

SUPPLEMENTARY MATERIAL

Wavelength trends of photoproduction of reactive transient species by chromophoric dissolved organic matter (CDOM), under steady-state polychromatic irradiation

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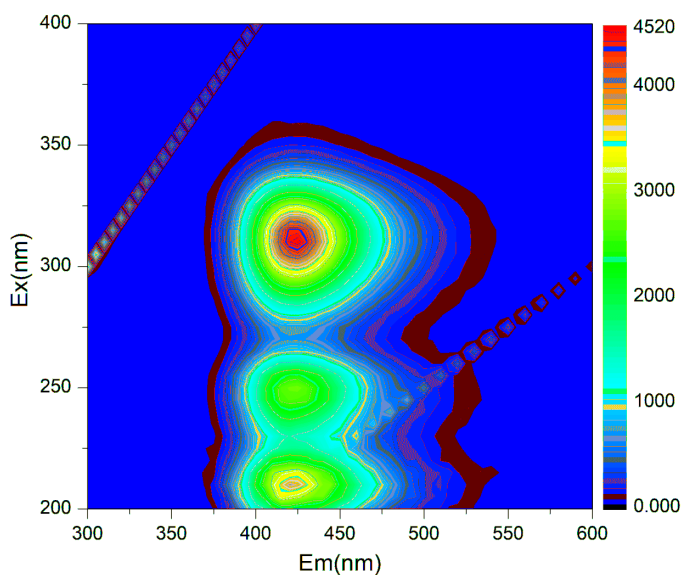


Figure S1. Excitation-emission matrix (EEM) fluorescence spectrum of 0.01 mM 2-hydroxyterephthalic acid. The spectrum was taken with a Hitachi F-7000 Fluorescence Spectrophotometer. The wavelength ranges of excitation and emission were 200-400 nm and 300-600 nm, respectively. The scanning speed was set at 1200 nm/min.

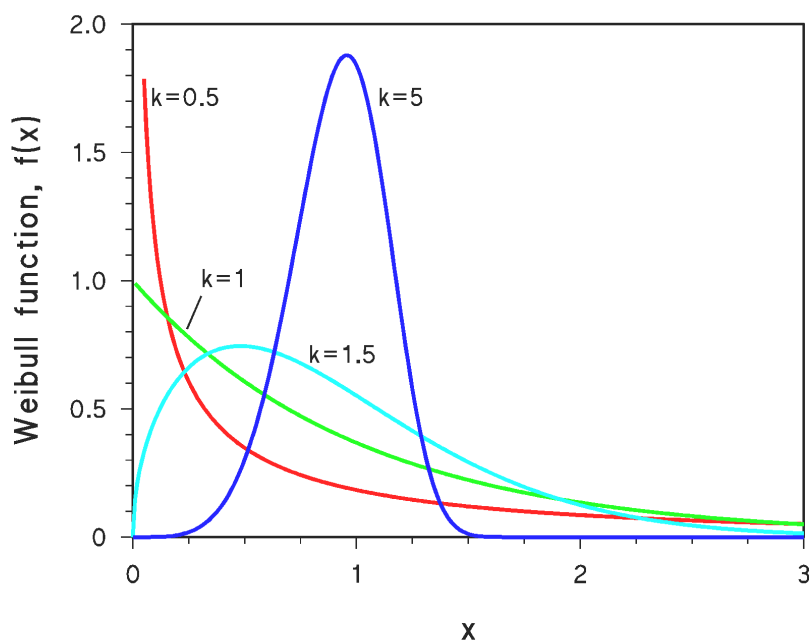


Figure S2. Trends of the simplified Weibull probability density function ($y = k x^{k-1} e^{-x^k}$), for different values of the k parameter.

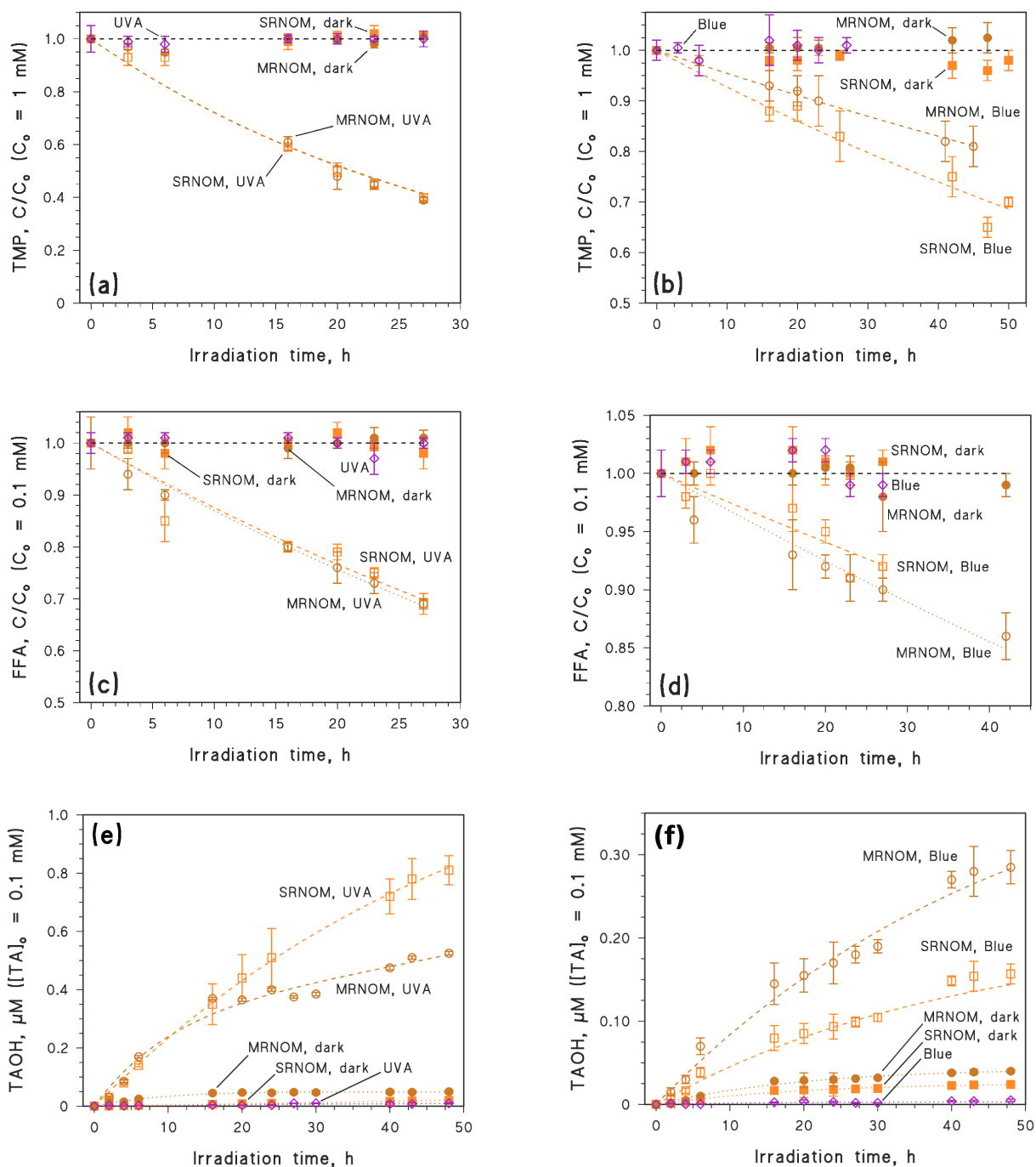


Figure S3. Time trends of the probe molecules, upon irradiation of the probes with SRNOM and MRNOM, of the probes alone, and of probes + SRNOM or MRNOM in the dark. **(a)** TMP, UVA irradiation; **(b)** TMP, irradiation under blue light; **(c)** FFA, UVA irradiation; **(d)** FFA, irradiation under blue light; **(e)** TAOH (from 0.1 mM TA), UVA irradiation; **(f)** TAOH (from 0.1 mM TA), irradiation under blue light. Note the zoomed Y-axis in panels b, c, d.

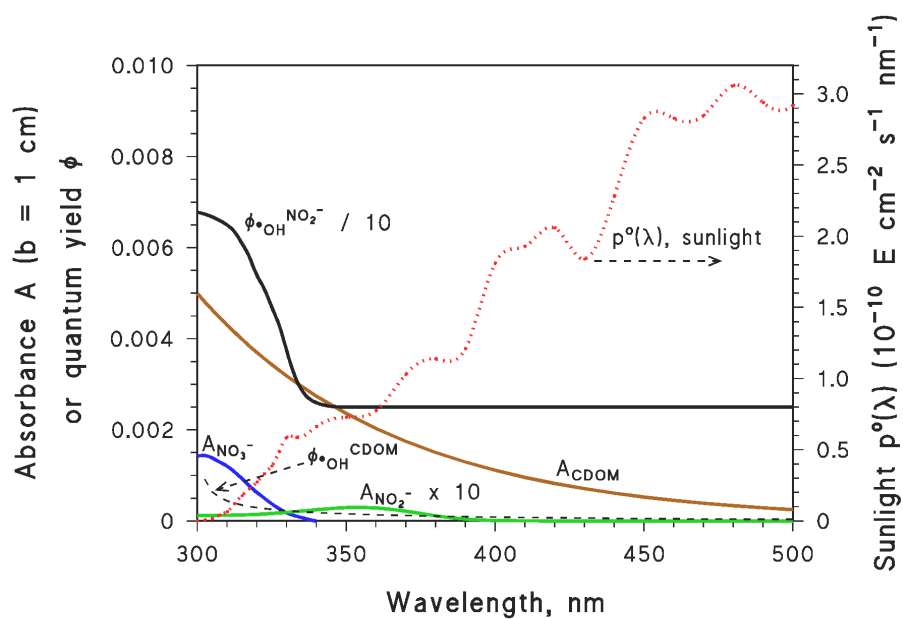


Figure S4. Wavelength trends of the absorbance values (optical path length $b = 1$ cm) of 0.18 mM nitrate, 1.3 μM nitrite and CDOM ($\text{DOC} = 1 \text{ mg}_C \text{ L}^{-1}$). $\bullet\text{OH}$ formation quantum yields from irradiated nitrite and CDOM. Incident spectral photon flux density of sunlight (equivalent to mid-latitude 15 July, at 9 am or 3 pm solar time).

Text S1. Computation of solar radiation and water-column photochemistry in the case of Lake Jyväsjärvi (Finland)

Lake Jyväsjärvi is located in the centre of the town of Jyväskylä in Finland. In Lake Jyväsjärvi, the concentration of nitrate + nitrite is $\sim 136 \mu\text{g L}^{-1}$ ($= 9.7 \mu\text{M}$; Vähätalo, unpublished data). The DOC value of water in the lake is $8\text{-}9 \text{ mg}_\text{C} \text{ L}^{-1}$. Here it was reasonably assumed that $[\text{NO}_2^-] = \frac{1}{100} [\text{NO}_3^-] = 0.097 \mu\text{M}$. **Figure S5** reports the logarithmic units of the absorption spectra of CDOM in Lake Jyväsjärvi, as well as the absorption coefficients of nitrate and nitrite.

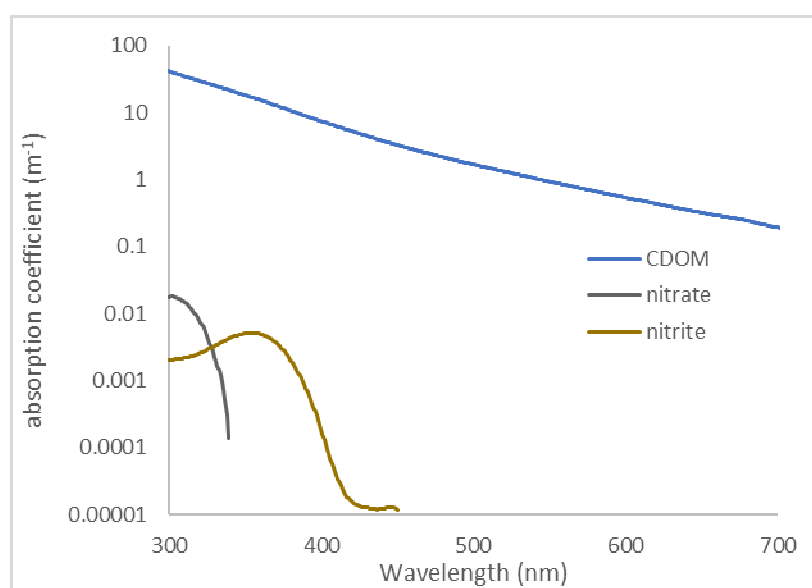


Figure S5. Logarithmic absorption coefficients ($\text{Log}_{10}[a(\lambda)]$) of CDOM in Lake Jyväsjärvi (Vähätalo, unpublished data), and of nitrate and nitrite.

The quantum yields used for calculations of $\bullet\text{OH}$ photoproduction are 0.01 (wavelength-independent) for nitrate, decreasing from 0.068 to 0.025 with increasing wavelength (see **Figure S4**) for nitrite, and wavelength-dependent (**Eq. 33** and **Figure 4** of the main manuscript) for CDOM.

Solar radiation ($p^\circ(\lambda)$) incident on the surface of Lake Jyväsjärvi was assumed as per 23 July 2019 at solar noon. The attenuation of solar radiation (290-500 nm) within the water column was calculated at 0.001 m steps down to 0.5 m, and at 0.01 m intervals from 0.5 m to 1.0 m depth. The solar radiation represents scalar photon flux density at each depth ($p_z^\circ(\lambda)$).

The rate of $\bullet\text{OH}$ photoproduction was calculated by integrating the relevant equations from 290 to 500 nm (from 301 nm in the case of CDOM), as follows:

$$R_{\text{OH}}^{\text{NO}_3^-} = \int_{\lambda} [p_z^{\circ}(\lambda) a_{\text{NO}_3^-}(\lambda) \Phi_{\text{NO}_3^-}(\lambda)] d\lambda \quad (\text{S1})$$

$$R_{\text{OH}}^{\text{NO}_2^-} = \int_{\lambda} [p_z^{\circ}(\lambda) a_{\text{NO}_2^-}(\lambda) \Phi_{\text{NO}_2^-}(\lambda)] d\lambda \quad (\text{S2})$$

$$R_{\text{OH}}^{\text{CDOM}} = \int_{\lambda} [p_z^{\circ}(\lambda) a_{\text{CDOM}}(\lambda) \Phi_{\text{CDOM}}(\lambda)] d\lambda \quad (\text{S3})$$

The calculation results are shown as **Figure 6** of the main manuscript.