Photosensitizing properties of 2,4-dichlorobenzoic acid and chlorinated biphenyl carboxylic acids, potentially key components of chromophoric dissolved organic matter.

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Absorbance of the model compounds of marine CDOM

Molar absorptivities of each compound were obtained from the slope of a linear fit to a plot of absorbance versus concentration at a particular wavelength in each of the solvents listed. Absorbance spectra were acquired on a Jasco V-530 spectrophotometer.

Table S1 Molar absorptivities of the model compounds in CH_3CN, H_2O (D_2O), and EtOH at 300, 266, and 254 nm.

Compound	Solvent	$\varepsilon_{300\,nm}$	$\varepsilon_{266\,nm}$	$\varepsilon_{254\,nm}$
2,4-DCBA	CH_3CN	40 ± 1	776 ± 7	nd
	EtOH	nd[a]	747 ± 3	nd
	H_2O (D_2O)[b]	25 ± 1	477 ± 8	1080 ± 20
BA	CH_3CN	< 1	750 ± 10	nd
	EtOH	nd	730 ± 3	nd
	H_2O (D_2O)	< 1	559 ± 1	711 ± 8
TCB	CH_3CN	42 ± 2	154 ± 4	93 ± 2
BPA	CH_3CN	2950 ± 40	21500 ± 200	nd
	EtOH	nd	21000 ± 70	nd
	H_2O (D_2O)	1400 ± 100	nd	15000 ± 1000
mono-Cl-BPA	CH_3CN	150 ± 10	12000 ± 100	14900 ± 100
	EtOH	nd	14200 ± 500	16400 ± 500
	H_2O (D_2O)	180 ± 10	nd	14700 ± 600
di-Cl-BPA	CH_3CN	3080 ± 30	12500 ± 100	nd
	EtOH	nd	27700 ± 800	nd
	H_2O (D_2O)	4400 ± 100	nd	16200 ± 400
PCB-47	CH_3CN	< 1	1640 ± 20	4770 ± 10

[a] nd = not determined. [b] 266 nm molar absorptivities were measured in D_2O.

Calculation of environmental half-lives

Environmental half-lives ($t_{1/2}$) were calculated according to Eq (S1).

$$t_{1/2} = \frac{\ln 2}{(\Sigma \varepsilon_\lambda L_\lambda)\Phi_{direct}} \tag{S1}$$

In Eq (S1), ε_λ are the molar absorptivities of the substrate at a given wavelength, L_λ values are the solar intensity obtained from Leifer for 30° N and represent a 24 hour average intensity.[1] The wavelength range of 296 – 440 nm was used, corresponding to environmentally relevant wavelengths.

Table S2 Aquatic environmental half-lives for model CDOM components based on direct photolysis.

Compound	$t_{1/2}{}^{a}$
2,4-DCBA	21 days
BPA	3 yrs
2'-Cl-BPA	4 hrs
3',4'-di-Cl-BPA	13 days

^{a} Calculated based on a 24 hour average sunlight intensity at 30° N.

Supporting Information References

1.   A. Leifer, *The Kinetics of Environmental Aquatic Photochemistry: Theory and Practice*. American Chemical Society: Washington, DC, 1988.