Supporting Information for

# Inhibitory Effect of Dissolved Organic Matter on the <br> Transformation of Selected Anilines and Sulfonamide Antibiotics Induced by the Sulfate Radical 

Silvio Canonica ${ }^{\dagger,}{ }^{,}$and Ursula Schönenberger ${ }^{\dagger}$

${ }^{\dagger}$ Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, CH-8600 Dübendorf, Switzerland

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## Table S1. List of abbreviations

| AOPs | Advanced oxidation processes |
| :---: | :---: |
| $\alpha$ | Slope of the linear regression line in competition kinetics plots. It corresponds to the ratio of $k_{\mathrm{SO}_{4}{ }^{-}, \mathrm{TC}}^{\mathrm{tr},{ }^{-}{ }^{-1}}$ to $k_{\mathrm{SO}_{4}{ }^{-}{ }^{-}, \mathrm{R}}^{\mathrm{tr}}$. |
| $\mathrm{CO}_{3}{ }^{-}$ | Carbonate radical (anion) |
| DOM | Dissolved organic matter |
| DOM ${ }_{\text {ox }}$ | Oxidized form of DOM resulting from the reaction of TC ${ }^{++}$with DOM |
| $[\mathrm{DOM}]_{1 / 2}$ | Concentration of DOM at which $I F=0.5$. It corresponds to the ratio of $k_{\mathrm{TC}}{ }^{\mathrm{ox}}$. to $k_{\mathrm{TC}}{ }^{\mathrm{r}, \text { DOM }}$ |
| $D_{\text {RIs }}$ | Parameter expressing the relative reactivity of a TC with RIsдом compared to $\mathrm{SO}_{4}{ }^{-}$in the frame of the developed kinetic model. It is defined as the ratio of $K_{\text {RIs }}$ to $k_{\mathrm{SO}_{4}{ }^{-}, \text {,TC }}^{\text {et }}$ |
| HPLC | High-performance liquid chromatography |
| $K_{\text {RIs }}$ | Parameter expressing the reactivity of a TC with $\mathrm{RIs}_{\text {dom }}$ in the frame of the developed kinetic model. It is defined as the ratio of the product of $k_{\mathrm{RIs}_{\text {DOM }}, \mathrm{TC}}^{\mathrm{tr}}$ and $k_{\mathrm{SO}_{4} \cdot-, \text {,DOM }}^{\mathrm{RIs}}$ to $k_{\mathrm{RIs}_{\text {DOM }}}^{\mathrm{d}}$ |
| $k_{\mathrm{RIs}_{\mathrm{DOM}}}^{\mathrm{d}}$ | First-order rate constant for the depletion of RIsdom |
|  | Second-order rate constants for the electron-transfer reaction of $\mathrm{SO}_{4}{ }^{*}$ with a TC leading to the formation of $\mathrm{TC}^{\cdot+}$ |
| $k_{\text {TC }}{ }^{\text {red }}$, Dom | Second-order rate constants for the reduction of TC ${ }^{+}$by DOM leading to the formation of TC |
|  | Second-order rate constants for the reaction of $\mathrm{SO}_{4}{ }^{--}$with DOM leading to the formation of RIsdom |
| $k_{\text {TC }}{ }^{\text {ox }}+$ | First-order rate constant for the transformation of $\mathrm{TC}^{\cdot+}$ to a stable oxidation product, $\mathrm{TC}_{\text {ox }}$ |
|  | Second-order rate constant for the scavenging of $\mathrm{SO}_{4}{ }^{--}$by DOM |
| $k_{\mathrm{RIs}_{\mathrm{DOM},}, \mathrm{TC}}^{\mathrm{tr}}$ | Second-order rate constants for the reaction of RIs ${ }_{\text {dom }}$ with TC leading to the transformation of TC to a product, $\mathrm{TC}_{\text {prod }}$ |
| $k_{\mathrm{SO}_{4}{ }^{-{ }^{-}, \mathrm{R}} \text { (r }}$ | Second-order rate constant for the reaction of $\mathrm{SO}_{4}{ }^{--}$with a competitor R leading to the transformation of R. In this study, IPU was used as R |


| $k_{\mathrm{SO}_{4}{ }^{-}, \mathrm{TC}}^{\text {trapp }}$ | Apparent second-order rate constants for the reaction of $\mathrm{SO}_{4}{ }^{--}$with a TC leading to the transformation of TC |
| :---: | :---: |
| EDC | Electron donating capacity |
| $E_{\text {red }}^{0}$ | Standard reduction potential |
| IF | Inhibition factor, defined as the ratio between second-order rate constants determined in the presence of a given concentration of DOM and in the absence of DOM |
| IPU | Isoproturon |
| $\cdot \mathrm{OH}$ | Hydroxyl radical |
| PLFA | Pony Lake fulvic acid |
| R | Reference compound or competitor |
| RIs | Reactive intermediates |
| RIs ${ }_{\text {dom }}$ | Secondary reactive intermediates formed through oxidation of DOM by $\mathrm{SO}_{4}{ }^{--}$ |
| SRFA | Suwannee River fulvic acid |
| SRHA | Suwannee River humic acid |
| $\mathrm{SO}_{4}{ }^{-}$ | Sulfate radical (anion) |
| TC | Target compound |
| TC ${ }^{+}$ | Reactive radical intermediate resulting from one-electron oxidation of TC |
| TCox | Stable oxidation product of TC |
| TC ${ }_{\text {prod }}$ | Product formed by reaction of TC with R $\mathrm{Is}_{\text {DOM }}$ |
| TMP | 2,4,6-Trimethylphenol |

Table S2. HPLC analysis parameters. ${ }^{\text {a }}$

| Target or reference compound | Eluent composition |  |  | Flow rate$\left[\mathrm{mL} \mathrm{~min}^{-1}\right]$ | Retention time [min] | Absorption wavelength [ nm$]^{\text {c }}$ | Excitation / emission wavelength [ nm ] ${ }^{\text {d }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | [vol \%] b |  |  |  |  |  |  |
|  | Acetonitrile | Water | Buffer ${ }^{\text {e }}$ |  |  |  |  |
| Aniline | 45 | 55 |  | 1.0 | 1.2 |  | 232 / 343 |
| 4-Cyanoaniline | 35 | 65 |  | 1.0 | 1.3 |  | 274/348 |
| 3,4-Dichloroaniline | 45 | 55 |  | 0.5 | 4.9 | 245 |  |
| $N, N$-Dimethylaniline | 45 | 55 |  | 1.0 | 3.4 |  | 251/360 |
| $N$-Ethylaniline | 45 | 55 |  | 0.5 | 5.2 |  | $235 / 340$ |
| $N$-Methylaniline | 37 | 63 |  | 0.5 | 5.1 |  | 232 / 343 |
| Sulfachloropyridazine | 22-50 |  | 78-50 | 0.7 | 3.2 | 272 |  |
| Sulfadiazine | 15-50 |  | 85-50 | 0.7 | 2.0 | 270 |  |
| Sulfadimethoxine | 20-45 |  | 80-55 | 0.7 | 4.4 | 272 |  |
| Sulfamethoxazole | 35 |  | 65 | 0.7 | 1.3 | 270 |  |
| Sulfathiazole | 15-50 |  | 85-50 | 0.7 | 2.1 | 288 |  |
| 2,4,6-Trimethylphenol | 55 | 45 |  | 0.7 | 2.5 |  | 225/316 |

Isoproturon ${ }^{\mathrm{f}}$
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Notes: ${ }^{\text {a }}$ All analyses were performed using a COSMOSIL Packed Column 5C18-MS-II, $100 \times 3 \mathrm{~mm}$ placed in a column oven that was maintained at a temperature of $25^{\circ} \mathrm{C} .{ }^{\mathrm{b}}$ Eluent composition ranges are given in the case gradient methods were used. ${ }^{\mathrm{c}}$ Absorbance measured using a photodiode array detector. ${ }^{e}$ Emission measured using a fluorescence detector. ${ }^{e}$ Composition: 0.675 mL of concentrated phosphoric acid (Fluka, puriss, p.a. $\geq$ $85 \%$ ) per liter of ultrapure water, corresponding to a total phosphate concentration of $10 \mathrm{mM}, \mathrm{pH} 2.1$. ${ }^{\mathrm{f}}$ Isoproturon was quantified in the same chromatograms used to quantify the target compounds, therefore methods used and retention times vary.

Text S1. Kinetic equations relevant to the sulfate radical-induced oxidation of a target compound and a reference compound (competitor).
A) Transformation of the target and reference compounds caused exclusively by reaction with the sulfate radical ( $\mathrm{SO}_{4}{ }^{--}$)

The rate equation for the depletion of a target compound (TC) induced by its reaction with $\mathrm{SO}_{4}{ }^{--}$is given by the following expression:

$$
\begin{equation*}
\frac{d[\mathrm{TC}]}{d t}=-k_{\mathrm{SO}_{4}-, \mathrm{TC}}^{\mathrm{tr}}\left[\mathrm{SO}_{4}{ }^{--}\right][\mathrm{TC}] \tag{S1}
\end{equation*}
$$

where square brackets refer to molar concentrations of the given species and $k_{\mathrm{SO}_{4}{ }^{-}, \mathrm{TC}}^{\mathrm{tr}}$ is the second-order rate constant for the reaction of $\mathrm{SO}_{4}{ }^{-}$with TC leading to a permanent transformation (expressed by the superscript "tr") of TC under the conditions and time scale of the kinetics experiments. Rearrangement and integration of Eq. S1 lead to Eq. S2.

$$
\begin{equation*}
\frac{1}{k_{\mathrm{SO}_{4}-, \mathrm{TC}}^{\mathrm{tr}}} \ln \frac{[\mathrm{TC}]_{0}}{[\mathrm{TC}]}=\int\left[\mathrm{SO}_{4}^{--}\right] d t \tag{S2}
\end{equation*}
$$

Applying the same procedure to the transformation of a reference compound (or competitor) R, present in the same solution as TC, one can derive Eq. S3.

$$
\begin{equation*}
\frac{1}{k_{\mathrm{SO}_{4}{ }^{--}, \mathrm{R}}^{\mathrm{tr}}} \ln \frac{[\mathrm{R}]_{0}}{[\mathrm{R}]}=\int\left[\mathrm{SO}_{4}^{--}\right] d t \tag{S3}
\end{equation*}
$$

Since the right-hand sides of Eqs. S2 and S3 are identical, one can equate the left-hand members of both equations, which, after rearrangement, leads to Eq. S4, a classical competition kinetics expression.

$$
\begin{equation*}
\ln \frac{[\mathrm{TC}]_{0}}{[\mathrm{TC}]}=\frac{k_{\mathrm{SO}_{4}}^{\mathrm{tr}} \cdot \mathrm{TT}}{k_{\mathrm{SO}_{4} \cdot-\mathrm{R}}^{\mathrm{tr}}} \ln \frac{[\mathrm{R}]_{0}}{[\mathrm{R}]} \tag{S4}
\end{equation*}
$$

This equation is analogous to Eq. 1 in the main paper with $\mathrm{R}=\mathrm{IPU}$ (isoproturon, which was used throughout this study as a competitor). In the main paper, $k_{\mathrm{SO}_{4}{ }^{-\quad}, \mathrm{TC}}^{\text {trapp }}$ is used instead of $k_{\mathrm{SO}_{4}{ }^{--}, \mathrm{TC}}^{\mathrm{tr}}$, in which the superscript "app" (for "apparent") was applied to allow for possible side-reactions in the transformation of TC, as discussed in the following paragraph B ) and Text S2.
B) Transformation of the reference compound caused exclusively by reaction with the sulfate radical; transformation of the target compound caused by reaction with the sulfate radical and by a side reaction that occurs in the presence of dissolved organic matter (DOM)

The kinetic treatment given in this section was performed making the following assumptions:
(a) The side reaction of the target compound is caused by radicals (represented here by a single lumped species RIsдом that result from the oxidation of DOM by $\mathrm{SO}_{4}{ }^{*-}$.
(b) RIs дом $^{\text {decays by a first-order process that is independent of the concentration of all }}$ other species considered in the kinetic treatment (including TC, R, DOM and all radical species).
(c) The transformation of the reference compound is not affected by side reactions.

The applicable reaction equations and rate constants are summarized below (Eqs. S5 - S9).

$$
\begin{align*}
& \mathrm{SO}_{4}{ }^{--}+\mathrm{R} \rightarrow \mathrm{SO}_{4}{ }^{2-}+\mathrm{R}_{\mathrm{ox}} \\
& \mathrm{SO}_{4}{ }^{-{ }^{-}}+\mathrm{TC} \rightarrow \mathrm{SO}_{4}{ }^{2-}+\mathrm{TC}_{\text {ox }}  \tag{S6}\\
& \mathrm{SO}_{4}{ }^{--}+\mathrm{DOM} \rightarrow \mathrm{SO}_{4}{ }^{2-}+\text { RIssom }_{\text {D }}  \tag{S7}\\
& \text { RIs }_{\text {DOM }}+\mathrm{TC} \rightarrow \mathrm{TC}_{\text {prod }}  \tag{S8}\\
& \begin{array}{l}
k_{\mathrm{SO}_{4}{ }^{--}, \mathrm{R}}^{\mathrm{tr}} \\
k_{\mathrm{SO}_{4}{ }^{-}, \mathrm{TC}}^{\mathrm{tr}} \\
k_{\mathrm{So}_{4}{ }^{--}, \mathrm{DOM}}^{\mathrm{RIs}} \\
k_{\mathrm{RIs}_{\mathrm{DOM},}, \mathrm{TC}}^{\mathrm{tr}} \\
k_{\mathrm{RII}_{\mathrm{DOM}}}^{\mathrm{d}}
\end{array}  \tag{S5}\\
& \text { RIs }_{\text {DOM }} \rightarrow \mathrm{DOM}_{\text {mod }} \tag{S9}
\end{align*}
$$

The products $\mathrm{R}_{\mathrm{ox}}, \mathrm{TC}_{\mathrm{ox}}$ and $\mathrm{TC}_{\text {prod }}$ of the reactions $\mathrm{S} 5, \mathrm{~S} 6$ and S 8 , respectively, are assumed to be formed irreversibly, excluding a reformation of TC or R. DOM mod represents the product of the decay of RIsдом and is denoted as "modified" DOM.

According to the reactions S5-S8, the following rate laws for the transformation of R and TC can be derived.

$$
\begin{align*}
\frac{d[\mathrm{R}]}{d t}= & -k_{\mathrm{SO}_{4}{ }^{--}, \mathrm{R}}^{\operatorname{tr}}\left[\mathrm{SO}_{4}{ }^{--}\right][\mathrm{R}]  \tag{S10}\\
\frac{d[\mathrm{TC}]}{d t}= & -k_{\mathrm{SO}_{4}-{ }^{-}, \mathrm{TC}}^{\mathrm{tr}}\left[\mathrm{SO}_{4}{ }^{-}\right][\mathrm{TC}]-k_{\mathrm{RIS}_{\mathrm{DOM},}, \mathrm{TC}}^{\mathrm{tr}}\left[\mathrm{RIs}_{\mathrm{DOM}}\right][\mathrm{TC}] \\
& =-\left\{k_{\mathrm{SO}_{4}{ }^{--}, \mathrm{TC}}^{\mathrm{tr}}\left[\mathrm{SO}_{4}{ }^{--}\right]+k_{\mathrm{RIS}_{\mathrm{DOM}}, \mathrm{TC}}^{\mathrm{tr}}\left[\mathrm{RIs}_{\mathrm{DOM}}\right]\right\}[\mathrm{TC}] \tag{S11}
\end{align*}
$$

Rearrangement and integration of Eqs. S10 and S11 yield the above-stated Eq. S3 as well as the new Eq. S12, respectively.

$$
\begin{equation*}
\ln \frac{[\mathrm{TC}]_{0}}{[\mathrm{TC}]}=k_{\mathrm{SO}_{4}^{\cdot-}, \mathrm{TC}}^{\operatorname{tr}} \int\left[\mathrm{SO}_{4}^{\cdot-}\right] d t+k_{\mathrm{RIs}_{\mathrm{DOM}}, \mathrm{TC}}^{\mathrm{tr}} \int\left[\mathrm{RIs}_{\mathrm{DOM}}\right] d t \tag{S12}
\end{equation*}
$$

The concentration of RIs som is controlled by its formation (reaction Eq. S7) and depletion (reaction Eq. S9), while the reaction of RIs $_{\text {dom }}$ with TC is considered to have a negligible effect on [RIsdom] (see the aforementioned assumption (b)). Making a steady-state assumption for RIs дом leads to the following equation:

$$
\begin{equation*}
k_{\mathrm{SO}_{4}^{--}, \mathrm{DOM}}^{\mathrm{RIs}}\left[\mathrm{SO}_{4}^{\cdot-}\right][\mathrm{DOM}]=k_{\mathrm{RIs}_{\mathrm{DOM}}}^{\mathrm{d}}\left[\mathrm{RIs}_{\mathrm{DOM}}\right] \tag{S13}
\end{equation*}
$$

Rearrangement of Eq. S13 yields:

Substituting Eq. S14 into Eq. S12 leads to Eq. S15.

Using Eq. S3, one can substitute the sulfate radical exposure ( $\int\left[\mathrm{SO}_{4}{ }^{-{ }^{-}}\right] d t$ ) into Eq. S 15 , which leads to Eq. S16.

We define the expression in braces as the apparent second-order rate constant for the transformation of TC induced, directly and indirectly through RIs ${ }_{\text {Dom }}$, by $\mathrm{SO}_{4}{ }^{--}$according to Eq. S17.

$$
\begin{equation*}
k_{\mathrm{SO}_{4}^{-}-\mathrm{TC}}^{\mathrm{tr}, \mathrm{TD}}=k_{\mathrm{SO}_{4}^{--}, \mathrm{TC}}^{\mathrm{tr}}+k_{\mathrm{RIs}_{\mathrm{DOM}, \mathrm{TC}}}^{\mathrm{tr}} \frac{k_{\mathrm{SO}_{4}-{ }^{-}, \mathrm{DOM}}[\mathrm{DOM}]}{k_{\mathrm{RIs}_{\mathrm{DOM}}}^{\mathrm{RIs}}} \tag{S17}
\end{equation*}
$$

The second term in the right-hand side of Eq. S17 can be considered as an apparent secondorder rate constant concerning exclusively the transformation of TC induced by RIs. ${ }_{\text {dom }}$. We define here the parameter $K_{\text {RIs }}$ by grouping the rate constants in this second term and obtain Eq. S18.

$$
\begin{equation*}
K_{\mathrm{RIs}}=\frac{k_{\mathrm{RIS}_{\mathrm{DOM}}, \mathrm{TC}}^{\mathrm{tr}} \times k_{\mathrm{SO}_{4}}^{\mathrm{RIs}-, \mathrm{DOM}}}{k_{\mathrm{RIS}_{\mathrm{DOM}}}^{\mathrm{d}}} \tag{S18}
\end{equation*}
$$

Substituting Eq. S18 into Eq. S17 yields:

$$
\begin{equation*}
k_{\mathrm{SO}_{4}^{-}-, \mathrm{TC}}^{\mathrm{tr}}=k_{\mathrm{SO}_{4}^{-}, \mathrm{TC}}^{\mathrm{tr}}+K_{\mathrm{RIs}} \times[\mathrm{DOM}] \tag{S19}
\end{equation*}
$$

For a given DOM, $K_{\text {RIs }}$ can be used to obtain the relative values of $k_{\mathrm{RIs}_{\mathrm{DOM}}, \mathrm{TC}}^{\mathrm{tr}}$ for various TCs.

Text S2. Inhibitory effect of dissolved organic matter on the second-order rate constant of the sulfate radical-induced oxidation of target compounds.

The previously elaborated one-channel model for the DOM-inhibited oxidation of a target compound (TC) is applied in this section to the derivation of the dependence of $k_{\mathrm{SO}_{4}{ }^{-} \text {, TC }}^{\mathrm{tr}}$ (see Text S1 for the definition of this second-order rate constant) on DOM concentration. We first consider the case in which the transformation of TC is exclusively initiated by $\mathrm{SO}_{4}{ }^{--}$(i.e., side-reactions of TC can be neglected). As explained in the main paper, the inhibitory effect of DOM on the oxidation of TC is rationalized in terms of the following reaction equations (which are identical with Eqs. 4-6 of the main paper and whose meaning has been explained in detail in the main paper).

$$
\begin{array}{ll}
\mathrm{SO}_{4}{ }^{--}+\mathrm{TC} \rightarrow \mathrm{SO}_{4}{ }^{2-}+\mathrm{TC}^{\cdot+} & k_{\mathrm{SO}_{4}^{--}, \mathrm{TC}}^{\mathrm{et}} \\
\mathrm{TC}^{\cdot+} \rightarrow \mathrm{TC}_{\mathrm{ox}} & k_{\mathrm{TC} \cdot}^{\mathrm{ox}} \\
\mathrm{TC}^{\cdot+}+\mathrm{DOM} \rightarrow \mathrm{TC}+\mathrm{DOM}_{\mathrm{ox}} & k_{\mathrm{TC}} \mathrm{red}^{++}, \mathrm{DOM}
\end{array}
$$

The rate equations for TC and $\mathrm{TC}^{\bullet+}$ can be expressed as follows.

$$
\left.\begin{array}{l}
\frac{d[\mathrm{TC}]}{d t}=-k_{\mathrm{SO}_{4}^{{ }^{-}}, \mathrm{TC}}^{\mathrm{et}}\left[\mathrm{SO}_{4}{ }^{\bullet-}\right][\mathrm{TC}]+k_{\mathrm{TC}^{+}, \mathrm{DOM}}^{\mathrm{red}}\left[\mathrm{TC}^{\bullet+}\right][\mathrm{DOM}] \\
\frac{d\left[\mathrm{TC}{ }^{+}\right]}{d t}=k_{\mathrm{SO}_{4}{ }^{-}, \mathrm{TC}}^{\mathrm{et}}\left[\mathrm{SO}_{4}{ }^{\bullet-}\right][\mathrm{TC}]-k_{\mathrm{TC}}{ }^{\mathrm{red}, \mathrm{DOM}} \tag{S24}
\end{array} \mathrm{TC}^{\bullet+}\right][\mathrm{DOM}]+k_{\mathrm{TC}} \mathrm{ox}^{\mathrm{ox}}\left[\mathrm{TC}^{\bullet+}\right] .
$$

Applying the steady-state assumption for $\mathrm{TC}^{\cdot+}$ leads to the following equation.

Substituting $\left[\mathrm{TC}^{+}\right]$from Eq. S25 into Eq. S23 and rearranging yields Eq. S24.

$$
\begin{equation*}
\frac{d[\mathrm{TC}]}{d t}=-\frac{k_{\mathrm{SO}_{4}-{ }^{-}, \mathrm{TC}}^{\mathrm{et}}}{1+\left(k_{\mathrm{TC}}{ }^{\text {red }+ \text { DOM }} \cdot k_{\mathrm{TC}}{ }^{\mathrm{ox}}{ }^{+}\right)[\mathrm{DOM}]}\left[\mathrm{SO}_{4}^{\cdot-}\right][\mathrm{TC}] \tag{S26}
\end{equation*}
$$

Comparing Eqs. S1 and S26 leads to the identity:

$$
\begin{equation*}
k_{\mathrm{SO}_{4}{ }^{-}, \mathrm{TC}}^{\mathrm{tr}}=\frac{k_{\mathrm{So}_{4}^{--}, \mathrm{TC}}^{\mathrm{et}}}{1+\left(k_{\mathrm{TC}}{ }^{+}, \mathrm{DOM}^{\mathrm{e}} / k_{\mathrm{TC}}{ }^{\mathrm{ox}}++[\mathrm{DOM}]\right.} \tag{S27}
\end{equation*}
$$

Note that in the case of $[\mathrm{DOM}]=0, k_{\mathrm{SO}_{4}{ }^{-}, \mathrm{TC}}^{\mathrm{tr}}=k_{\mathrm{SO}_{4}{ }^{-}, \mathrm{TC}}{ }^{\mathrm{et}}$. For the inhibition factor, defined in Eq. 3 of the main paper, Eq. S28 (corresponding to Eq. 7 in the main paper) holds.

$$
\begin{equation*}
I F([\mathrm{DOM}])=\frac{k_{\mathrm{SO}_{4}{ }^{-}, \mathrm{TC}}^{\mathrm{tr}}([\mathrm{DOM}])}{k_{\mathrm{SO}_{4}-, \mathrm{TC}}^{e t}}=\frac{1}{1+\left(k_{\mathrm{TC}}{ }^{\mathrm{red}+, \mathrm{DOM}} / k_{\mathrm{TC}}{ }^{\mathrm{ox}}+{ }^{+}\right)[\mathrm{DOM}]} \tag{S28}
\end{equation*}
$$

It should be recalled here that Eq. S28 is valid for the case in which the transformation of TC is exclusively initiated by $\mathrm{SO}_{4}{ }^{-}$. In the more complex case in which the transformation of TC is partly due to a side reaction with radicals generated from the oxidation of DOM by $\mathrm{SO}_{4}{ }^{--}$ (i.e., the radicals mentioned above in Text S 1 and in the main paper, which were called RIs ${ }_{\text {dom }}$, one can insert Eq. S27 into Eq. S19 (derived in Text S1, Part B), which leads to:

$$
\begin{equation*}
\left.k_{\mathrm{SO}_{4}^{-}, \mathrm{TC}}^{\mathrm{tr}, \mathrm{app}}=\frac{k_{\mathrm{SO}_{4}-, \mathrm{TC}}^{\mathrm{et}}}{1+\left(k_{\mathrm{TC}} \mathrm{TC}^{+}, \mathrm{DOM}\right.} k_{\mathrm{TC}} \mathrm{TC}^{++}\right)[\mathrm{DOM}] \quad K_{\mathrm{RIs}} \times[\mathrm{DOM}] \tag{S29}
\end{equation*}
$$

The inhibition factor is then obtained by dividing this expression by $k_{\mathrm{SO}_{4}}^{\mathrm{et}}{ }^{-{ }^{-}, \mathrm{TC}}$, which yields Eq. S30.

$$
\begin{equation*}
I F([\mathrm{DOM}])=\frac{1}{1+\left(k_{\mathrm{TC}} \mathrm{red}+\mathrm{DOM}^{2} / k_{\mathrm{TC}}{ }^{\mathrm{ox}}+{ }^{+}\right)[\mathrm{DOM}]}+\frac{K_{\mathrm{RIS}}}{k_{\mathrm{SO}_{4}}^{\mathrm{et}, \mathrm{TC}}} \times[\mathrm{DOM}] \tag{S30}
\end{equation*}
$$

One can substitute the parameter $[\mathrm{DOM}]_{1 / 2}=k_{\mathrm{TC}} \mathrm{ox}{ }^{++} / k_{\mathrm{TC}}{ }^{\mathrm{red}, \mathrm{DOM}}$ into Eq. S30 (see also the main paper), obtaining Eq. S31, which corresponds to Eq. 11 in the main paper.

$$
\begin{equation*}
I F([\mathrm{DOM}])=\frac{1}{1+[\mathrm{DOM}] /[\mathrm{DOM}]_{1 / 2}}+\frac{K_{\mathrm{RIs}}}{k_{\mathrm{SO}_{4}-,, \mathrm{TC}}^{\mathrm{et}}} \times[\mathrm{DOM}] \tag{S31}
\end{equation*}
$$



Figure S1. Inhibition factors (IF, equation 3) for 2,4,6-trimethylphenol measured at various DOM concentrations in the range of $0.0-5.0 \mathrm{mg}_{\mathrm{C}} \mathrm{L}^{-1}$ for aqueous solutions ( pH 8.0 ) of Suwannee River humic acid (a), Suwannee River fulvic acid (b) and Pony Lake fulvic acid (c). Data points correspond to $I F$ values obtained by applying equation 3 to $k_{\mathrm{SO}_{4}{ }^{-}, \mathrm{TC}}^{\mathrm{tr}}{ }^{\text {, }}$ ([DOM] $)$
 two independent experiments. Error bars represent $95 \%$ confidence intervals obtained from
linear regression and by applying Gaussian error propagation. Straight lines represent linear regressions performed using the data points in the range of $[D O M]=0-1.5 \mathrm{mgC}_{\mathrm{C}} \mathrm{L}^{-1}$ (filled symbols), while the data points for $[\mathrm{DOM}]>1.5 \mathrm{mg}_{\mathrm{C}} \mathrm{L}^{-1}$ (open symbols) were not included in the regression analysis.

Table S3. Parameter values for the secondary reactive intemediates effects obtained by linear regression of the $I F$ values for 2,4,6-trimethylphenol (see Figure S1).

| DOM <br> isolate | $I F_{0}{ }^{\mathrm{a}}$ <br> (intercept) | $D_{\text {RIs }}{ }^{\text {a }}$ <br> $/ 10^{-1} \mathrm{~L} \mathrm{mgc}^{-1}$ | $K_{\text {RIs }}{ }^{\text {a }}$ <br> $/ 10^{9} \mathrm{~L} \mathrm{mgc}^{-1} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ | $r^{2}$ |
| :--- | :---: | :---: | :---: | :---: |
| SRHA | $1.10 \pm 0.06$ | $0.97 \pm 0.08$ | $3.39 \pm 0.27$ | 0.929 |
| SRFA | $1.02 \pm 0.02$ | $0.56 \pm 0.02$ | $1.96 \pm 0.08$ | 0.983 |
| PLFA | $1.00 \pm 0.02$ | $0.31 \pm 0.03$ | $1.08 \pm 0.01$ | 0.914 |

${ }^{\text {a }}$ Standard errors are used.

## Text S3. Determination of the second-order rate constant for the reaction of the sulfate radical with dissolved organic matter.

The dependence of the initial transformation rate of the competitor, isoproturon (IPU), on DOM concentration was used to obtain the second-order (scavenging, see superscript "s") rate constant for the reaction of $\mathrm{SO}_{4}{ }^{--}$with $\mathrm{DOM}, k_{\mathrm{SO}_{4}{ }^{-}, \text {DOM }}$. Analogously to Eq. S1, the rate expression for the transformation of IPU is given by:

$$
\begin{equation*}
\frac{d[\mathrm{IPU}]}{d t}=-k_{\mathrm{SO}_{4}^{--}, \mathrm{IPU}}^{\mathrm{tr}}\left[\mathrm{SO}_{4}{ }^{--}\right][\mathrm{IPU}] \tag{S30}
\end{equation*}
$$

The sulfate radical reacts, besides with DOM, with several species, termed scavengers ( $\mathrm{S}_{i}, i=$ $1,2, \ldots$ ), which are listed in Table S 4 together with their second-order rate constants for the reaction with $\mathrm{SO}_{4}{ }^{--}\left(k_{\mathrm{SO}_{4}-{ }^{-}, \mathrm{S}_{i}}^{\mathrm{S}}\right)$ and their initial concentrations valid for the experiments performed in this study. We define the formation rate of $\mathrm{SO}_{4}{ }^{\bullet-}$ (following photolysis of persulfate) as $r_{\mathrm{SO}_{4}}^{\mathrm{f}}{ }^{\bullet-}$. The depletion of $\mathrm{SO}_{4}{ }^{--}$is controlled by its scavengers (including DOM) and can be quantified as pseudo-first-order scavenging rate constant, $k_{\mathrm{SO}_{4}}^{\prime \mathrm{s}}{ }^{--}$according to Eq. S31.

$$
\begin{equation*}
k_{\mathrm{SO}_{4}{ }^{--}}^{\mathrm{s}}=\left[\mathrm{SO}_{4}^{\cdot-}\right]\left(k_{\mathrm{SO}_{4}^{--}, \mathrm{DOM}}^{\mathrm{s}}[\mathrm{DOM}]+\sum_{i} k_{\mathrm{SO}_{4}^{--}, \mathrm{S}_{i}}^{\mathrm{s}}\left[\mathrm{~S}_{i}\right]\right) \tag{S31}
\end{equation*}
$$

Applying the steady-state assumption for $\mathrm{SO}_{4}{ }^{--}$, one obtains the following expression:

$$
\begin{equation*}
\left[\mathrm{SO}_{4}^{--}\right]=\frac{r_{\mathrm{SO}_{4}^{--}}^{\mathrm{f}}}{k_{\mathrm{SO}_{4}{ }^{--}, \mathrm{DOM}}{ }^{\mathrm{DOM}]+\sum_{i} k_{\mathrm{SO}_{4}}^{\mathrm{s}}, \mathrm{~s}_{i}}\left[\mathrm{~S}_{i}\right]} \tag{S32}
\end{equation*}
$$

Substituting Eq. S32 into Eq. S30 leads to:

Dividing both sides of Eq. S33 by [IPU] and inverting yields:

$$
\begin{equation*}
[\mathrm{IPU}] /\left(-\frac{d[\mathrm{IPU}]}{d t}\right)=\frac{1}{k_{\mathrm{SO}_{4}{ }^{--}, \mathrm{IPU}} \times r_{\mathrm{SO}_{4}}^{\mathrm{f}}} \times\left(k_{\mathrm{SO}_{4}{ }^{--}, \mathrm{DOM}}^{\mathrm{s}}[\mathrm{DOM}]+\sum_{i} k_{\mathrm{SO}_{4}{ }^{--}, \mathrm{S}_{i}}^{\mathrm{s}}\left[\mathrm{~S}_{i}\right]\right) \tag{S34}
\end{equation*}
$$

Eq. S34 is strictly valid only at the beginning of the reaction, when no additional scavengers resulting from the transformation of the various compounds are present. Considering that during the experiments only a small decrease in the initial concentration of target and reference compounds was observed, we substitute the left-hand side of the equation with $k_{\mathrm{IPU}}^{\mathrm{obs}^{-1}}$, the inverse of the pseudo-first-order rate constant determined from the isoproturon
transformation kinetics runs. After this substitution and regrouping, Eq. S34 transforms to Eq. S35,
 a linear regression of $k_{\mathrm{IPU}}^{\mathrm{obs}^{-1}}$ vs. [DOM], provided $r_{\mathrm{SO}_{4}}^{\mathrm{f}}{ }^{-}$- remains constant for the series of experiments considered. This condition was satisfactorily fulfilled in the present study. Before regression, $k_{\mathrm{IPU}}^{\mathrm{obs}}$ values were corrected for light screening caused by DOM by applying the methods described in detail by Leresche et al. (Ref. 18 of the main paper). The second-order rate constant for the scavenging of $\mathrm{SO}_{4}{ }^{--}$by DOM can be obtained as:

$$
\begin{equation*}
k_{\mathrm{SO}_{4}--, \mathrm{DOM}}^{\mathrm{s}}=\frac{B}{A} \times \sum_{i} k_{\mathrm{SO}_{4}{ }^{--}, \mathrm{S}_{i}}^{\mathrm{s}}\left[\mathrm{~S}_{i}\right] \tag{S36}
\end{equation*}
$$

From the fit parameter $A$ of the linear regression the formation rate of $\mathrm{SO}_{4}{ }^{-}$can also be obtained according to Eq. S37.

$$
\begin{equation*}
r_{\mathrm{SO}_{4}}^{\mathrm{f}}{ }^{--}=\frac{\sum_{i} k_{\mathrm{SO}_{4}--, \mathrm{s}_{i}}^{\mathrm{s}}\left[\mathrm{~S}_{i}\right]}{A \times k_{\mathrm{SO}_{4}{ }^{-}, \mathrm{IPU}}^{\mathrm{tr}}} \tag{S37}
\end{equation*}
$$





Figure S2. Linear regression diagrams according to eq S35 to determine the second-order rate constants for the reaction of the sulfate radical with the three studied DOM isolates:

Suwannee River humic acid (SRHA, upper row), Suwannee River fulvic acid (SRFA, central row), Pony Lake fulvic acid (PLFA, lower row). Pseudo-first-order rate constants were corrected for light screening caused by DOM as described in Text S3. The regression parameters (slope and intercept) are displayed in Table S 5 together with the calculated values


Table S4. Rate constants for the scavenging of the sulfate radical by dissolved compounds in the studied solutions.

| Compound ( $\mathrm{S}_{i}$ ) | $k_{\mathrm{SO}_{4}{ }^{-}, \mathrm{s}_{i}}^{\mathrm{s}} / \mathrm{M}^{-1} \mathrm{~s}^{-1}$ | $\left[\mathrm{~S}_{i}\right] / \mathrm{M}$ | $k_{\mathrm{SO}_{4}{ }^{-}, \mathrm{s}_{i}}^{\mathrm{s}} \times\left[\mathrm{S}_{i}\right] / \mathrm{s}^{-1}$ | $\sum_{i} k_{\mathrm{SO}_{4}{ }^{-}, \mathrm{s}_{i}}^{\mathrm{s}}\left[\mathrm{S}_{i}\right] \mathrm{a} / \mathrm{s}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{H}_{2} \mathrm{O}$ | $1.19 \times 10^{1}$ | $5.55 \times 10^{1}$ | $6.6 \times 10^{2 \mathrm{~b}}$ |  |
| $\mathrm{OH}^{-}$ | $(1.4-8.3) \times 10^{7 \mathrm{c}}$ | $1.0 \times 10^{-6}$ | $5.6 \times 10^{1 \mathrm{~d}}$ |  |
| $\mathrm{HPO}_{4}{ }^{2-}$ | $1.2 \times 10^{6 \mathrm{e}}$ | $4.3 \times 10^{-4}$ | $5.2 \times 10^{2}$ |  |
| $\mathrm{~S}_{2} \mathrm{O}_{8}{ }^{2-}$ | $6.3 \times 10^{5 \mathrm{~b}}$ | $5.0 \times 10^{-4}$ | $3.2 \times 10^{2}$ |  |
| $t$-Butanol | $9.1 \times 10^{5 \mathrm{f}}$ | $2.5 \times 10^{-4}$ | $2.3 \times 10^{2}$ |  |
| Isoproturon | $2.9 \times 10^{9 \mathrm{~g}}$ | $1.0 \times 10^{-6}$ | $2.9 \times 10^{3}$ |  |
| 4-Cyanoaniline | $2.7 \times 10^{9 \mathrm{~h}}$ | $1.0 \times 10^{-6}$ | $2.7 \times 10^{3}$ | $7.4 \times 10^{3}$ |
| Sulfamethoxazole | $8.7 \times 10^{8 \mathrm{~h}}$ | $1.0 \times 10^{-6}$ | $8.7 \times 10^{2}$ | $5.5 \times 10^{3}$ |
| 2,4,6-Trimethylphenol | $3.5 \times 10^{9 \mathrm{~h}}$ | $1.0 \times 10^{-6}$ | $3.5 \times 10^{3}$ | $8.2 \times 10^{3}$ |

${ }^{\text {a }}$ The summation includes all first six components (from $\mathrm{H}_{2} \mathrm{O}$ to isoproturon) plus the term of a single target compound (either 4-cyanoaniline, or sulfamethoxazole, or 2,4,6-trimethylphenol. ${ }^{\mathrm{b}}$ Ref. 1. ${ }^{\mathrm{c}}$ Refs. 1-5. ${ }^{\mathrm{d}}$ Average of five values employed. ${ }^{\mathrm{e}}$ Ref. 6. ${ }^{\mathrm{f}}$ Ref. 4. ${ }^{\mathrm{g}}$ Ref. 7. ${ }^{\mathrm{h}}$ This study.

Table S5. Linear regression parameters (eq S35) and rate constants for the scavenging of the sulfate radical by dissolved compounds in the studied solutions.

| DOM isolate | Target compound series | $A^{\mathrm{a} / \mathrm{s}} \quad$ (intercept) | $B^{\mathrm{a}} / \mathrm{L} \mathrm{mgC}^{-1} \mathrm{~s} \quad$ (slope) |  |
| :---: | :---: | :---: | :---: | :---: |
| SRHA | 4-cyanoaniline | $897 \pm 166$ | $1074 \pm 88$ | $8.9 \pm 1.4$ |
|  | sulfamethoxazole | $2982 \pm 725$ | $4871 \pm 585$ | $9.1 \pm 1$ |
|  | 2,4,6-trimethylphenol | $2513 \pm 496$ | $5032 \pm 377$ | $16.4 \pm 3.5$ |
|  | average ( $\pm$ st. dev.) |  |  | $11.5 \pm 4.3$ |
| SRFA | 4-cyanoaniline | $1358 \pm 106$ | $1016 \pm 81$ | $5.57 \pm 0.62$ |
|  | sulfamethoxazole | $2734 \pm 248$ | $1965 \pm 188$ | $4.00 \pm 0.53$ |
|  | 2,4,6-trimethylphenol | $2020 \pm 161$ | $2860 \pm 122$ | $11.6 \pm 1.1$ |
|  | average ( $\pm$ st. dev.) |  |  | $7.1 \pm 4.0$ |
| PLFA | 4-cyanoaniline | $4332 \pm 146$ | $1895 \pm 111$ | $3.25 \pm 0.22$ |
|  | sulfamethoxazole | $2557 \pm 87$ | $1930 \pm 66$ | $4.20 \pm 0.20$ |
|  | 2,4,6-trimethylphenol | $2858 \pm 298$ | $635 \pm 226$ | $1.82 \pm 0.68$ |
|  | average ( $\pm$ st. dev.) |  |  | $3.1 \pm 1.2$ |

${ }^{\text {a }}$ Standard errors from linear regression are given. ${ }^{\text {b }}$ Calculated using eq S36 and the applicable summation values given in Table S 4 (last column).
Standard errors, calculated by applying Gaussian error propagation, are given, except for overall averages, for which standard deviations are used.

## References

1. Herrmann, H.; Reese, A.; Zellner, R. Time-resolved UV/VIS diode array absorption spectroscopy of $\mathrm{SO}_{\mathrm{x}}^{-}(\mathrm{x}=3,4,5)$ radical anions in aqueous solution. J. Mol. Struct. 1995, 348, 183-186.
2. Chawla, O. P.; Fessenden, R. W. Electron spin resonance and pulse radiolysis studies of some reactions of $\mathrm{SO}_{4}$. J. Phys. Chem. 1975, 79 (24), 2693-2700.
3. Redpath, J. L.; Willson, R. L. Chain reactions and radiosensitization - Model enzyme studies. Int. J. Radiat. Biol. 1975, 27 (4), 389-398.
4. Hayon, E.; Treinin, A.; Wilf, J. Electronic spectra, photochemistry, and autoxidation mechanism of the sulfite-bisulfite-pyrosulfate systems. The $\mathrm{SO}_{2}{ }^{-}, \mathrm{SO}_{3}{ }^{-}, \mathrm{SO}_{4}{ }^{-}$, and $\mathrm{SO}_{5}^{-}$ radicals. J. Am. Chem. Soc. 1972, 94 (1), 47-57.
5. Roebke, W.; Renz, M.; Henglein, A. Pulsradiolyse der Anionen $\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}$ und $\mathrm{HSO}_{5}{ }^{-}$in wässriger Lösung. Int. J. Radiat. Phys. Chem. 1969, 1, 39-44.
6. Maruthamuthu, P.; Neta, P. Phosphate radicals - Spectra, acid-base equilibria, and reactions with inorganic compounds. J. Phys. Chem. 1978, 82 (6), 710-713.
7. Canle Lopez, M.; Fernandez, M. I.; Rodriguez, S.; Santaballa, J. A.; Steenken, S.; Vulliet, E. Mechanisms of direct and $\mathrm{TiO}_{2}$-photocatalysed UV degradation of phenylurea herbicides. ChemPhysChem 2005, 6 (10), 2064-2074.

[^0]:    * Corresponding Author:

    E-mail: silvio.canonica@eawag.ch. Telephone: +41-58-765-5453. Fax: +41-58-765-5028.

