Electronic Supporting Information

Controls on the photochemical production of hydrogen peroxide in Lake Erie

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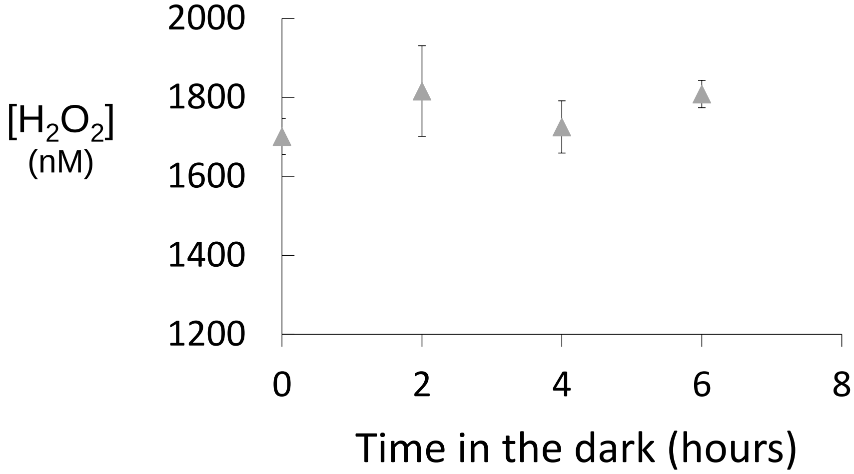

Figure S1: H_2O_2 concentrations (average ± 1 standard error) in filtered Lake Erie water in the dark at room temperature. The slope of the linear regression was not significantly different than zero ($p > 0.05$).

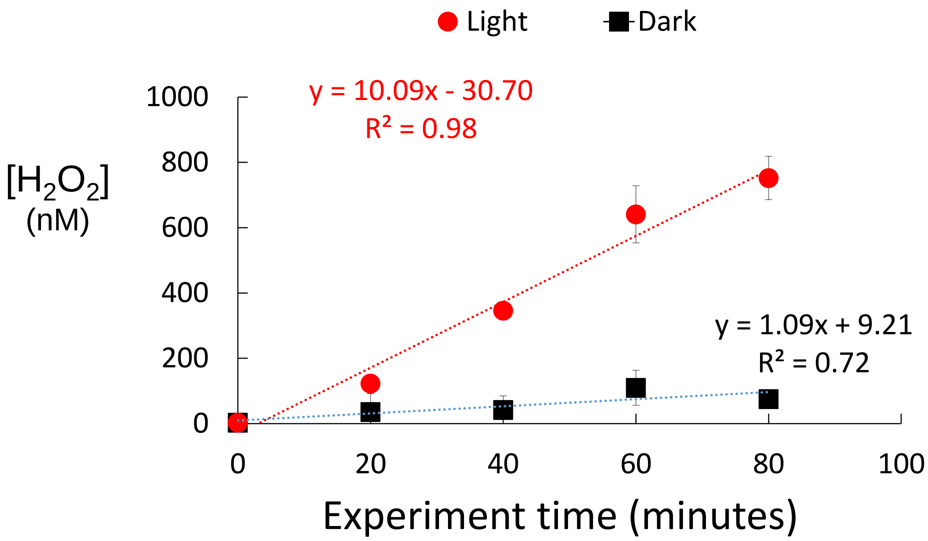

Figure S2: H_2O_2 concentrations (average ± 1 standard error, n = 3) increased linearly ($p < 0.05$) in filtered Lake Erie water exposed to simulated sunlight. Lake Erie water was collected from site WE2 on 23-July-2019.

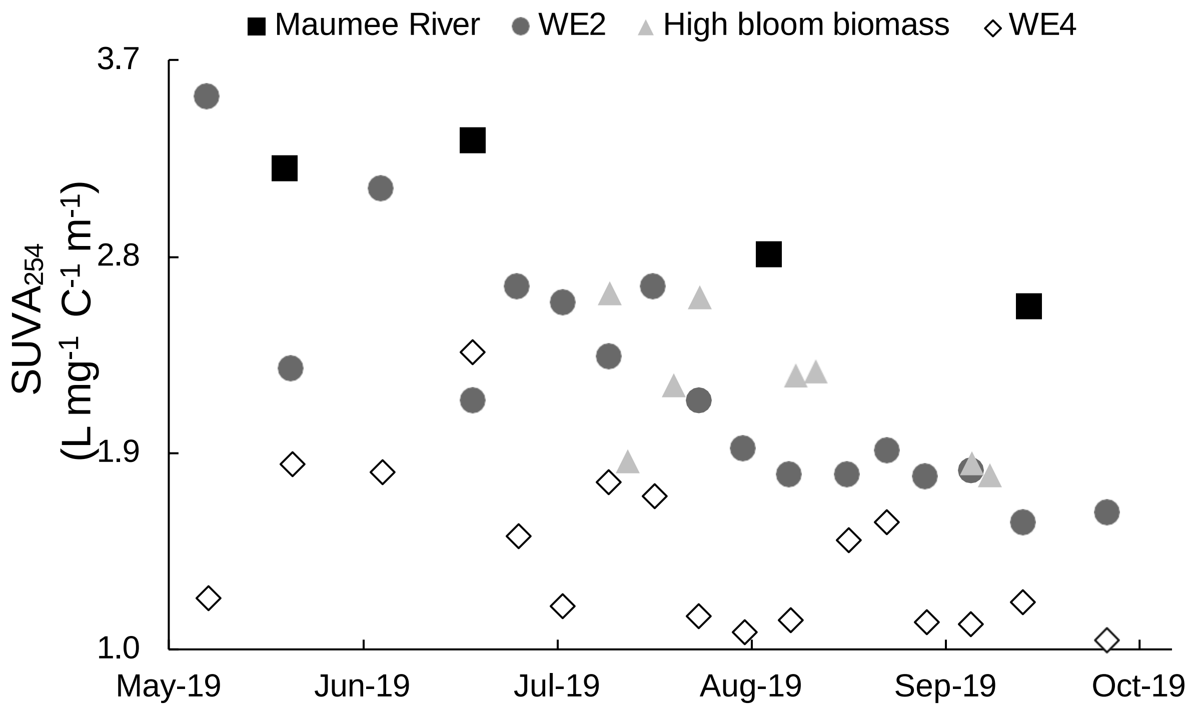

Figure S3: SUVA $_{254}$ in the Maumee River and Lake Erie during summer 2019.

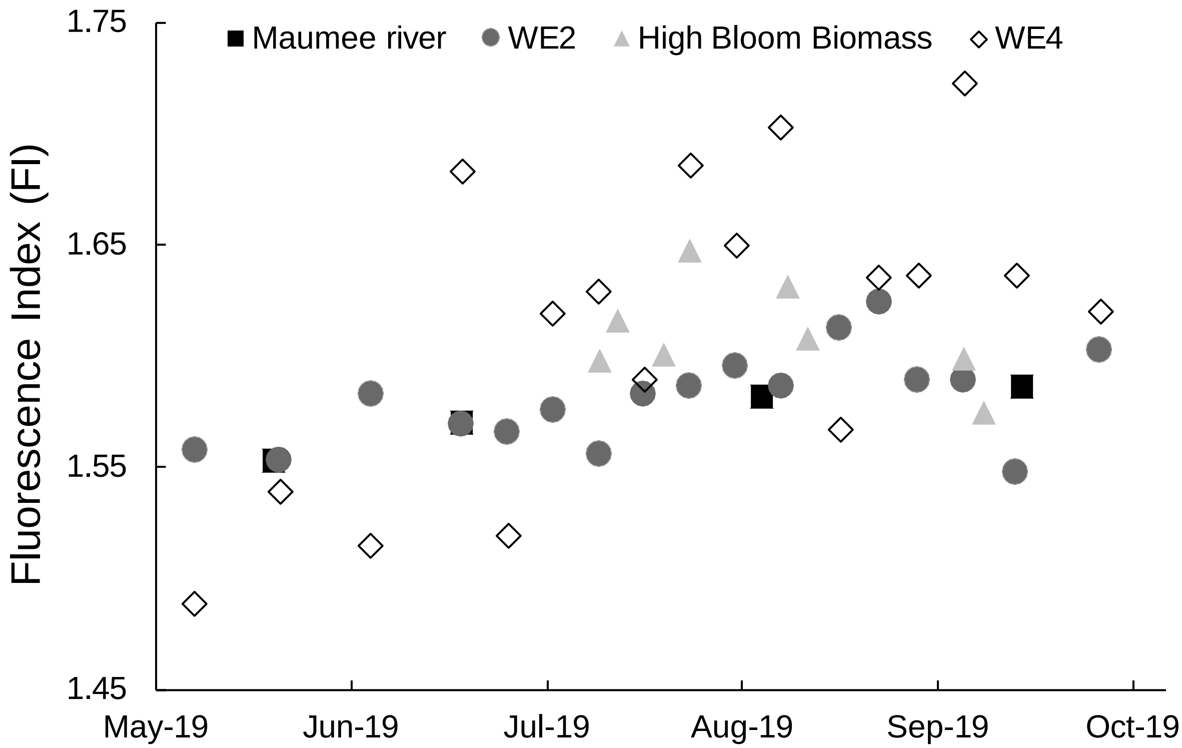

Figure S4: Fluorescence Index (FI) in the Maumee River and Lake Erie during summer 2019.

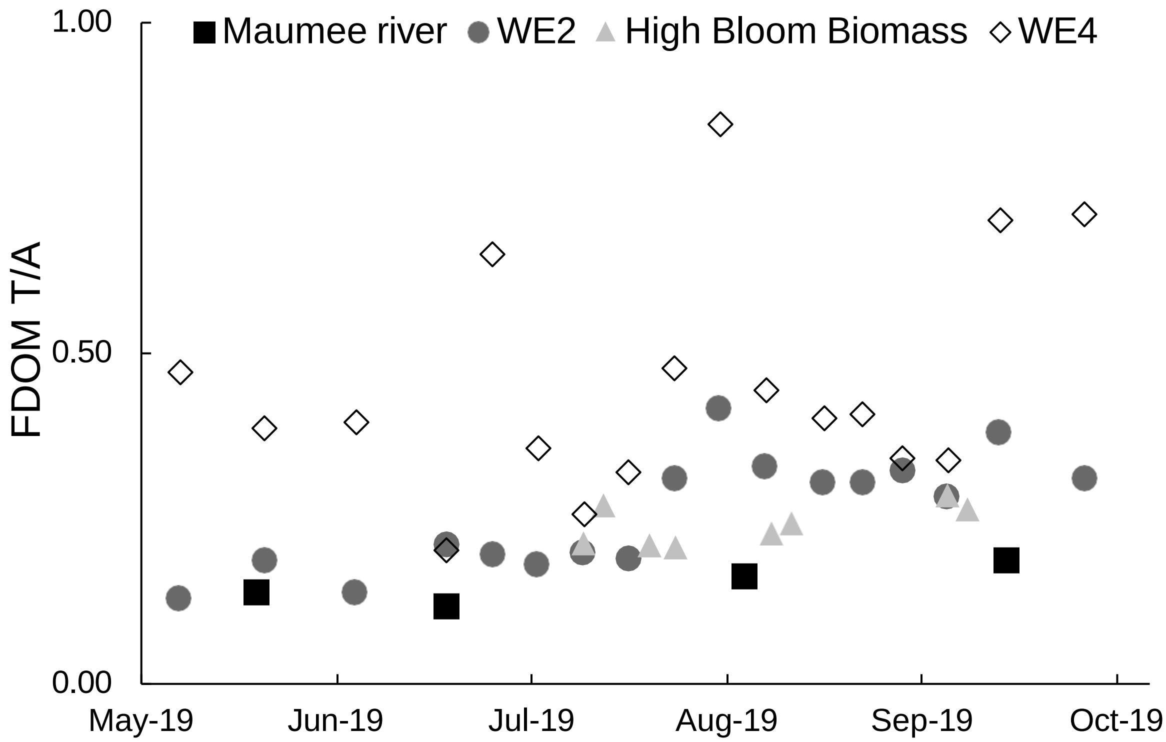

Figure S5: FDOM T/A ratio in the Maumee River and Lake Erie during summer 2019.

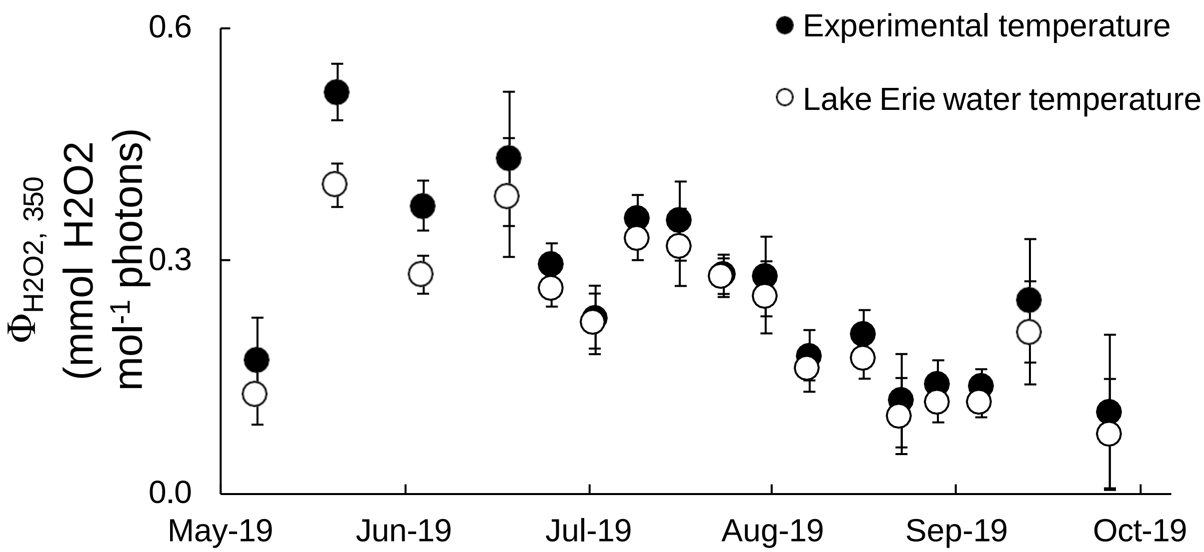

Figure S6: Apparent quantum yield for H_2O_2 production at 350 nm ($\Phi_{H2O2,350}$) measured in water from site WE2 corrected to Lake Erie water temperatures are within the analytical uncertainty of measurements of H_2O_2 concentrations by Amplex® Red method except for water collected in June. Error bars show ± 1 standard error of experimental replicates (n =3).

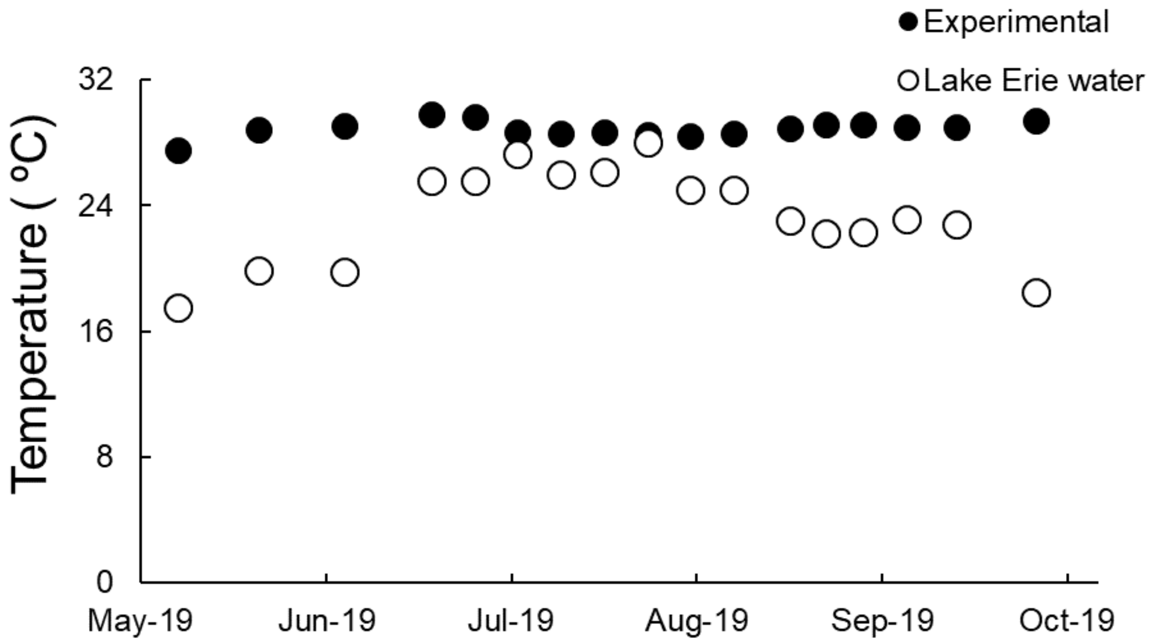

Figure S7: Water temperatures measured during water sampling at WE2 compared to experimental temperatures when quantifying $\Phi_{H2O2,\lambda}$.

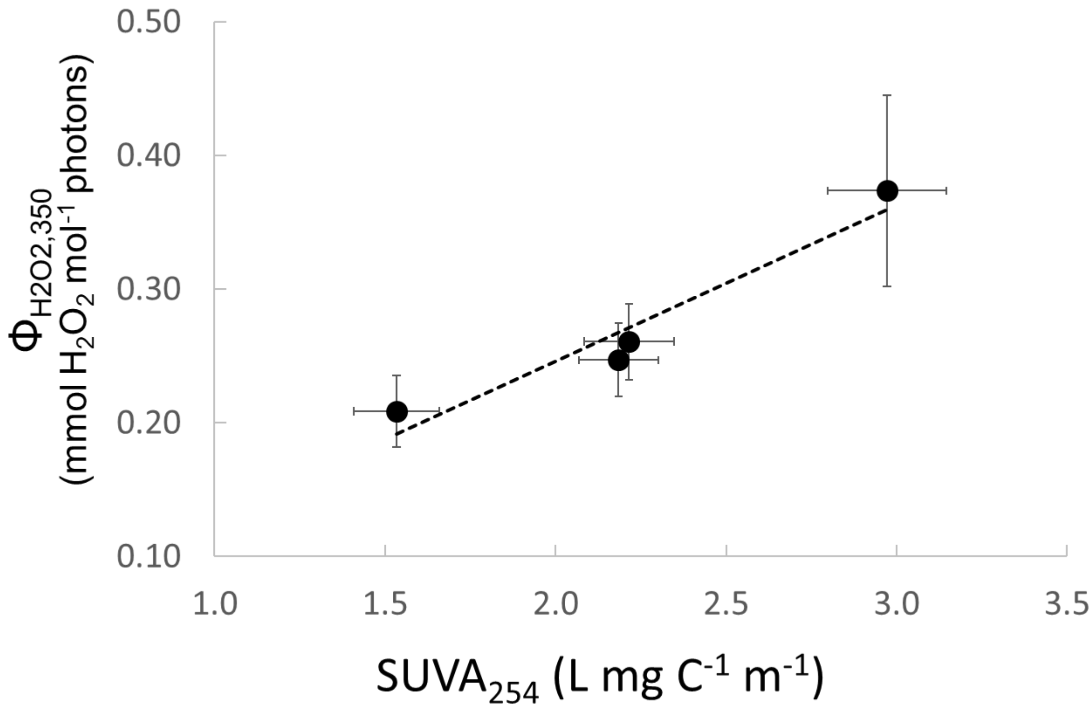

Figure S8: Average $\Phi_{H2O2,350}$ at each site vs. average $SUVA_{254}$ at each site (Maumee River, Bloom Chase, WE2, WE4). Error bars show standard error of all water samples at each site. Line shows linear regression ($p < 0.05$).

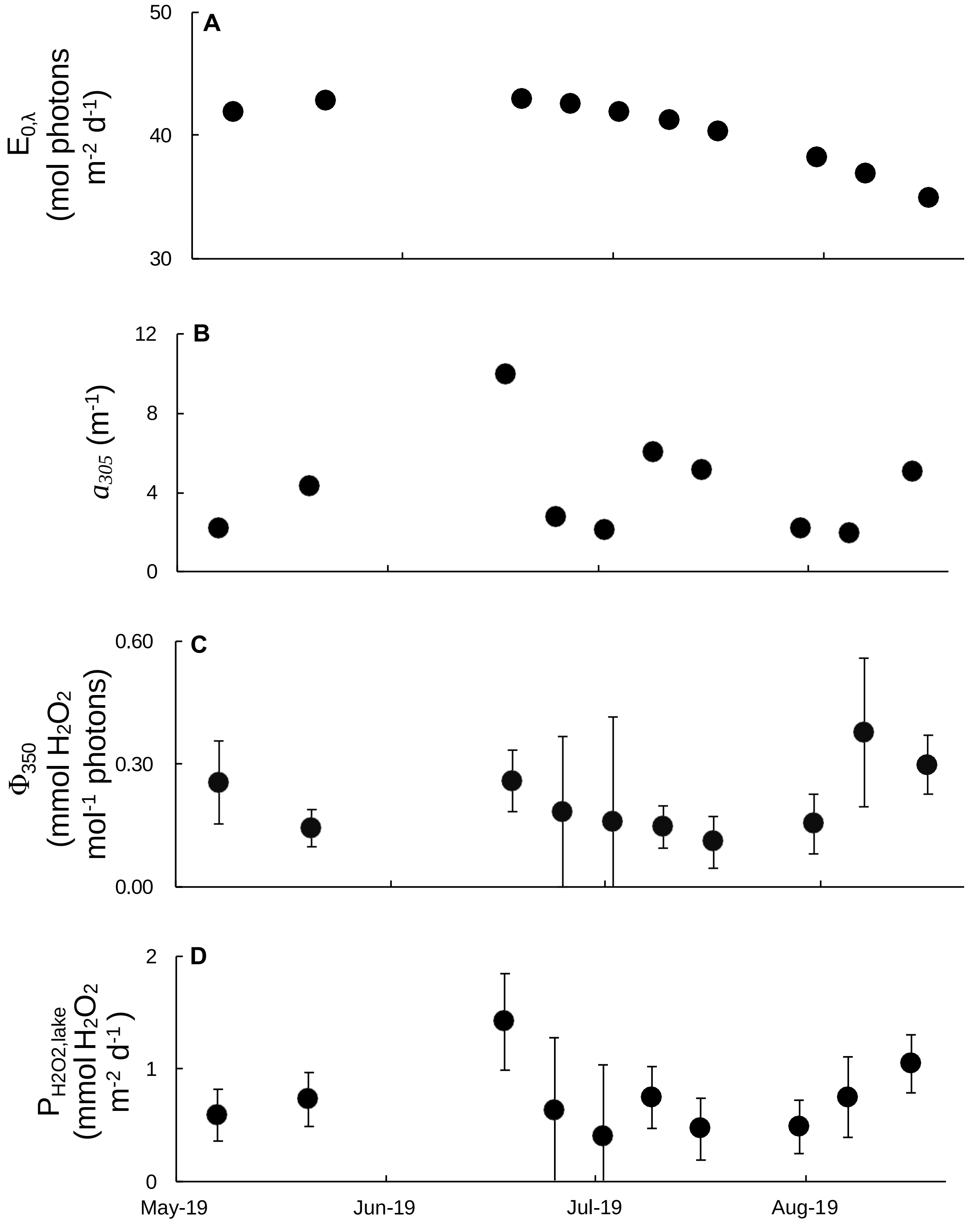

Figure S9. Photochemical production of H_2O_2 by CDOM over depth of 1 m at WE4 in Lake Erie in summer 2019. A) Daily total photon flux reaching the surface of Lake Erie ($E_{0,\lambda}$ modeled for 7am-7pm Eastern Standard Time). B) CDOM absorption coefficient at 305 nm (a_{305}). C) Apparent quantum yield for H_2O_2 production at 350 nm ($\Phi_{H2O2,350}$). D) Photochemical production rate of H_2O_2 at WE4 in Lake Erie ($P_{H2O2,lake}$). Error bars show ± 1 standard error of experimental replicates (n = 3).

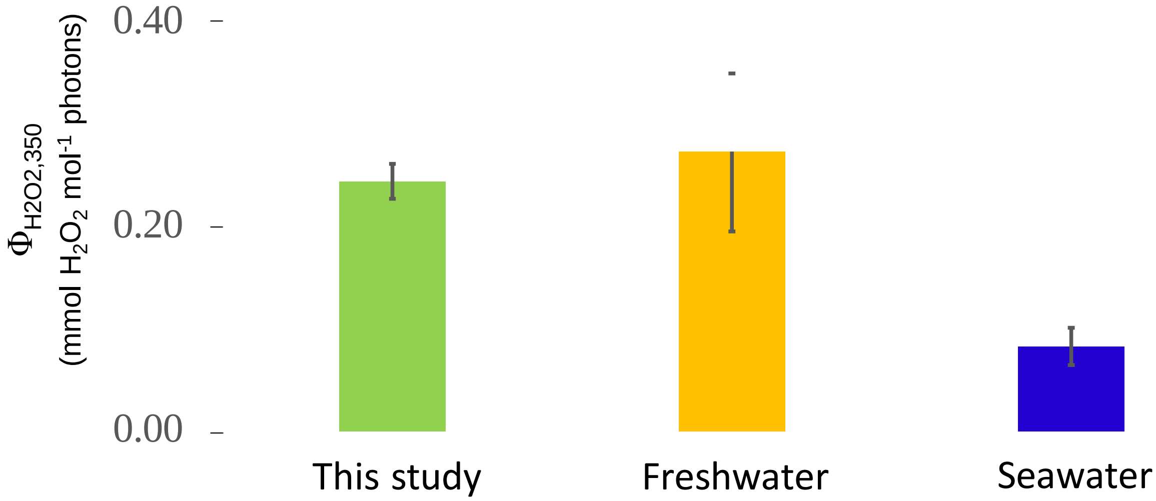

Figure S10: Apparent quantum yield for H_2O_2 production at 350 nm ($\Phi_{H2O2,350}$) from freshwaters sampled for this study compared to an average apparent quantum yield for H_2O_2 production at ~ 350 nm aggregated from other freshwaters and a pooled seawater average (from Andrews et al. 2000, Cooper et al. 1988, Scully et al.1996 O'Sullivan et al. 2005, and Powers & Miller 2014 as cited in the main text). Error bars show ± 1 standard error (n = 39 water samples of Lake Erie; n= 4 $\Phi_{H2O2,350}$ reported on freshwaters in the literature).

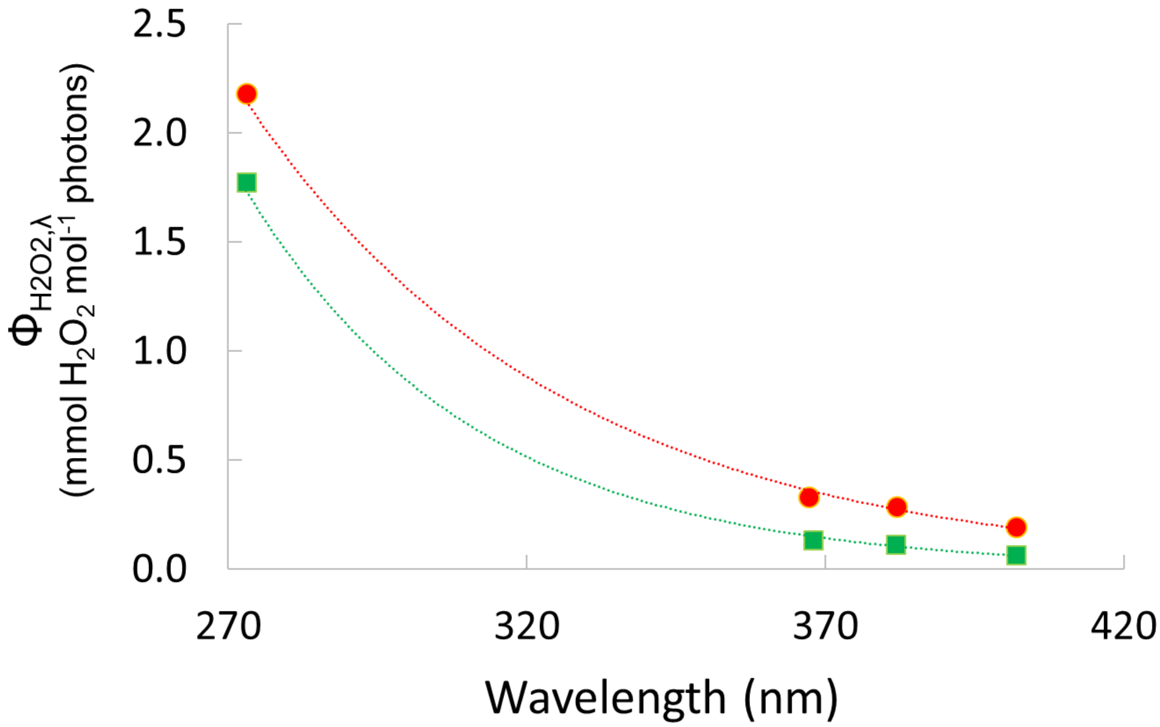

Figure S11: Apparent quantum yield for H_2O_2 production ($\phi_{H2O2,\lambda}$) quantified by the LED method for the Maumee River (6-July-2021) and site WE2 in in Lake Erie (14-July-21). $\Phi_{H2O2,\lambda}$ shown as average at each LED wavelength. Error bars (smaller than point size) show ± 1 standard error (n = 2 replicates at each wavelength). Each line shows the best fit (exponential decay).

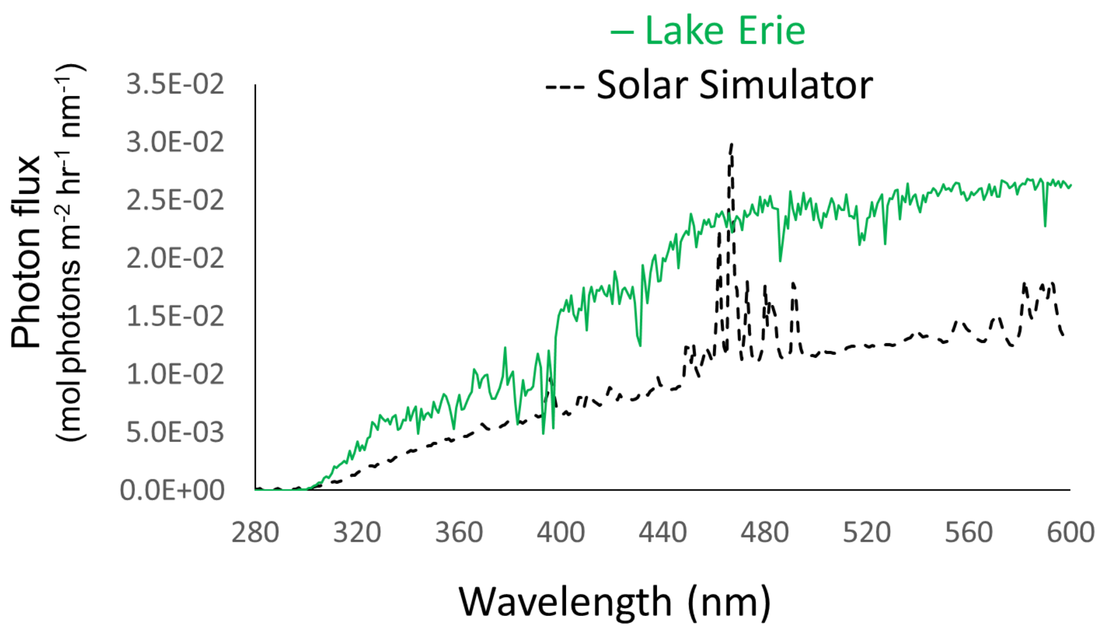

Figure S12. Photon flux reaching the surface of Lake Erie at 1pm local time on 17-June-2019 and from the Atlas Solar Simulator (set to 750 W m^{-2}). Lake Erie photon flux was modeled from NCAR TUV calculator for clear sky conditions (see main text and Cory et al. 2016).

Table S1: Average, maximum and minimum CDOM concentration at 305 nm (a_{305}), apparent quantum yield at 350 nm ($\Phi_{H2O2,350}$) and daily photon flux integrated over all wavelengths ($E_{0,280\text{-}600}$) used in the sensitivity analysis at Lake Erie sites WE2 and WE4.

			WE2	
Term	Units	Average	Maximum	Minimum
a_{305}	m^{-1}	9	37	2
$\Phi_{H2O2,350}$	mol H_2O_2 mol^{-1} photons	0.3	0.5	0.1
$E_{0,280\text{-}600}$	mol photons m^{-2} s^{-1}	38	43	24
			WE4	
a_{305}	m^{-1}	3	11	0.9
$\Phi_{H2O2,350}$	mol H_2O_2 mol^{-1} photons	0.2	0.4	0.1
$E_{0,280\text{-}600}$	mol photons m^{-2} s^{-1}	38	43	24

The average, maximum and minimum CDOM concentration was obtained from a dataset of summertime measurements collected from 2014-2020. Data from 2014-2015 published in Cory et al. 2016, and 2019 data are in this study (Figure 3 and S7). The 95% confidence interval on the average CDOM concentration at 305 nm is ± 1 m^{-1} at WE2 and 0.3 m^{-1} at WE4. Uncertainty in the $\Phi_{H2O2,350}$ is presented in the main text and in Figures 2, 3 and S7. Uncertainty was not assessed for the integrated daily photon flux spectra ($E_{0,280\text{-}600}$) which was obtained from NCAR TUV calculator for clear sky conditions as described in the methods section.

Comparison of experimental H_2O_2 production rates ($P_{H2O2,exp}$) by Amplex® Red and Felume methods

To understand whether H_2O_2 production observed in dark controls is an experimental artifact associated with Amplex® Red method, we compared H_2O_2 production rates in light-exposure and dark control treatments using the Amplex® Red method and a chemiluminescence flow injection (Felume) method (King et al. 2007, as cited in the main text) in a river water sample (Huron River) relatively high in CDOM, and in a Lake Erie water sample, relatively low in CDOM. Light treatment samples were exposed to simulated sunlight for 80 minutes (See Methods) in triplicates in 80 mL quartz tubes alongside dark controls in 60 mL amber HDPE bottles wrapped in aluminum foil. H_2O_2 concentrations were measured by both Amplex® Red and Felume method within 24 hours of the experiment. Light-dark experimental rate of H_2O_2 production ($P_{H2O2,exp}$) was quantified (See Methods).

There was no significant difference ($p < 0.05$) in $P_{H2O2,exp}$ measured by Amplex® Red method and Felume method in Huron River water (Table S1). In Lake Erie water, $P_{H2O2,exp}$ quantified by Amplex® Red method was significantly higher than Felume method (Table S1). The methodological difference in $P_{H2O2,exp}$ observed in Lake Erie water mainly due to dark H_2O_2 production quantified by the Amplex® Red method.

The Amplex® Red method showed significant dark H_2O_2 production in both Huron River water and Lake Erie water, while the Felume method showed no detectable dark H_2O_2 production (Table S1). These results suggest that dark H_2O_2 production is likely an artifact associated with Amplex® Red method, as has been observed by others using similar reagents to quantify H_2O_2 in natural waters (Zhang et al. 2016). Further support that dark H_2O_2 production is an artifact of the Amplex® Red method was similar dark H_2O_2 production in Huron River water and in Lake Erie water (16 nmol m^{-3} s^{-1}; Table S1).

Dark H_2O_2 production was 5% of the H_2O_2 production in light treatment in Huron River water (Table S1). In contrast to high CDOM river water, dark production of H_2O_2 was up to 18% of the H_2O_2 production in light treatment of lower CDOM Lake Erie water. Thus, lower $P_{H2O2, exp}$ associated with low CDOM waters are more sensitive to dark production quantified from the Amplex® Red method compared to higher H_2O_2 production quantified from higher CDOM waters. Based on these results, dark production from the Amplex Red method had little impact on $P_{H2O2, exp}$ in waters where $aCDOM_{305}$ was greater than 7 m^{-1}.

Table S2: The average experimental rate of H_2O_2 production ($P_{H2O2,exp}$; nmol $m^{-3}s^{-1}$) measured by Amplex® Red and Felume methods in Huron River water and Lake Erie water. Error show ± 1 standard error of experimental replicates (n = 3).

	Amplex® Red			Felume		
	Light-treatment	Dark control	$P_{H2O2,exp}$	Light-treatment	Dark control	$P_{H2O2,exp}$
Huron River	324 ± 20	16 ± 4	308 ± 20	295 ± 41	0 ± 0	295 ± 41
Lake Erie	91 ± 5	16 ± 6	75 ± 7	56 ± 4	0 ± 0	56 ± 4

References

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