence, co-occurring with an increase in the degree of oxidation and in aliphatic content (0.5 < O/C < 2 and 1 < H/C < 3), are often observed in various AOPs.^{139,225,231–233} DOM with a lower H/C ratio and greater aromaticity is more readily degraded in the UV/chlorine process rather than UV/H₂O₂ or UV/PS processes.²³² A recent study indicates that DOM moieties with lower H/C ratios (i.e., more aromatic) are favorable for ozone reactions, while those with high H/C ratios (i.e., more aliphatic) are favorable for [•]OH reactions.²²⁴ Additionally, diverse transformation products have been observed after AOP treatment. [•]OH often reacts via radical addition and produces numerous hydroxylated, oxygenated, and ring-cleavage products after reacting with DOM.^{224,234} SO₄^{•-} preferentially attacks the carboxyl-rich molecules in DOM via single electron transfer pathways and the stabilization of intermediate cationic radicals is often associated with decarboxylation reactions.^{223,234} Chlorine photolysis transforms DOM via multiple pathways and produces more aliphatic organics and it is difficult to characterize high molecular weight chlorine-containing products.⁸⁰

The composition of oxidized DOM can affect the subsequent water treatment processes and water qualities receiving the effluent. The polar and lower molecular weight organic byproducts (e.g., aldehydes, ketones, and carboxylic acids) are often biodegradable. Assimilable organic carbon (AOC), a measure of the labile fraction of DOC, is frequently observed to increase after UV/H₂O₂, UV photocatalysis, and

O_3/H_2O_2 treatment, though discrepancy exists.^{235–237} AOC is a critical parameter for controlling bacterial regrowth potential in water distribution systems, and the increases in AOC values suggest the reduction of water biostability after AOPs treatment. $\bullet OH$ -induced decarboxylation and deamination seem to reduce and enhance the assimilability, respectively, whereas both increases and decreases in assimilability are observed for hydroxylation and dealkylation reactions.²³⁵ There is some consensus about the order of magnitude of AOC concentrations that constitute biostable water. AOC levels from below 10 to 100 $\mu g/L$ are often considered to support only low levels bacterial growth in drinking water.²³⁸ Biological activated carbon or biological filters after AOPs can be helpful to reduce AOC levels.²³⁹ Further studies are suggested to evaluate the assimilability of AOP treated water and the dependence on water quality and radical exposure.

Additionally, low molecular weight carbonyls (LMWCs), such as α,β -unsaturated enedials and oxoalens, can form from DOM's phenolics during UV/ H_2O_2 treatment.^{81,223} The unsaturated carbonyl compounds, in particular α,β -unsaturated aldehydes, may pose potential health risks because of their high reactivity via nucleophilic addition to biomolecules.

The understanding of the DOM transformation is essential as it affects not only the elimination efficiency of TrOCs but also the environmental risks in receiving waters. The combination of bulk analytical methods, augmented with high-resolution MS, is needed to gain further unknown DOM transformation byproducts. Building upon prior work, there is evidence that improved molecular identification can be improved by applying hydrophilic interaction chromatography and high-performance size exclusion chromatography to separate DOM into fractions before analysis.^{240,241} The combination of chromatograph separation, multidimensional NMR, and FT-ICR MS can be helpful to improve the understanding of the transformation of DOM at molecular levels in the AOPs.

4.2. The Formation of Toxic Halogen Containing Byproducts. Halogenated organic byproducts (X-OBPs) can form as DOM transforms during AOPs, and X-OBPs are of high concern because of their potential human health risks.^{242–244} X-OBPs can form through multiple pathways in AOPs, including reactions of DOM with halogen radicals and/or hypohalous acid/hypohalite (HOX/OX^-). Halides in the water can be oxidized by primary radicals ($\bullet OH$, $SO_4^{\bullet -}$, etc.) to form halogen radicals. Chain reactions among halogen radicals and the oxidation of halides by common oxidants (e.g., ozone, PMS), reaction intermediates (e.g., Co^{3+}), and activation reagents (e.g., $CuFeO_2$) all produce HOX and/or OX^- .^{245–248} The generation of X-OBPs from HOX/OX^- is well-known, but debates continue regarding whether halogen radicals can react with DOM to form X-DBPs.^{87,249–251} Recent work in our group provides direct evidence of the difference of chlorine and bromine radicals in forming X-OBPs.^{56,135} Chlorine radicals (Cl^\bullet and $Cl_2^{\bullet -}$) react with DOM to form Cl-OBPs. The maximum total organic chlorine (TOCl) was around 1 μM and ~ 3 –7 μM at an oxidant exposure (CT value) of 4 – $8 \times 10^{-12} M s^{-1}$ for Cl^\bullet and 1.1 – $2.2 \times 10^{-10} M s^{-1}$ for $Cl_2^{\bullet -}$, respectively. In contrast, bromine radicals (Br^\bullet and $Br_2^{\bullet -}$) barely form Br-OBPs from reactions with DOM (i.e., $<0.5 \mu M$ at CT value of $\sim 10^{-9} M s^{-1}$ for $Br^\bullet/Br_2^{\bullet -}$).^{56,135} As such, $HOBr/OBr^-$ is the dominant oxidant to form Br-OBPs, whereas $Cl^\bullet/Cl_2^{\bullet -}$ and $HOCl/OCl^-$ can all contribute to Cl-OBP formation. So limiting HOX/OX^- formation in

AOPs is a crucial step in controlling X-OBP formation, especially for Br-OBPs. The formation of X-OBPs in different AOPs can vary significantly. For example, H_2O_2 -based AOPs do not usually form significant concentrations of X-OBPs because of the low level of both halogen radicals (because of the reversible reactions between $\bullet OH$ and Cl^- and the reduction by H_2O_2) and HOX/OX^- (because of the reduction by H_2O_2).^{62,135,252,253} In $SO_4^{\bullet -}$ -based AOPs, PMS is more reactive with background Cl^- and Br^- than PDS to generate $HOCl/OCl^-$ and $HOBr/OBr^-$, resulting in X-OBP formation.^{3,254} For AOPs using chlorine as the activating chemical (e.g., UV/chlorine), X-OBP is of great concern because of the DOM reactions with HOX/OX^- added or generated from bromide/iodide oxidation.²⁵⁵ $Cl^\bullet/Cl_2^{\bullet -}$ can not only contribute to Cl-OBP formation but also transform DOM to either increase or decrease Cl-OBP precursors.⁵⁶ More information about oxidation byproduct formation in AOPs can be found in an excellent review compiled by Ike and his colleagues.⁸⁷ Notably, despite the difference in the concentrations and formation mechanisms of X-OBPs in different AOPs, DOM is the major precursor of X-OBPs. Eliminating DOM concentrations is generally beneficial for controlling X-OBPs.

The formation of inorganic byproducts such as chlorite, chlorate, and bromate is also a concern in AOPs.^{83,256,257} Being different from X-OBPs, they are not derived from DOM. Instead, the quenching of their precursors (e.g., halogen radicals and HOX/OX^-) by DOM and DOM-derived reducing species (e.g., $O_2^{\bullet -}$, semiquinone radicals, excited state of DOM)^{10,217,258} could significantly reduce the formation of inorganic byproducts (Figure 6).^{82,83,257,259,260} For example, DOM inhibits chlorate formation in the Co^{2+}/PMS AOP by scavenging chlorine radicals and $HOCl/OCl^-$.⁸² DOM inhibits bromate formation in UV/PDS because of the elimination of bromine radicals and $HOBr/OBr^-$ by $O_2^{\bullet -}$ formed from UV irradiation of DOM, and the reduction of bromine radicals by DOM to Br^- .^{260,261} The presence of DOM also inhibits bromate formation in ozonation or ozone-based AOPs because of competitive reactions with $O_3/\bullet OH$ and the reactions with the formed $HOBr/OBr^-$.²⁵² However, Br-OBP formation increases instead.²⁵⁹ Forasmuch, the formation of both X-OBPs and halogen containing oxyanions should be considered in AOPs. Integrated processes, such as combination with membrane filtration, activated carbon adsorption, and ion exchange, can be desirable to reduce the adverse effects of these toxic byproducts.

4.3. The Necessity of Toxicity Assessment. Toxicity studies are highly recommended to evaluate the potential adverse health effects of treated water and wastewater, which are missing in majority of the studies. A few studies investigating the trade-offs between the effectiveness of AOPs in eliminating TrOCs versus the formation of toxic transformation products have produced conflicting toxicity observations. For example, after AOP treatment of Suwannee River DOM in a UV/chlorine AOP, a Chinese hamster ovary cell assay showed enhanced cytotoxicity.²²⁶ However, a reduction in toxicity has been reported when UV irradiation is combined with chlorine.^{255,262–264} Some studies have reported the increases in genotoxic activity after UV/ O_3 , UV/ O_3/H_2O_2 , O_3/H_2O_2 , and UV/ H_2O_2 treatment,^{235,265–267} while other studies have not.^{267,268} The differences in toxicity might be attributable to different water contaminants, the UV applied (LPUV or MPUV), oxidant dosage, or the bioassays used in the toxicity tests. *In chemico*, *in vitro*, and *in vivo* assays

may be applied to target health-relevant end points.^{269,270} For halogenated DBPs, the calculation of the sum of potency-weighted DBP concentrations can be used as an estimate of the cell cytotoxicity associated with known DBPs.²⁷¹ Moreover, establishing linkages between the transformation of specific functional groups with the changes of toxicological effects can provide important guidance on optimizing engineering designs. For example, granular activated carbon adsorption after AOP treatment effectively reduces toxicity by physically removing the transformation byproducts (typically carboxylic acids and aldehydes).^{19,266,272,273}

5. THE WAY FORWARD

5.1. Predicting the Abatement of TrOCs in AOPs. Mechanistic and machine learning models of TrOC degradation in AOPs are emerging.^{274–278} The degradation of TrOCs in an AOP is governed by the oxidant exposure (eqs 17–19). Models developed to predict the degradation of TrOCs in surface water and wastewater effluents show good predictive power with $\bullet\text{OH}$ -based AOPs such as the $\text{O}_3/\text{H}_2\text{O}_2$ and UV/ H_2O_2 systems.^{77,279} A key limitation has been parameterization of the DOM component of such models, as most require probe compound experiments to first obtain water-specific oxidant exposures during the treatment. While *in situ* probe measurement techniques are improving, most still require off-line experiments.^{279–282} For example, the decay of O_3 and the $\bullet\text{OH}$ probe compound such as *p*-chlorobenzoic acid needs to be measured first to get $\int[\text{O}_3]dt$ and $\int[\bullet\text{OH}]dt$ values before using eq 17 to predict the degradation.^{5,77} The steady-state concentrations of $\bullet\text{OH}$ must also be obtained using *p*-chlorobenzoic acid or rhodamine B as a probe compound before using eq 18.^{283,284} For AOPs with many types of RS, all the steady-state RS concentrations are needed (eq 19).

$$-\ln\left(\frac{[\text{TrOC}]}{[\text{TrOC}]_0}\right) = k_{\text{O}_3} \int[\text{O}_3]dt + k_{\bullet\text{OH}} \int[\bullet\text{OH}]dt \quad (17)$$

$$-\ln\left(\frac{[\text{TrOC}]}{[\text{TrOC}]_0}\right) = H \times k_{\text{UV}} + [\bullet\text{OH}]_{\text{SS}} \times k_{\bullet\text{OH},\text{TrOCs}} \times t \quad (18)$$

$$k' = k_{\text{RS},\text{TrOCs}} \times [\text{RS}]_{\text{SS}} \quad (19)$$

Few full-scale AOPs applications yet modify operations based on such models (e.g., digital twins) and rarely determine oxidant exposure or RS concentrations in their continuous flow reactors. Digital twins are emerging as viable design and operational tools for water treatment.²⁸⁵ For AOPs, the major uncertainty lies in the different DOM characteristics and their different reactivity with oxidants. The behavior of RS with ubiquitous inorganic ions such as Cl^- , Br^- , and CO_3^{2-} is better understood. Correlating DOM properties with RS may be a step forward to predicting the impacts of DOM composition on an AOP. Machine learning methods using fluorescence excitation–emission data describing the DOM already offers accurate prediction of the abatement of TrOCs in the ozonation of drinking water and wastewater effluent.²⁸⁶

Adjusting the oxidant dose and the intensity of illumination based on water quality promises attractive in energy cost savings while still achieving treatment goals, but it needs integrated online monitoring of DOM properties and their connection with reactivity. Further integration of existing mechanistic models that predict TrOC degradation pathways

and rate constants accounting for both synergistic and antagonistic effects is now the frontier for improving AOP models.^{274,275,287,288}

5.2. Understanding the Fundamental Reaction Mechanisms of DOM with Reactive Species. There are fundamental mechanisms in the reactions of DOM components that remain unclear. The role of DOM^* in AOPs is often neglected primarily for want of appropriate analytical methods. Though long-lived DOM radicals such as phenoxyl, alkoxy, peroxy, and percarboxyl radicals are known to have lower reactivity than RS such as $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, they can possibly outcompete the RS because of their higher concentrations. The presence of long-lived radicals has been verified using electron paramagnetic resonance and time-resolved spectroscopy determinations.^{51,289} However, methods for quantifying DOM^* levels are not available. There are even no published methods for measuring the specific PhO^* , RO^* , or ROO^* concentrations. Additionally, the reactions in the confined volumes of DOM – TrOCs and catalyst – DOM interactions are not yet well understood. In heterogenous AOPs the reactions happen on the catalyst's surface, in the solid–liquid boundary layer, or in the bulk solution.²⁹⁰ The role of DOM components on the surface or in the boundary layer is barely known. Heterogeneous distribution of $^1\text{O}_2$ and $\bullet\text{OH}$ on a microscale during solar irradiation of DOM has been found to accelerate the degradation of target TrOCs,⁶⁹ but the radical reaction chemistry in that microscale environment is not yet well studied. As such, localized quantification methods for DOM^* and radicals are badly needed.

5.3. Developing AOPs that Exploit DOM. The typical focus of an AOP is on designing better catalysts that generate more RS. Exploiting DOM has only rarely been considered. Insulating target TrOCs from DOM can reduce DOM's inhibitory effects. In doing so, rational structural design to improve selectivity (size-selective properties for example, or selective surface interactions) is critical.^{19,291–294} When the pore sizes of the materials are tailored to separate DOM from the TrOCs by size-exclusion, the DOM's impacts on TrOCs adsorption and oxidation can be minimized. This is how yolk–shell Co/C nanoscale reactors work.^{291,292,295} Conjugating molecularly imprinted materials with photocatalysts can also improve the efficiency of photocatalytic processes.²⁹⁶ Another approach to consider is to take advantage of the diversity of DOM's properties. It can perhaps provide metal ligands for complexing oxidants and reductants or serve as an organic activator for some Fenton-like reactions. Opportunities exist to make DOM serve to accelerate the degradation of TrOCs in AOPs. DOM's quinones and quinone-like moieties are redox-active, and they can be exploited in reactions to generate RS or degrade TrOCs.²⁹⁷ A recent study has shown their role in activating H_2O_2 to generate $\bullet\text{OH}$ and $^1\text{O}_2$.¹⁹⁴ Another has demonstrated that they can reduce Fe(III) to Fe(II) to activate PMS in $\text{SO}_4^{\bullet-}$ generation.^{109,194} DOM is ubiquitous. It should be exploited to promote TrOC removal.

5.4. Improving Understanding the Formation of Byproducts and Their Toxicity. AOP development also needs to attend more to the formation of oxidation byproducts and to their toxicity. Many halogenated organic byproducts are regulated in certain jurisdictions, but pharmaceuticals rarely are.²⁴² Tools such as transient spectroscopy, ultra-high-resolution mass spectrometry, and three-dimensional NMR spectroscopy can help to elucidate the relationships between byproduct formation and DOM transformation at nanosecond

to microsecond time scales and on the molecular level.^{41,56,80,111,138,224,298–300} In terms of toxicity, the commonly used effect-directed analysis inevitably causes a loss of volatile and/or polar components from the samples.³⁰¹ Reactivity-directed analysis using organic electrophilic molecules may be a better choice for determining the toxicity of byproducts generated from DOM.^{81,302} Bioassays employing bacteria, invertebrates, algae, plants, fish, and different water compositions should be employed to evaluate the toxicity from multiple perspectives. A multidimensional understanding of byproduct formation is required. The mutual relationships involved in DOM's transformation, concentrations, the types of byproducts generated, and their cytotoxicity and genotoxicity are all important.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.2c01017>.

UV–vis absorbance spectra of some nanoscale materials, main reactive species produced in different AOPs, second-order reaction rate constants of water components and DOM with radicals, and characteristics of source water and secondary wastewater effluent from different sources (PDF)

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Notes

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■ ABBREVIATIONS

DOM	Dissolved organic matter
SRFA	Suwannee River fulvic acid
FAs	Fulvic acids
HAs	Humic acids
NOM	Natural organic matter
AOPs	Advanced oxidation processes
TrOCs	Trace organic contaminants
•OH	Hydroxyl radical
SO ₄ ^{•-}	Sulfate radical
O ₂ ^{•-}	Superoxide ion
¹ O ₂	Singlet oxygen
H ₂ O ₂	Hydrogen peroxide
PMS	Peroxymonosulfate
PDS	Peroxydisulfate
HOCl	Hypochlorous acid
NH ₂ Cl	Monochloramine
NHCl ₂	Dichloramine
Cl•	Chlorine atom
Cl ₂ ^{•-}	Dichloride radical anion
RS	Reactive species
CO ₃ ^{•-}	Carbonate radical
Br•	Bromine atom
Br ₂ ^{•-}	Dibromide radical anion
EfOM	Effluent organic matter
³ DOM*	Triplet excited state of DOM
DOM•	DOM radicals
[RS] _{ss}	Steady-state concentration of reactive species
r _{RS} ^f	Generation rate of RS
k _{RS} ^d	Consumption rate of RS
SUVA ₂₅₄	The specific UV absorbance at 254 nm
ε ₂₅₄	Molar absorptivity value at 254 nm
AC	Activating chemicals
f _{DOM}	DOM's relative contribution to radical scavenging
F	The attenuation of light absorption by DOM competition
LPUV	Low pressure UV
MPUV	Medium pressure UV
k _{•OH,DOM}	The second-order reaction rate constant of •OH with DOM
k _{SO₄^{•-},DOM}	The second-order reaction rate constant of SO ₄ ^{•-} with DOM
k _{Cl•,DOM}	The second-order reaction rate constant of Cl• with DOM
k _{Cl₂^{•-},DOM}	The second-order reaction rate constant of Cl ₂ ^{•-} with DOM
k _{Br•,DOM}	The second-order reaction rate constant of Br• with DOM
k _{Br₂^{•-},DOM}	The second-order reaction rate constant of Br ₂ ^{•-} with DOM
k _{CO₃^{•-},DOM}	The second-order reaction rate constant of CO ₃ ^{•-} with DOM

E2/E3	The absorbance at 254 nm divided by the absorbance at 365 nm
PAHs	Polycyclic aromatic hydrocarbons
PFAS	Perfluorooctanesulfonate
P ^{•+}	Intermediate radical cation
P _(-H) [•]	Neutral intermediate radical
P _{ox}	Oxidation products of intermediate radical
DOM _{ao}	Antioxidants in the DOM
Trp ^{•+}	Tryptophan radical cation
DMABN ^{•+}	4-(dimethylamino) benzonitrile radical cation
ADN _(-H) [•]	Neutral adenine radical
SRNOM	Suwannee River NOM
PhO [•]	Phenoxy radicals
RO [•]	Alkoxy radicals
ROO [•]	Peroxy radicals
SQ ⁻	Semiquinone radicals
NMR	Nuclear magnetic resonance
LMWCs	Low molecular weight carbonyls
X-OBPs	Halogenated organic byproducts
HOX/OX ⁻	Hypohalous acid/hypohalite

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