Supporting Information

PHOTOCHEMICAL PRODUCTION AND PHOTOLYSIS OF ACRYLATE IN SEAWATER

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Supporting Information is 10 pages including 6 figures and 1 table

S1 Determination of Hourly Rates. Average, clear-sky photochemical production rates were determined by first dividing the nM of acrylate produced during a photochemical experiment by the hours samples were exposed to solar radiation. Observed hourly rates were then scaled to rates that would be expected under cloudless, clear-sky conditions on days that the photochemical experiments were conducted. This was done by dividing hourly rates by the ratio of the photon exposure determined by nitrite actinometry to the clear-sky photon exposure between 330-380 nm determined by the Simple Model of the Atmospheric Radiative Transfer of Sunshine (SMARTS) model version 2.9.5[1] (https://www.nrel.gov/grid/solar-resource/smarts.html) for the days each photochemical experiment was conducted. Data used for these calculations are presented in Table S1.

The SMARTS hourly spectral irradiance (local time 07:00–17:00) for each irradiation day was modeled following the protocol in Zhu and Kieber.[2] Two input parameters were used in the SMARTS model: aerosol optical depth at 550 nm (AOD_{550nm}) and total column ozone concentrations. The daily AOD_{550nm} was from the Moderate-Resolution Imaging Spectroradiometer (MODIS) and the total column ozone concentrations were from the Aura Ozone Monitoring Instrument (OMI) monthly averaged data. Both the ozone and AOD_{550nm} data were from NASA's Goddard Earth Sciences Data and Information Services Center (https://disc.gsfc.nasa.gov/).

Table S1 Data used to calculate average, clear-sky photochemical production rates. All irradiations were performed in Syracuse NY, except for the Mo'orea samples that were irradiated at the Gump Research Station in Mo'orea, French Polynesia. Nitrite actinometry and the SMARTS model integrated photon exposure between 330-380 nm. GOM denotes the Gulf of Mexico

Irradiation dates	Sample	Hours irradiated	Acrylate produced (nM)	Nitrite photon exposure (μmol quanta cm^{-2})	SMARTS photon exposure (μmol quanta cm^{-2})	Nitrite/ SMARTS	Clear-sky rate (nM h^{-1})
April 7	Mo'orea Pacific Ocean	10.0	0.51	225.2	259.8	0.867	0.059
April 16-17	Mo'orea coral reef	20.0	0.66	405.5	491.7	0.825	0.040
April 18-20	Mo'orea Pacific Ocean	30.0	1.34	580.7	726.7	0.799	0.056
April 24-25	Mo'orea coral reef	20.0	0.94	309.4	468.7	0.660	0.071
August 20	GOM coastal	8.5	1.16	231.8	244.4	0.948	0.144
August 24	Delaware Estuary	9.0	0.95	236.5	242.6	0.975	0.108
September 4	Georges Bank	8.6	0.88	208.8	223.4	0.935	0.109
September 10	GOM open ocean	8.8	0.48	206.9	214.2	0.966	0.056
September 20	North Pacific Ocean	8.0	0.47	176.2	188.6	0.934	0.063
September 24	coastal Rhode Island	8.0	0.79	161.4	180.3	0.895	0.110
October 23-25	Sargasso Sea	18.5	0.47	236.8	317.5	0.746	0.034

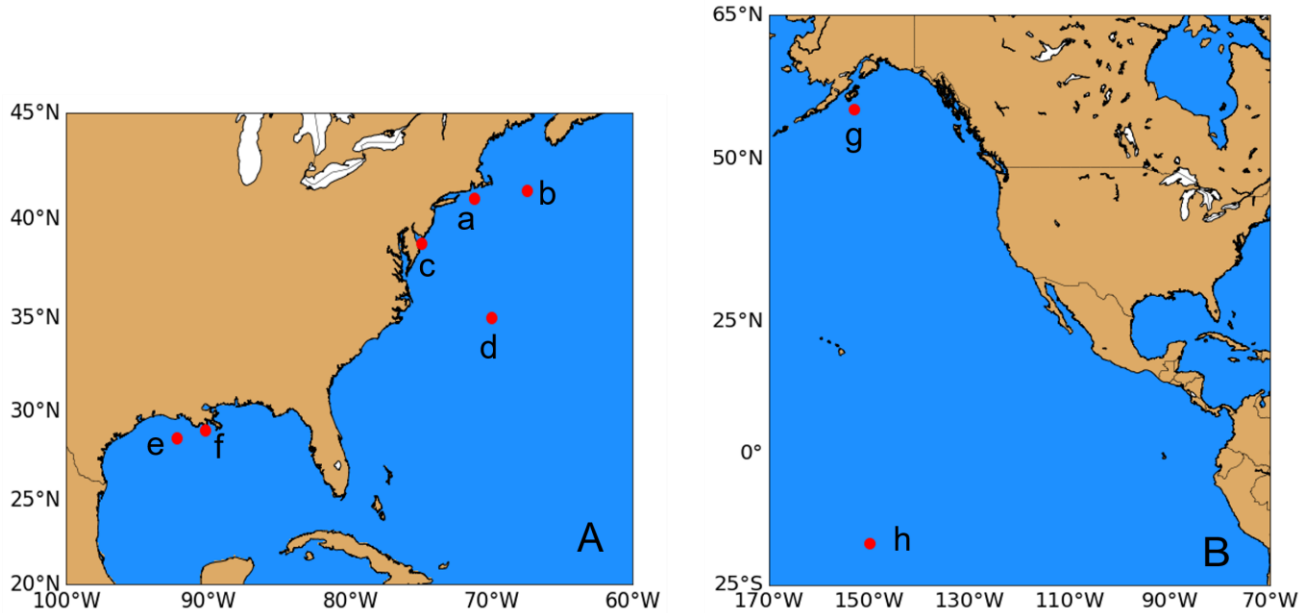

Figure S1 Hydrographic stations in the (A) Atlantic and (B) Pacific Ocean where samples were collected for photochemical experiments. Station notation: a, coastal Rhode Island; b, Georges Bank; c, mouth of the Delaware Estuary; d, Sargasso Sea; e, Gulf of Mexico, open ocean; f, Gulf of Mexico, coastal; g, North Pacific; h, coral reef and Pacific Ocean waters off the island of Mo'orea, French Polynesia.

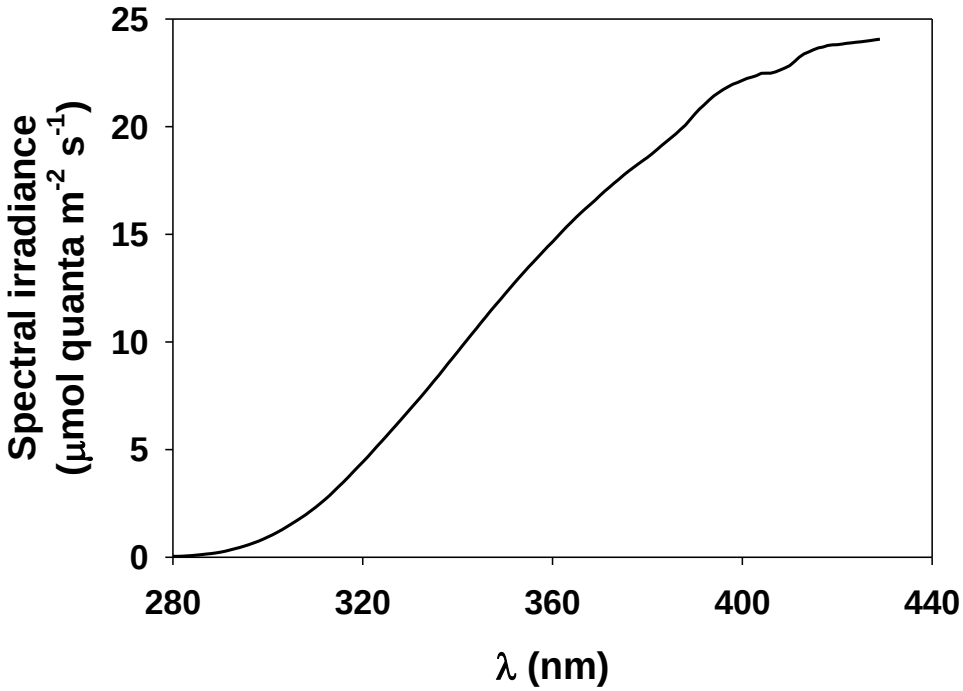

Figure S2 Spectral irradiance output from the 300 W xenon lamp between 280 and 430 nm after it passed through Milli-Q water to remove IR and a Pyrex plate to remove UV radiation less than 290 nm.

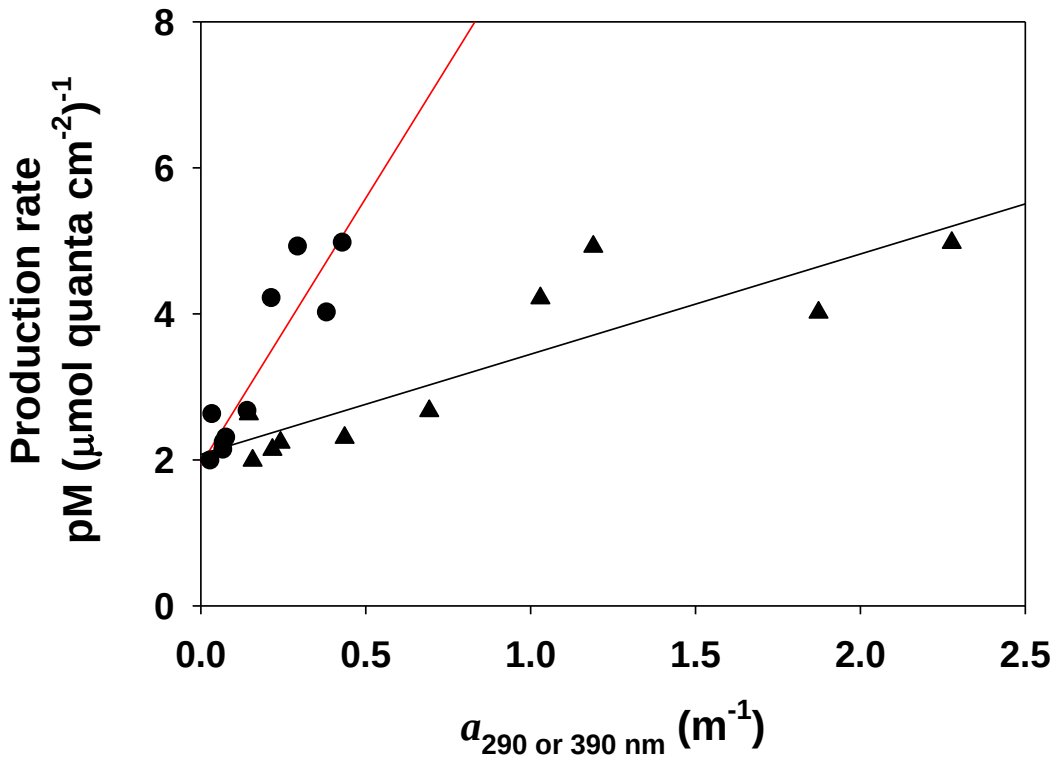

Figure S3 Nitrite-based photochemical production rates of acrylate in the same samples shown in Figure 2 plotted against the CDOM absorption coefficient at 290 (a_{290nm}, triangle) or 390 nm (a_{390nm}, circle). The solid black and red lines are the best fit from linear regression analysis. The slopes and y-intercepts ± std errors are: 1.37 ± 0.27 pM m (µmol quanta $cm^{-2})^{-1}$ and 2.08 ± 0.30 pM (µmol quanta $cm^{-2})^{-1}$ for 290 nm (black line) and 7.29 ± 1.18 pM m (µmol quanta $cm^{-2})^{-1}$ and 1.94 ± 0.26 pM (µmol quanta $cm^{-2})^{-1}$ for 390 nm (red line).

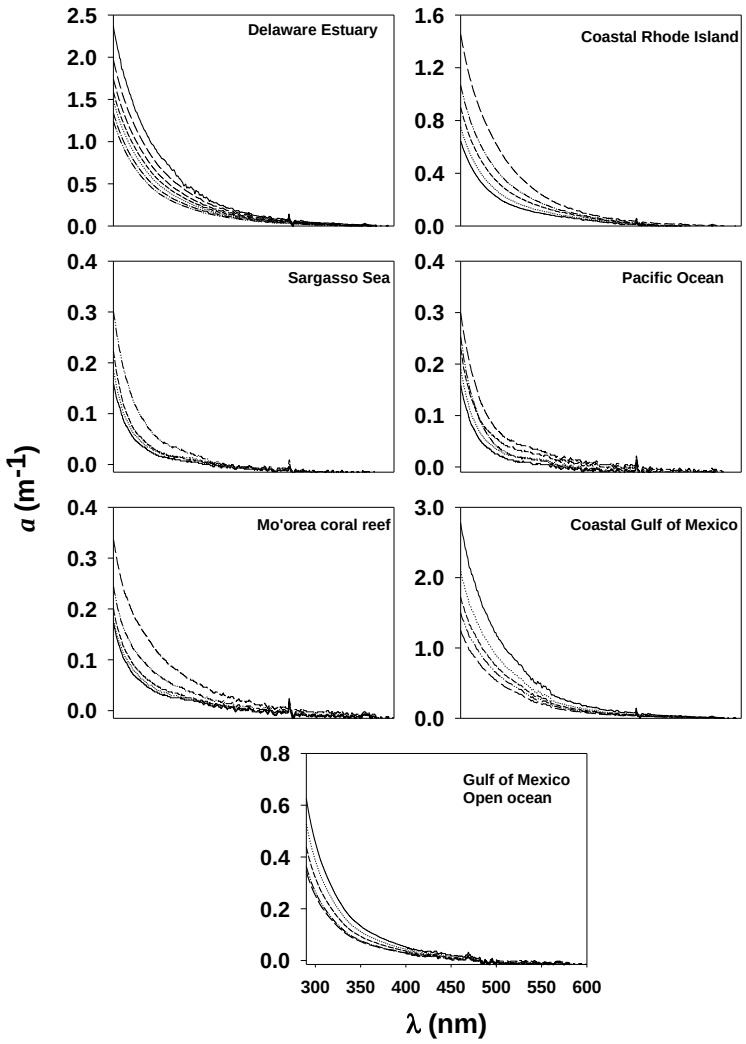

Figure S4 Decrease in the wavelength-dependent CDOM absorption coefficient during the irradiation of seawater samples using the solar simulator. For each seawater sample, wavelength-dependent absorption coefficients decreased from the initial spectrum to subsequent spectra at irradiation times of 2, 4, 7, and 10 h. All absorbance spectra were determined using an Ocean Optics spectrophotometer (model, SD-2000). The hourly photon exposure between 330 and 380 nm as determined by nitrite actinometry in the quartz flasks was 0.22 ± 0.01 mmol quanta cm^{-2}.

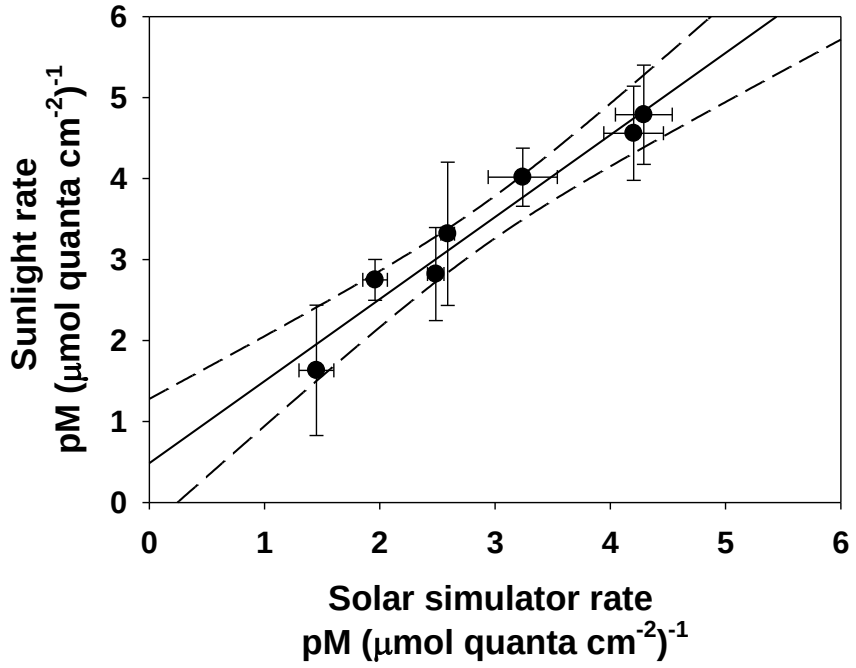

Figure S5 Acrylate photoproduction rate determined in seawater samples exposed to sunlight plotted against the rate determined in the same seawater samples exposed to the solar simulator. Both rates were calculated based on the photon exposure determined by nitrite actinometry. The solid line is the best fit line determined from linear regression analysis with a slope ± std error = 0.94 ± 0.09, a y-intercept ± std error = -0.32 ± 0.33 pM (μmol quanta $cm^{-2})^{-1}$, and r = 0.98. The dashed lines denote the 95% confidence interval. Vertical and horizontal error bars denote the standard deviation of replicate samples (n = 3 or 4).

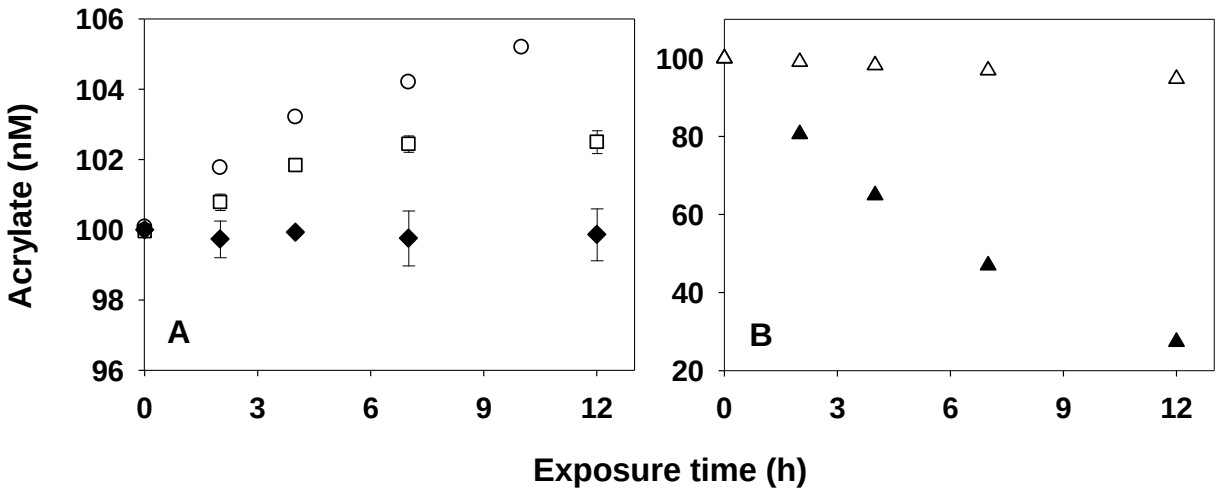

Figure S6 (A) Observed photochemical production of acrylate in 0.2 µm-filtered seawater samples collected from coastal Rhode Island (circles) and the Sargasso Sea (squares) exposed to the solar simulator for up to 12 h. Solid diamonds denote the observed change in the acrylate concentration in Milli-Q water during exposure to the solar simulator for 12 h; the initial acrylate concentration used in the Milli-Q water experiment was 100 nM. (B) Modeled photochemical loss of 100 nM acrylate using the published first-order rate constant ($k_{photolysis}$) of 3×10^{-6} s^{-1} (Wu et al.[3]; solid triangles) and 1.3×10^{-7} s^{-1} (Bajt et al.[4]; open triangles). The Bajt et al.[4] $k_{photolysis}$ was based on 15% loss of acrylate after exposure of a seawater sample to sunlight for 30 days assuming first-order kinetics. The Wu et al.[3] and Bajt et al.[4] $k_{photolysis}$ rates constants were normalized to the solar simulator spectral output between 330 and 380 nm (~7.5 suns). For all solar simulator experiments, the hourly photon exposure between 330 and 380 nm was 0.22 ± 0.01 mmol quanta cm^{-2}.

References

(1) Gueymard, C. A. Parameterized transmittance model for direct beam and circumsolar spectral irradiance. *Sol. Energy* **2001**, *71*, 325−346.

(2) Zhu, Y.; Kieber, D. J. Global model for depth-dependent carbonyl photochemical production rates in seawater. *Global Biogeochem. Cy*. **2020**, *34*, e2019GB006431.

(3) Wu, X.; Liu, C.-Y.; Li, P.-F. Photochemical transformation of acrylic acid in seawater. *Mar. Chem*. **2015**, *170*, 29–36.

(4) Bajt, O.; Šket, B.; Faganeli, J. The aqueous photochemical transformation of acrylic acid. *Mar. Chem*. **1997**, *58*, 255–259.