Photosensitizing and inhibitory effects of ozonated dissolved organic matter on triplet-induced contaminant transformation

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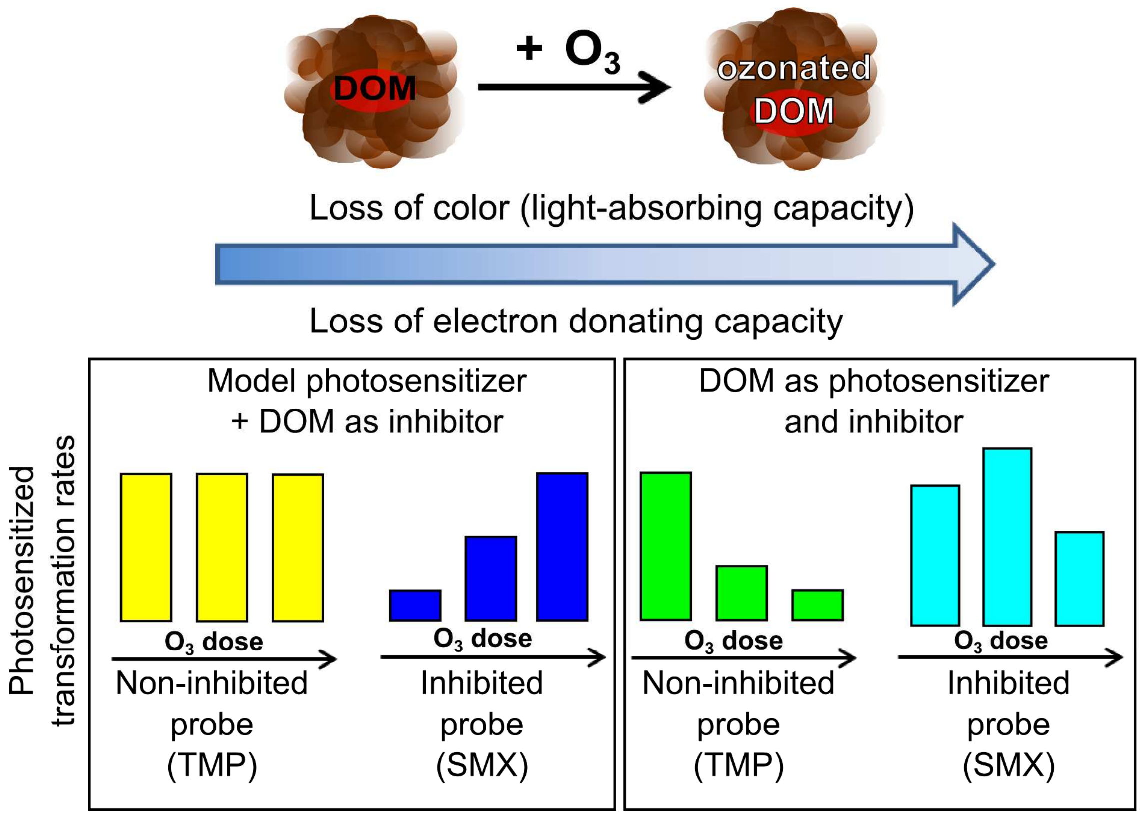

Graphical Abstract

Abstract

Dissolved organic matter (DOM) is both a promoter and an inhibitor of triplet-induced organic contaminant oxidation. This dual role was systematically investigated through photochemical experiments with three types of DOM of terrestrial and aquatic origins that were pre-oxidized to varying extents by ozonation. The inhibitory effect of DOM was assessed by determining the 4-carboxybenzophenone photosensitized transformation rate constants of two sulfonamide antibiotics (sulfamethoxazole and sulfadiazine) in the presence of untreated or pre-oxidized DOM. The inhibitory effect decreased with increasing extent of DOM pre-oxidation, and was correlated to the loss of phenolic antioxidant moieties, as quantified electrochemically, and to the loss of DOM ultraviolet absorbance. The triplet photosensitizing ability of pre-oxidized DOM was determined using conversion of the probe compound 2,4,6-trimethylphenol (TMP), which is unaffected by DOM inhibition effects. DOM-photosensitized transformation rate constants of TMP decreased with increasing DOM pre-oxidation and were correlated to the concomitant loss of chromophores (i.e., photosensitizing moieties). The combined effects of DOM pre-oxidation on the inhibiting and photosensitizing properties were assessed by phototransformation experiments of the sulfonamides in DOM-containing solutions. At low extents of DOM pre-oxidation, sulfonamide phototransformation rate constants remained either unchanged or slightly increased, indicating that the removal of antioxidant moieties had larger effects than the loss of photosensitizing moieties. At higher extents of DOM pre-oxidation, transformation rates declined, mainly reflecting the destruction of photosensitizing moieties.

Introduction

Dissolved organic matter (DOM) is a heterogeneous, complex mixture of organic molecules and is ubiquitous in natural waters.[1] DOM plays a central role in aquatic photochemical processes[2-4] that are important for biogeochemical element cycles as well as pollutant dynamics. While DOM has long been known to enhance organic pollutant phototransformation by acting as a sensitizer, it was recently demonstrated that DOM may also play the role of an inhibitor of triplet-induced contaminant transformation [5-7] as well as direct photooxidation reactions.[8]

The formation of excited triplet states of DOM ($^3DOM^*$) is initiated by the absorption of light by chromophoric moieties of DOM followed by the formation of excited singlet states of DOM ($^1DOM^*$). Subsequent rapid intersystem crossing converts $^1DOM^*$ to $^3DOM^*$. The latter are key reactive species initiating the oxidative transformation of various aquatic contaminants.[3, 9, 10] The importance of $^3DOM^*$ as photooxidants was verified by using low molecular weight aromatic ketones as models mimicking the photosensitizing characteristics of DOM.[11-14]

More recently, the inhibitory properties of DOM on $^3DOM^*$-induced contaminant transformations were recognized.[5-7] Inhibition is hypothesized to result from contaminant intermediates, formed via the oxidation of the parent compound through a reactive encounter with $^3DOM^*$, being transformed back to the parent compound by accepting an electron from antioxidant moieties present in the DOM. More specifically, phenolic moieties are considered to be the major antioxidant groups in DOM.[15] The importance of phenols as antioxidants in DOM was supported by demonstrating that low molecular weight model phenolic compounds at micromolar concentrations were capable of inhibiting triplet-induced reactions.[7]

Despite the successful use of model aromatic ketones and phenolic compounds, the detailed chemical structure and nature of the moieties responsible for the photosensitizing and inhibiting effects of the DOM on triplet-induced contaminant transformation remain to be clarified in more detail. A promising approach to identify a specific group of moieties in the DOM involves exposing DOM to specific chemical reactants that inactivate the target moieties. Such an approach was recently used by Blough, del Vecchio and coworkers who assessed the role of aromatic ketones and quinone moieties in the electronic absorption and fluorescence spectra of DOM.[16] Treatment of the DOM with the reducing agent sodium borohydride ($NaBH_4$) transformed the target carbonyl groups into hydroxy (alcohol) groups, resulting in a preferential loss of DOM absorption in the visible range as well as an enhanced fluorescence with blue-shifted spectra. These results support the hypothesis that DOM electronic absorption in the visible range is largely due to donor-acceptor complexes between electron-rich aromatic donors and carbonyl-containing acceptors.[4, 17, 18] Two follow-up studies showed that borohydride treatment reduced the rate of the triplet-induced transformation of the probe compound 2,4,6-trimethylphenol[19] and of photosensitized singlet oxygen production,[20] reinforcing the role of aromatic ketones as key DOM photosensitizer moieties in these processes.

The main motivation for the present study was to selectively deplete the antioxidant moieties in the DOM to test their involvement in the inhibition of triplet-induced transformations of contaminants. With this objective in mind, in a recent study, we oxidized different DOMs with three chemical oxidants, namely ozone, chlorine and chlorine dioxide, that are currently used in water treatment.[21] Both the electronic absorption spectrum and the electron donating capacity (EDC) of treated and untreated DOM were measured to characterize the chemical changes of the DOM. The EDC was measured using mediated electrochemical oxidation (MEO) as described elsewhere.[22] It expresses the number of electrons that can be withdrawn from a unit mass of material under well-defined applied reduction potentials and solution pH. EDC values are well suited as quantitative descriptors of the antioxidant capacities of a material,[23-25] and, for DOM, they were shown to be well correlated to DOM phenolic contents.[15] Treatment of DOM with any of the three aforementioned oxidative methods led to decreases in the EDC values and, at the same time, in the UV and visible absorption. The differential decreases in EDC values and absorption coefficients indicated that not only antioxidant moieties, but also further chromophoric DOM components were lost by oxidation.

In this study, we investigated the effect of DOM ozonation on the triplet-induced transformation of sulfamethoxazole (SMX) and sulfadiazine (SD), two sulfonamide antibiotics chosen as representatives for contaminants exhibiting concomitantly promotion and inhibition of the transformation rates in the presence of DOM.[5-7] In a first series of kinetics experiments, the model photosensitizer 4-carboxybenzophenone (CBBP) was employed to induce the phototransformation in the presence of untreated and ozone-treated DOM. This set of experiments assessed the inhibitory effects of the DOM. In a second, analogous experimental series, untreated and O_3-treated DOM served as both photosensitizer and inhibitor of the phototransformation. Besides SMX and SD, the well-established photochemical probe compound 2,4,6-trimethylphenol (TMP),[11] which is not affected by inhibition, was used to benchmark the modified photosensitizing strength of the treated DOMs.

Materials and Methods

Chemicals and humic substances. All chemicals were from commercial sources and used as received: 2,4,6-trimethylphenol (TMP) [CAS 527-60-6] (EGA Chemie, 99%), sulfamethoxazole (SMX) [723-46-6], sulfadiazine (SD) [68-35-9] (≥99%), 4-carboxybenzophenone (CBBP) [611-95-0] (>99%, all Sigma-Aldrich), *tert*-butanol (t-BuOH) [75-65-0] (≥99.7%), all inorganic chemicals were either from Fluka or Merck. Humic substances: Suwannee River humic acid (SRHA, catalogue number: 2S101H), Suwannee River fulvic acid (SRFA, 2S101F) and Pony Lake fulvic acid (PLFA, 1R109F) were obtained from the International Humic Substances Society (IHSS, St. Paul, MN). Chemicals used for electrochemical analyses are specified elsewhere.[22]

Preparation of solutions. Aqueous solutions (including ozone stock solutions and HPLC eluents) were prepared using deionized water from Milli-Q (Millipore) or Barnsteadt water purification systems. Organic chemical stock solutions (all 1 mM) and standard DOM stock solutions (100 $mg_C\ L^{-1}$) were prepared with buffered water (5 mM phosphate, pH 8). Ozone stock solutions were produced and standardized as described previously.[21]

Ozonation. DOM solutions (nominal concentration after reagent mixing of 0.83 $mmol_C\ L^{-1}$ = 10 $mg_C\ L^{-1}$) and blank solutions (containing no DOM) at pH 7 (all 50 mM phosphate buffer) were ozonated in a series of identical glass reaction vessels (50 or 100 mL, Schott, Germany) in the absence and presence (5 mM) of t-BuOH as a hydroxyl radical scavenger. Aliquots of the ozone stock solution were added to reaction vessels under vigorous mixing at volumes yielding specific ozone doses of 0–1.12 $mmol_{ozone}\ (mmol_C)^{-1}$. After addition of ozone, the vessels were closed, removed from the stirrer and stored at room temperature (22 °C) for 2h. Subsequently, residual ozone was removed by purging with helium for 20 min. The effect of t-BuOH as a hydroxyl radical scavenger on changes in EDC and optical properties during ozonation was discussed in detail in our previous study.[21]

Irradiation experiments. A merry-go-round photoreactor system was employed equipped with a medium pressure mercury lamp (Heraeus Noblelight model TQ 718, operated at 500W) and a 0.15 M sodium nitrate filter solution that minimizes direct phototransformation reactions. The experimental setup was described in detail previously.[6] Aliquots of ozonated DOM solutions and blanks were supplemented either with only the target compounds (i.e., SMX, SD and TMP) or additionally with the excited triplet state sensitizer CBBP and diluted to yield final concentrations of 0.19 $mmol_C$ L^{-1} = 2.3 mg_C L^{-1} for DOMs, 5 μM for target compounds and 50 μM for CBBP. The solution pH was adjusted to 7.0 by addition of phosphoric acid (11.5 mM final buffer concentration) prior to irradiation. This pH was chosen to match the pH used in EDC measurements.[21] A 20 mL sample of each solution was filled into capped quartz-glass tubes and irradiated for 5 min (all CBBP – target compound combinations), 100 min (DOMs – TMP), 225 min (DOMs – SMX/SD). These irradiation times were determined based on preliminary kinetic irradiation experiments. During irradiation six aliquots of each 400 μL were withdrawn at equidistant time intervals and analyzed, immediately or stored at 4°C, by high-performance liquid chromatography (HPLC). Details on HPLC equipment and methods employed to quantify the concentration of the target compounds (SMX, SD and TMP) are available elsewhere.[6, 7] To confirm that t-BuOH had no effect on the phototransformation kinetics of the target compounds, control irradiation experiments were conducted with DOM solutions that were ozonated in the absence of t-BuOH but were subsequently amended with 5 mM t-BuOH prior to the irradiations.

Kinetic data analysis. Pseudo-first-order rate constants for the transformation of the target compounds were determined by linear regression of natural logarithmic concentration data versus irradiation time. These rate constants were submitted to correction depending on the type of experiment, as described in the following. (1) Irradiation experiments with CBBP as the photosensitizer: The correction procedure is described in detail elsewhere.[6] Briefly, in a first step, the rate constant for CBBP-photoinduced transformation was corrected for contributions from other phototransformation pathways (i.e., sensitization by DOM and direct photolysis), as detailed in the Supporting Information (SI), Tables S4–S9. In a second correction step, the light screening by DOM was accounted for (see correction factors in the SI, Tables S1–S3). The obtained corrected rate constants are denoted as $k^{(2)}_{CBBP,DOM,(O_3-dose)}$ (s^{-1}), the subscript '(O_3-dose)' indicating the ozone dose used to treat the DOM prior to the irradiation experiments. (2) Irradiation experiments with untreated and ozonated DOM as the photosensitizer: The rate constants were corrected for light screening following a previously described method[6] (see correction factors in the SI, Tables S1–S3). Subsequently, the contributions from direct phototransformation, which became important in experiments conducted with highly ozonated DOM, were subtracted from the rate constants. The corrected rate constants after these two correction steps are denoted as $k^{(2)}_{DOM,(O_3-dose)}$, in analogy to the terminology used above.

Results and Discussion

Inhibitory effect of untreated or ozonated DOM on CBBP-induced phototransformations. The phototransformation kinetics of TMP, SMX and SD were measured using CBBP as a model photosensitizer and untreated or ozonated DOM as potential inhibitors. CBBP was chosen because its photoexcited triplet state was previously employed to investigate the inhibitory effect of DOM on the triplet-induced oxidation of aquatic contaminants.[5, 6] From the pseudo-first-order rate constants, obtained and corrected as described in the previous section (see SI, Tables S4–S9 for the rate constant values), the inhibition factor, *IF*, was calculated according to equation 1.

$$IF = k^{(2)}_{CBBP,DOM,(O_3-dose)} / k^{(2)}_{CBBP} \quad (1)$$

where $k_{CBBP}^{(2)}$ is the corrected rate constant determined for samples without DOM. The results of the present series of experiments are displayed in Figure 1 in terms of *IF* versus the ozone dose applied in the pre-oxidation treatment of each DOM. Note that an *IF* value of unity describes systems in which DOM has no inhibitory effect. *IF* values <1 and >1 signify inhibited and enhanced transformation in the presence of DOM, respectively.

We first consider the *IF* of DOM for the transformation of TMP, a commonly used probe compound for excited triplet states in the aquatic environment[19, 26, 27] that is not subject to inhibition by DOM.[5] Inhibition factors for TMP were close to unity and independent of the ozone dose used for DOM pre-treatment (Figure 1a–c), demonstrating that neither the excited triplet state of CBBP ($^3CBBP^*$) nor the transformation of TMP were affected by untreated and ozonated DOM. Independent direct evidence that the lifetime of $^3CBBP^*$ is not affected by the presence of DOM at concentrations <30 mg_C L^{-1} has been provided in a recent $^3CBBP^*$ quenching study.[28]

In contrast to the TMP data, *IF* values for SMX and SD were significantly lower than unity in experiments with untreated DOMs (Figure 1d–f), revealing the inhibitory effect of the DOM. The *IF* values increased monotonically − and hence inhibition decreased − with increasing specific O_3 doses for DOM pre-treatment. The differential increase in *IF* values became smaller at higher specific ozone doses. All DOMs showed similar trends with one exception, for which we currently do not have an explanation: the *IF* values of SRHA ozonated in the presence of the hydroxyl radical scavenger t-BuOH exhibited a maximum of $IF \approx 0.8$ at a specific O_3 dose of ≈0.25 $mmol_{ozone}$ $mmol_C^{-1}$ and subsequently decreased for more extensive ozonation (Figure 1d). The initial *IF* values for untreated SRHA and SRFA were ~0.3, whereas for PLFA they varied between 0.53 (SMX) and 0.7 (SD). These values confirm previous findings[6] showing that allochthonous (terrestrially-derived) aquatic DOMs, such as

SRHA or SRFA, are better inhibitors than mostly autochthonous aquatic DOMs such as PLFA. Moreover, for SRFA and PLFA *IF* values appeared to reach a limit of ≈1 at high ozone doses (Figure 1e, f), indicating that the inhibitory effect was entirely eliminated. In general, for SMX the increases in *IF* values with an increasing degree of DOM ozonation were more pronounced for ozonation in the presence of t-BuOH than in its absence (Figure 1d–f). Furthermore, for SMX the *IF* values slightly exceeded unity for pre-treatment of PLFA with high ozone doses in the presence of t-BuOH. Values larger than unity may have resulted from the formation of DOM moieties with photosensitizing character, which could enhance the phototransformation of SMX. In general, however, for the phototransformation of SMX and SD the increases in *IF* values with increasing specific ozone doses applied in DOM pre-oxidation are consistent with the expectation: Antioxidant moieties of the DOM were increasingly removed at increasing oxidant doses, resulting in decrease of the inhibitory effects of DOM on triplet-induced transformation of SMX and SD.

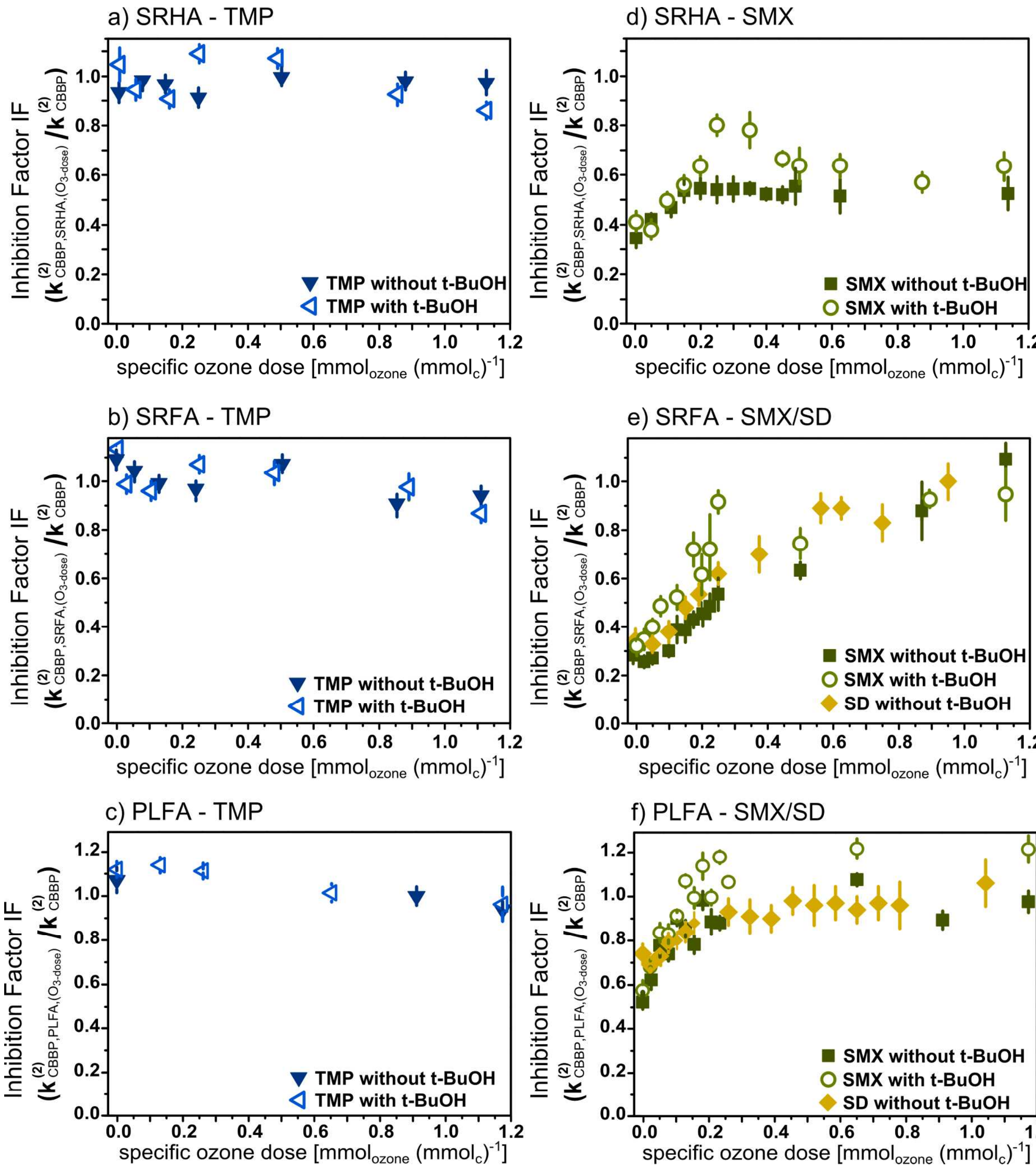

Figure 1. Inhibition factor (*IF*) of dissolved organic matter (DOM, 2.3 mg_C L^{-1}) on the $^3CBBP^*$-induced phototransformation of the target compounds 2,4,6-trimethylphenol (TMP), sulfamethoxazole (SMX) and sulfadiazine (SD) as a function of the specific ozone dose ($mmol_{ozone}$ $(mmol_C)^{-1}$). The three standard DOMs Suwannee River humic acid (SRHA), Suwannee River fulvic acid (SRFA) and Pony Lake fulvic acid (PLFA) were investigated. Ozonation was carried out both in the absence and presence of t-BuOH. a–c (left-hand side

panels): Data for TMP in the presence of the selected DOMs. d–f (right-hand side panels): Data for SMX/SD in the presence of the selected DOMs. Experiments for the combination SD/SRHA were not conducted. Error bars give 95% confidence intervals.

Relationship between inhibition factor (*IF*) for CBBP-induced phototransformation and electron donating capacity (EDC) of ozonated DOM. In our previous studies,[6, 7] the *IF* values for the triplet-induced transformation of anilines and sulfonamide antibiotics were shown to be related to the concentration of a specific DOM or model antioxidant (AO). For both SMX and SD, a one-channel reaction model[6] and the corresponding equation (of the type of the following equation 2) were found to satisfactorily fit the data.

$$IF([\mathrm{AO}]) = \frac{1}{1 + [\mathrm{AO}]/[\mathrm{AO}]_{1/2}} \quad (2)$$

where $[\mathrm{AO}]_{1/2}$ is the concentration of antioxidant needed to slow down the reaction by 50%. While the concentration and type of antioxidant moieties in the untreated and ozonated DOM are not characterized in detail, the electron donating capacity (EDC) is a useful indicator of such moieties[15] and is available from a recent study.[21] In a simple model, we assume the EDC for a given type of DOM, untreated or subjected to ozonation, to be directly proportional to the concentration of antioxidant moieties in the same DOM, as expressed by the proportionality constant κ (equation 3).

$$EDC = \kappa \times [\mathrm{AO}] \quad (3)$$

Inverting equation 2 and substituting [AO] using equation 3 leads to the following linear relationship between (1/*IF*) and *EDC* (equation 4):

$$\frac{1}{IF} = 1 + EDC / EDC_{1/2} \quad (4)$$

with $EDC_{1/2} = \kappa \times [AO]_{1/2}$.

Figure 2a displays plots of (1/*IF*) versus *EDC* values for the tested DOMs and the corresponding linear regression lines (see SI, Table S10 for a collection of fitting parameters). Linear regression fits were performed grouping data for SRFA and PLFA as well as data with and without t-BuOH used in the ozonation pre-treatment of DOM. The SRHA data were fitted separately from the two fulvic acids because of markedly different trends between SRHA the fulvic acids. SMX and SD data were also treated separately, given that $[AO]_{1/2}$ (see equations 2-4) are expected to be compound-specific.[5-7] Data fits were satisfactory in all cases. This is particularly true for the fulvic acid data that yielded high coefficients of determination ($R^2 \approx 0.92$). These high R^2 values suggest that EDC is an adequate descriptor variable of the inhibition efficiency of DOM on the triplet-induced phototransformation of these sulfonamides. For SMX, the slope parameter value (i.e., $1/EDC_{1/2}$) determined for SRHA was significantly smaller (i.e., by a factor of ≈2.8) than that determined for the fulvic acids. This finding implies that a much larger decrease in the EDC of the humic acid than of fulvic acids was required to obtain the same effect on *IF*, suggesting a more effective inhibition by the antioxidant moieties in the fulvic acids than in SRHA. This conclusion is consistent with the stronger inhibition (i.e., smaller *IF*) obtained with untreated SRFA than with untreated SRHA (see Figure 1d, e), even though the EDC of SRHA is much larger (by about 80%) than that of SRFA.[15] For SD almost the same slope parameter value was obtained as for SMX, confirming the similarity in the photochemical behavior of these two sulfonamides that has been recently described elsewhere.[29] The ordinate intercepts of the regression lines in Figure 2a are generally below the value of 1 predicted by equation 4 and indicate a deviation of the experimental data from the simple model described above. It is possible that the deviation resulted from the presence of antioxidant moieties in the DOMs that contributed to the EDC (measured by MEO) but that were not reactive with triplet-induced transformation intermediates of SD and SMX. Regressions were also performed for the individual data sets (see SI, Figure S1 and Tables S11-S13). The results of these regressions were consistent with those obtained from the regressions of the pooled data but had larger errors in the fitting parameters, reflecting the smaller data sets.

As EDC changes were found to be positively correlated with the specific absorption coefficient (SUVA) changes during ozonation of the three DOMs used in this study,[21] $SUVA_{254}$ (the coefficient for the wavelength of 254 nm) was employed as a secondary proxy to predict inhibition of triplet-induced transformations. Corresponding overall correlations and linear regression lines as for the EDC are displayed in Figure 2b. While the trends in Figure 2b are in good qualitative agreement with those shown in Figure 2a (see the preceding discussion), the scattering of the data is larger and the quality of the fits lower (see SI, Table S14). For the individual data sets (see SI, Figure S2 and Tables S15-S17) the larger scattering in the data as compared to the regressions using the EDC is confirmed. Despite the weaker performance of $SUVA_{254}$ than EDC as a predictor of inhibition of triplet-induced transformation, $SUVA_{254}$ might be a useful proxy when EDC data are missing and/or cannot be readily determined.

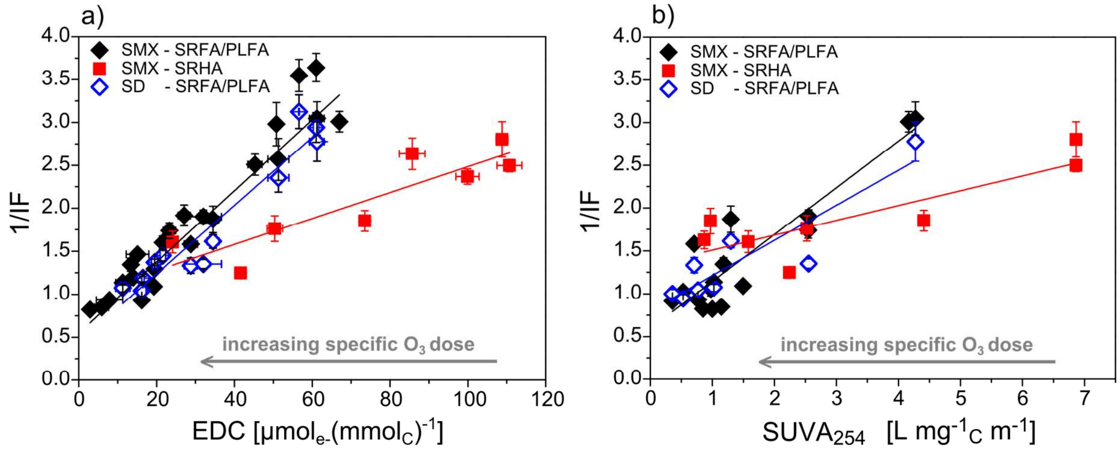

Figure 2. Correlations between the inverse inhibition factor (1/*IF*) and a) the electron donating capacity (*EDC*) and b) the specific absorption coefficient ($SUVA_{254}$) of DOMs ozonated in the presence and absence of t-BuOH for the CBBP-induced phototransformation of sulfamethoxazole (SMX) and sulfadiazine (SD). For SMX, separate correlations were performed for the pooled SRFA/PLFA data and for the SRHA data. Horizontal error bars correspond to the standard deviations of two duplicate EDC measurements. Vertical error bars give 95% confidence intervals of single kinetic measurements. 1/IF > 1: Inhibition; 1/IF < 1: Enhanced transformation.

Phototransformation sensitized by ozonated DOM. Figure 3 displays the pseudo-first-order rate constants for the transformation of TMP and SMX photosensitized by increasingly ozonated SRHA, SRFA and PLFA, normalized to the respective rate constants obtained in experiments with the corresponding non-ozonated DOMs, i.e. $k^{(2)}_{DOM,(O_3-dose)} / k^{(2)}_{DOM,(O_3-dose)=0}$ (see the SI, Figures S3–S5 for the raw kinetic data, and Tables S18–S23 for the numerical values of the rate constants and the applied corrections, according to the details given in the *Material and Methods* section). The relative rate constants of TMP transformation decreased with increasing specific ozone doses in a similar manner for all three DOMs (Figure 3a–c).

DOMs treated with high specific ozone doses retained a residual photochemical activity for TMP transformation (i.e., 7–20% in terms of rate constants with respect to untreated DOM). This activity was possibly associated with photosensitizing moieties in the DOM that either reacted slowly with ozone and/or were newly formed during ozonation. Aromatic ketones are plausible candidates for such photosensitizing moieties resistant to ozone and formed during ozonation of DOM.[30] In general, the indirect phototransformation rates of TMP were expected to correlate to DOM light absorption – and therefore to the absorption coefficient of the DOM – and to the capability of the chromophores to form oxidizing excited triplet states. We previously reported the specific spectral absorption coefficients a_λ (L mg_C^{-1} m^{-1}) for all three studied DOMs, both for the untreated and the ozonated materials.[21] We here used the reported coefficients to calculate wavelength-weighted specific absorption coefficient ratios $\frac{\bar{a}_{DOM,(O_3-dose)}}{\bar{a}_{DOM,(O_3-dose)=0}}$ (Figure 3a–c; calculation details and numerical values are provided in the SI, Text S1 and Tables S24 and S25). Except for SRHA ozonated in the absence of t-BuOH, the specific absorption coefficient ratios decreased more strongly with increasing ozone dose than the relative TMP indirect phototransformation rate constants. This finding is also evidenced by the non-linear dependence of TMP rate constants versus absorption coefficient ratios shown in the SI, Figure S6 (panels b and c). It may indicate that chromophores involved in the indirect phototransformation of TMP were more resistant to ozonation than the whole ensemble of DOM chromophores absorbing at the considered wavelengths. A similar finding was recently reported for ozonated wastewaters irradiated with simulated solar light: the quantum yield of singlet oxygen formation increased with increasing applied ozone doses.[31]

Compared to TMP, the relative rate constants of SMX (Figure 3d–f) showed very different dependencies on the specific ozone doses (see also the SI, Figure S6 for an alternative representation of the data). For SRHA and SRFA (both ozonation treatments), and PLFA ozonated in the absence of t-BuOH, at low specific doses (i.e., <0.2 $mmol_{ozone}$ $(mmol_C)^{-1}$) the relative rate constants of SMX were nearly unchanged, at values of approximately 1−1.25. At higher specific ozone doses these relative rate constants tended to decrease, albeit to smaller extents than determined for TMP. The data set for PLFA ozonated in the presence of t-BuOH deserves special consideration as relative SMX phototransformation rate constants reached much higher values than in the absence of t-BuOH. The relative rate constants for PLFA ozonated in the presence of t-BuOH doubled at low specific ozone doses with respect to untreated PLFA, decreased markedly at specific doses larger than 0.2 $mmol_{ozone}$ $(mmol_C)^{-1}$), and finally converged with the values measured for PLFA ozonated in the absence of t-BuOH. The marked increase in the rate constants at low specific ozone doses for the O_3/t-BuOH-treated PLFA correlates well with the observed strong reduction in EDC of treated PLFA[21] and virtual disappearance of any inhibition of CBBP-induced phototransformation of SMX (Figure 1f). In conclusion, the higher relative rate constants for SMX than for TMP phototransformation observed with ozonated DOM may be explained by the partial removal of antioxidant moieties, which weakens the inhibitory effect of DOM on SMX phototransformation.

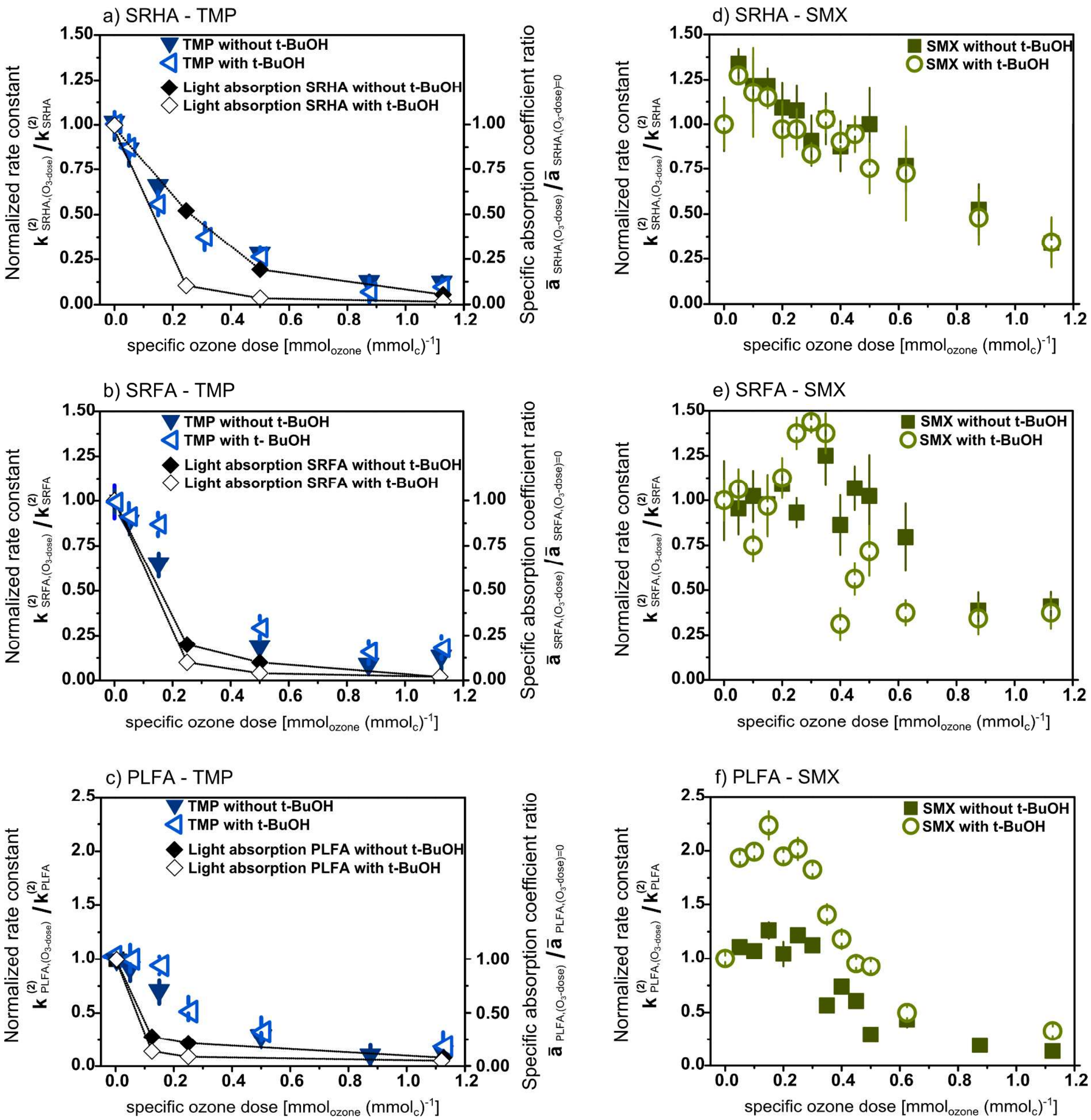

Figure 3. Normalized phototransformation rate constants, $k^{(2)}_{DOM,(O_3-dose)} / k^{(2)}_{DOM,(O_3-dose)=0}$, of (a–c) 2,4,6-trimethylphenol (TMP) and (d–f) sulfamethoxazole (SMX) sensitized by the three standard DOMs, Suwannee River humic acid (SRHA), Suwannee River fulvic acid (SRFA) and Pony Lake fulvic acid (PLFA), as a function of the specific ozone dose applied during DOM pre-oxidation (in the presence or absence of t-BuOH as a hydroxyl radical scavenger). The specific absorption coefficient ratios (see text for definition) of the treated DOMs are

also shown in (a–c) for comparison (second y-axis). Note the different y-axes scales for PLFA. Error bars indicate 95% confidence intervals.

In the following we present an attempt to assess exclusively the inhibitory effect of pre-oxidized DOM on the phototransformation of SMX, using the data from Figure 3 and compensating for the changes in photosensitizing activity of the DOM. TMP is assumed to be unaffected by the inhibitory effect of untreated or pre-oxidized DOM, as supported by the results of previous studies and of the experiments with CBBP presented above (Figure 1). Let us further assume that the rate constants for the transformation of SMX photosensitized by untreated and ozonated DOM are directly proportional to the corresponding rate constants for TMP. Then, the ratio of the normalized rate constants for SMX and TMP, as given in Figure 4, can be considered as a relative inhibition factor (normalized to the inhibition factor of the untreated DOM). Since the data set for SMX was larger than the one for TMP, the relative rate constants for the phototransformation of TMP were linearly interpolated from its data in Figure 3 to match the specific ozone dose values of the DOM used for SMX phototransformation. Figure 4 shows that treatment of all three DOMs with low specific ozone doses (smaller than ≈0.3 $mmol_{ozone}$ $(mmol_C)^{-1}$) resulted in a marked monotonic increase in the ratio of the relative rate constants. This trend is qualitatively similar to the one observed for the CBBP photosensitization experiments (Figure 1). The ratio of relative rate constants tended to level off or progress through a maximum for the DOMs treated with higher specific ozone doses. The maximum of the ratios was particularly pronounced for PLFA ozonated in the presence of t-BuOH (Figure 4c). For this data series, the enhancement of SMX phototransformation upon PLFA ozonation reached much higher values (≈ 3.8) than the maximum enhancement factor observed in CBBP experiments (≈ 1.9, Figure 1f). Such an additional enhancement can either be attributed to a stronger inhibition of the DOM antioxidant moieties on $^{3}DOM^{*}$-induced than on $^{3}CBBP^{*}$-induced transformation of SMX, or to the formation of photosensitizing moieties during DOM pre-treatment with ozone. Carbonyl compounds are one example of such possible photosensitizing moieties, since they are known to be produced by reaction of ozone with unsaturated organic compounds such as olefins and aromatics.[30, 32]

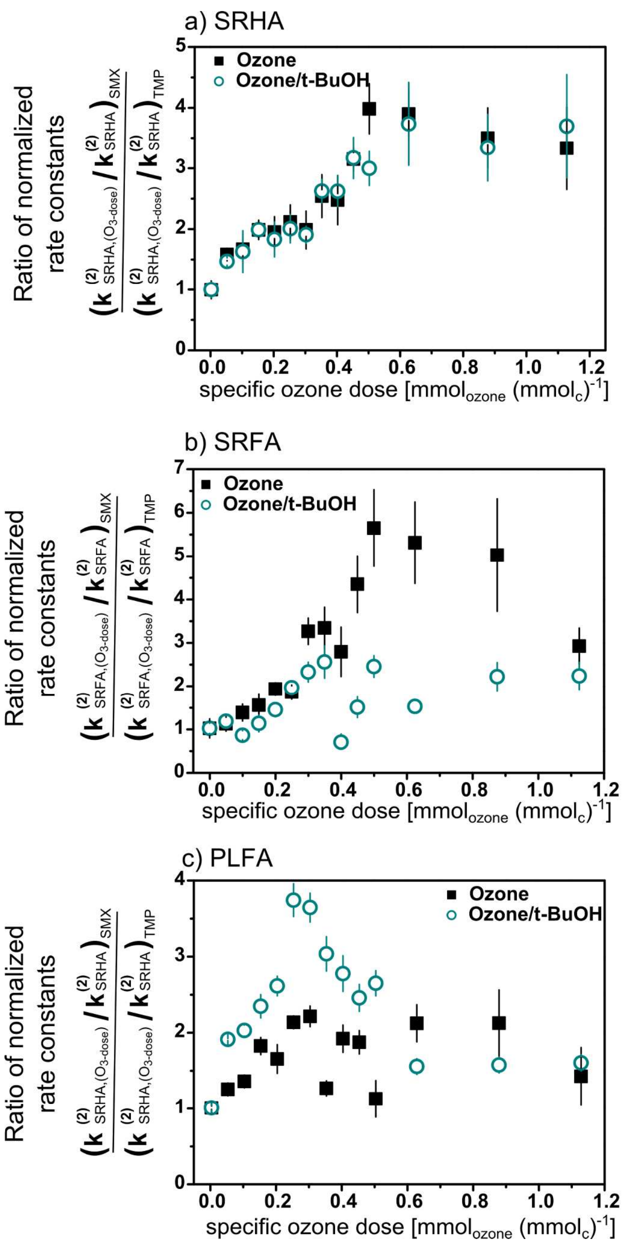

Figure 4. Ratio of normalized phototransformation rate constants of sulfamethoxazole (SMX) and 2,4,6-trimethylphenol (TMP) sensitized by the three standard DOMs, (a) Suwannee River humic acid (SRHA), (b) Suwannee River fulvic acid (SRFA) and (c) Pony Lake fulvic acid (PLFA), versus the specific ozone dose applied during DOM pre-oxidation. Error bars were calculated using the Gaussian error propagation law from the original rate constants and are shown as 95% confidence intervals.

Environmental implications

The results of this study have provided solid evidence that antioxidant moieties of DOM are involved in the inhibition of the triplet-induced transformation of two sulfonamide antibiotics, namely SMX and SD. Considering our previous investigations,[5-7] many other contaminants occurring in surface waters, particularly those exhibiting easily oxidizable aromatic nitrogen moieties, are expected to undergo the same kind of inhibition effect. For the $^3CBBP^*$-induced transformation of SMX and SD, we demonstrated a strong positive correlation between the inverse inhibition factors (expressing the inhibition capacity) and the EDC values of partially oxidized DOM. This correlation suggests that the concentration of electron-donating moieties (measured as EDC×DOC, DOC=dissolved organic carbon) in a natural water is a suitable proxy for its inhibitory effect on triplet-induced oxidations. Such a hypothesis will have to be verified experimentally for a consistent and representative collection of natural water samples.

Ozonation is being increasingly applied in advanced wastewater treatment for removal of micropollutants[33-36] and it is one of the main options, besides adsorption to powdered activated carbon, that will be implemented for the advanced treatment of municipal wastewater in Switzerland.[37] The results of the present study allow a qualitative prediction of the impact of ozonation of wastewater on the optical and photochemical properties of the receiving water bodies, provided that a final filtration step would not alter the characteristics of effluent organic matter (EfOM) significantly. Typical specific ozone doses that are applied in wastewater treatment range from 0.5 to 1.0 g_{ozone} $(g_C)^{-1}$ (C measured as DOC; on a molar base these doses correspond to 0.13–0.25 $mmol_{ozone}$ $(mmol_C)^{-1}$). While quantitative data on optical changes in EfOM during wastewater ozonation are available,[38, 39] integrative data sets addressing the optical and photochemical properties as well as EDC properties of EfOM during ozonation are, to the best of our knowledge, missing. In a recent study it was shown that EfOM undergoes similar changes in these properties upon ozonation as the studied fulvic acids.[40] By inspecting the fulvic acid data from our previous paper[21] and from Figure 3 (b, c, e, and f) the following changes after application of a specific ozone dose of 0.25 $mmol_{ozone}$ $(mmol_C)^{-1}$ are expected: (1) Absorption coefficients of DOM for the UV-A are reduced by >75%; (2) The rate constants for the phototransformation of TMP (indicative of the photosensitizing efficiency of DOM) are reduced by ≈50%; (3) EDC also decreases by ≈50%; (4) The rate constants for the phototransformation of SMX remain unchanged. Thus, the main effect of wastewater ozonation that may be relevant to phototransformation rate constants of contaminants in receiving surface waters is expected to be de-colorization of EfOM. Correspondingly, there will be an increase in transparency of receiving water bodies that goes along with an increase in direct phototransformation rate constants averaged over the photic zone, as compared to water bodies receiving non-ozonated wastewater. Predicting changes in triplet-induced phototransformation rate constants is more complex: While contaminants behaving like TMP, may show a decrease in rate constants, contaminants behaving like SMX may have higher rate constants and hence experience enhanced phototransformation. More detailed predictions can only be made after knowing the ratio of the released EfOM to the background DOM that is already present in the receiving water body. However, an ultimate quantitative assessment of phototransformation rate constants will require that the specific wastewaters and natural waters are investigated with the methods delineated in this work.

Associated content

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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