Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Photolysis of the Herbicide Dicamba in Aqueous Solutions and on Corn Surfaces:

Supporting Information

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Section 1:

First order kinetics plots for all rate constants. All plots show the natural log of dicamba concentration versus irradiation time in minutes. The data points are from the experiment described in the figure captions and the lines are the weighted linear regression used to obtain the rate constant, k.

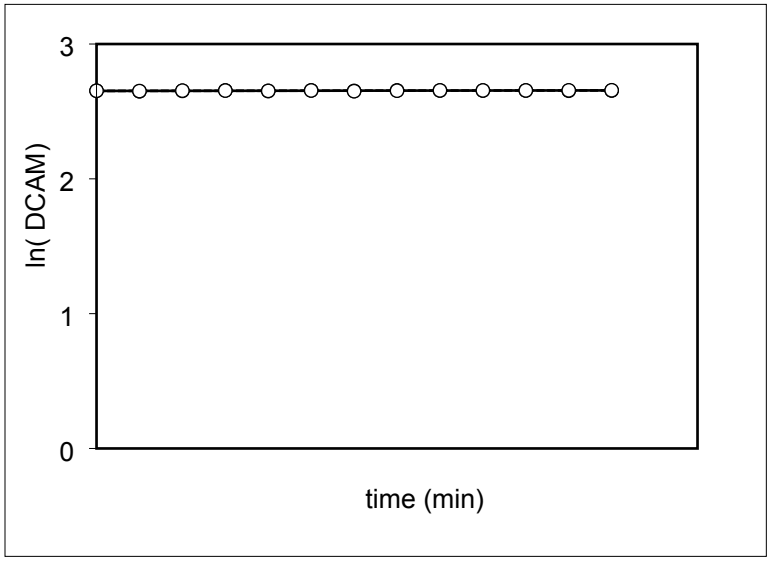

Figure S-1: Dark control – No irradiation of 15 mg/L dicamba solution. No reaction.

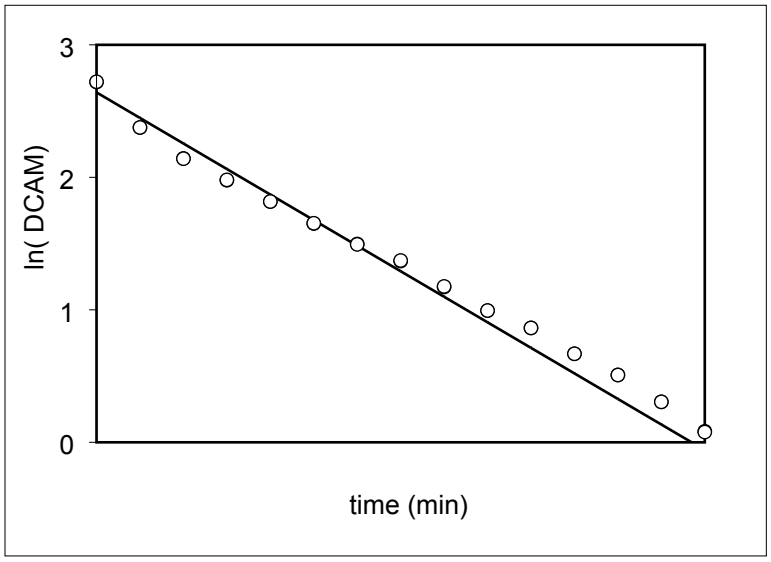

Figure S-2: Irradiation of 15 mg/L dicamba at pH 7 at 254 nm. k = 0.0386 min^{-1}. Line is the weighted linear regression line.

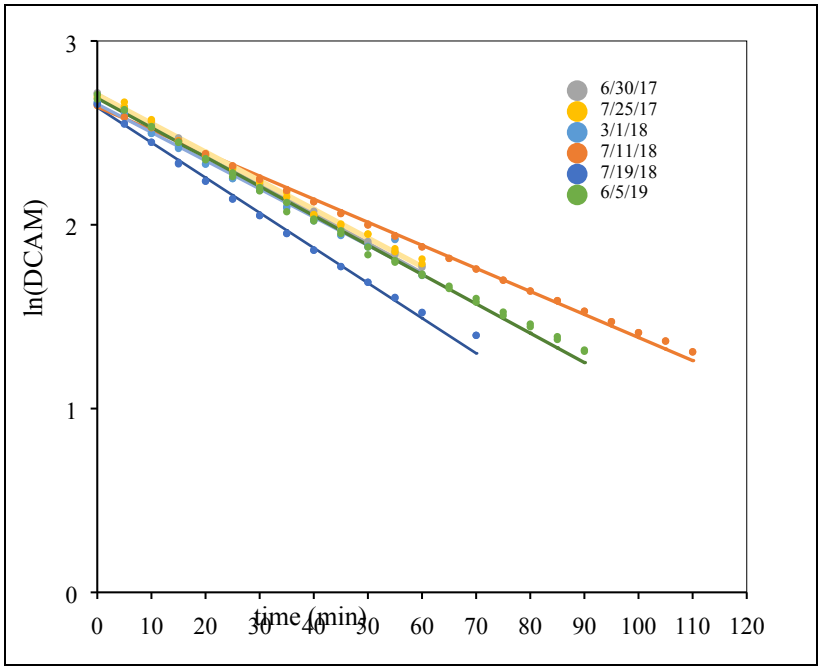

Figure S-3: Irradiation of 15 mg/L dicamba at pH 7 at 310 nm. All lines are weighted linear regression lines. Dates of experiments in legend (gray = 6/30/2017, yellow = 7/25/2017, light blue = 3/1/2018, orange = 7/11/2018, dark blue = 7/19/2018, and green = 6/5/2019). Average k=0.016 ± 0.002 min^{-1}.

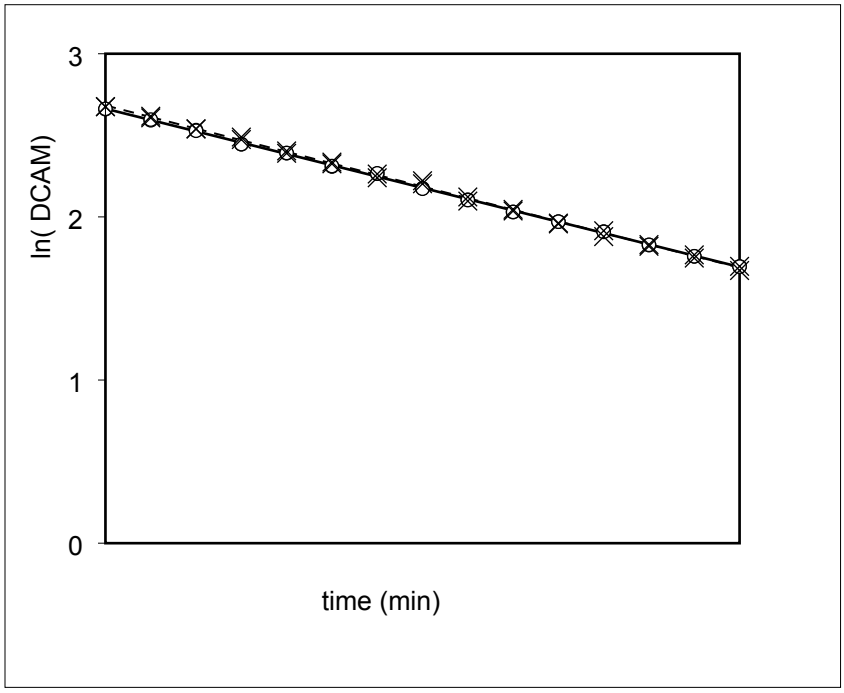

Figure S-4: Irradiation of 15 mg/L dicamba at pH 1 at 310 nm. Two experiments with average k = 0.014 ± 0.002 min^{-1}. X data points and dashed linear regression line from experiment on 7-10-2017 and circle data points and solid linear regression line from experiment on 6-20-2018.

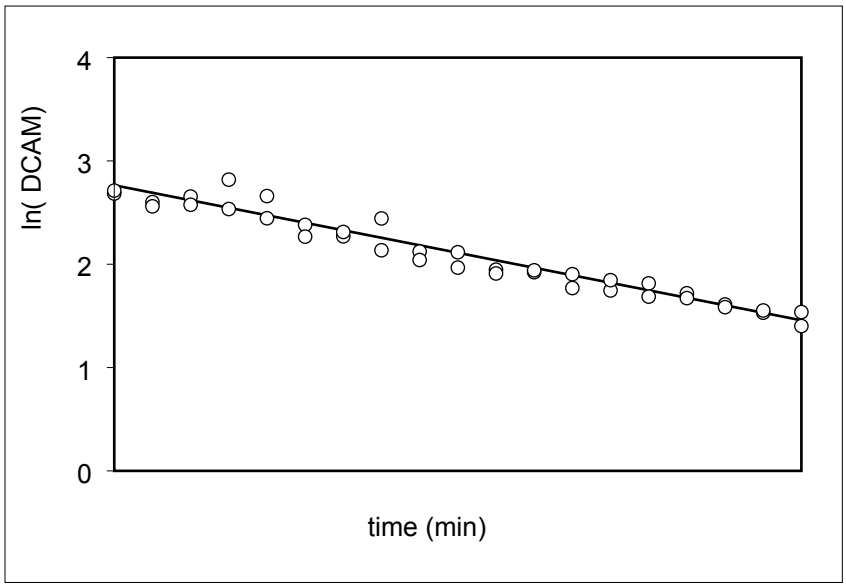

Figure S-5: Irradiation of 15 mg/L dicamba at pH 7 in oxygen saturated solution at 310 nm. k = 0.015 ± 0.001 min^{-1}.

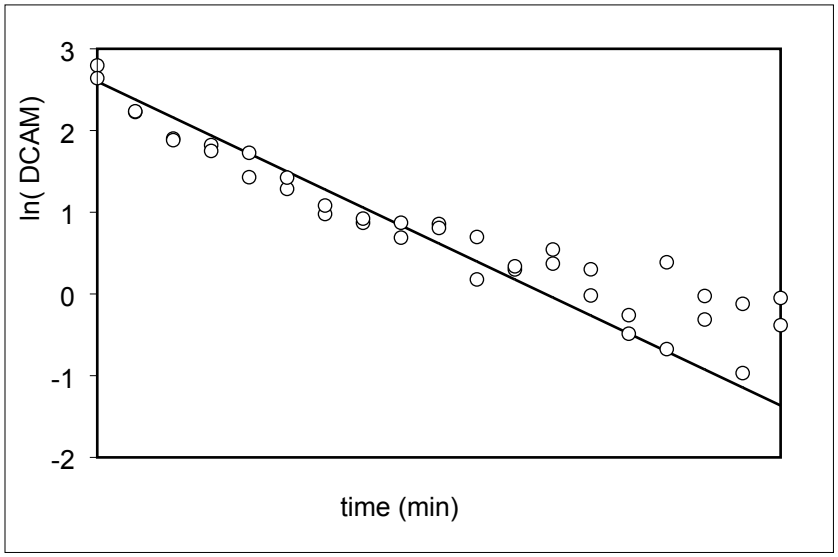

Figure S-6: Irradiation of 15 mg/L dicamba at pH 7 in nitrogen saturated solution at 310 nm. k = 0.044 ± 0.003 min^{-1}.

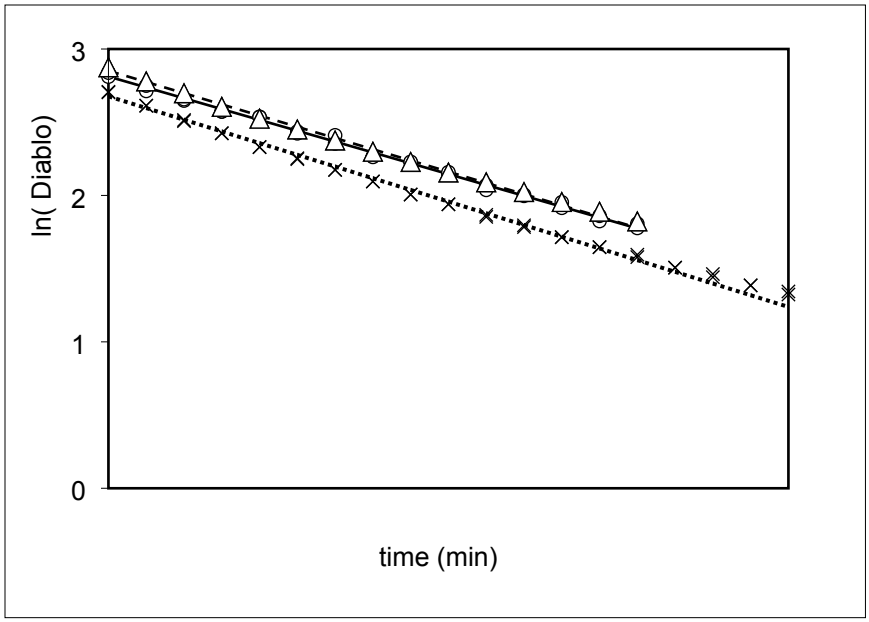

Figure S-7: Irradiation of 15 mg/L dicamba in commercial product Diablo at 310 nm. Three experiments with average k = 0.015 ± 0.001 min^{-1}. Circle data points and solid linear regression line from experiment on 8-10-2017, triangle data points and dashed linear regression line from experiment on 6-21-2018, and X data points and dotted regression line from experiment on 6-30-2020. Note that the initial concentration in 2020 was slightly lower, shifting the data points lower, but the slope is still the same as the other two experiments.

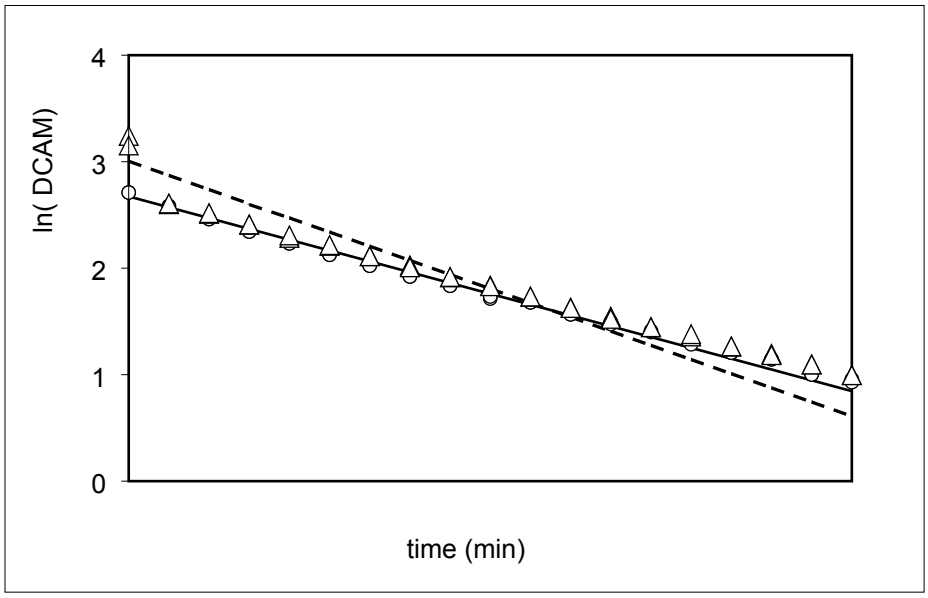

Figure S-8: Irradiation of 15 mg/L dicamba at pH 7 with 5 mg/L DA-6 adjuvant at 310 nm. Two experiments with average k = 0.023 ± 0.004 min^{-1}. X data points and dashed linear regression line from experiment on 6-26-2019 and circle data points and solid linear regression line from experiment on 6-30-2020.

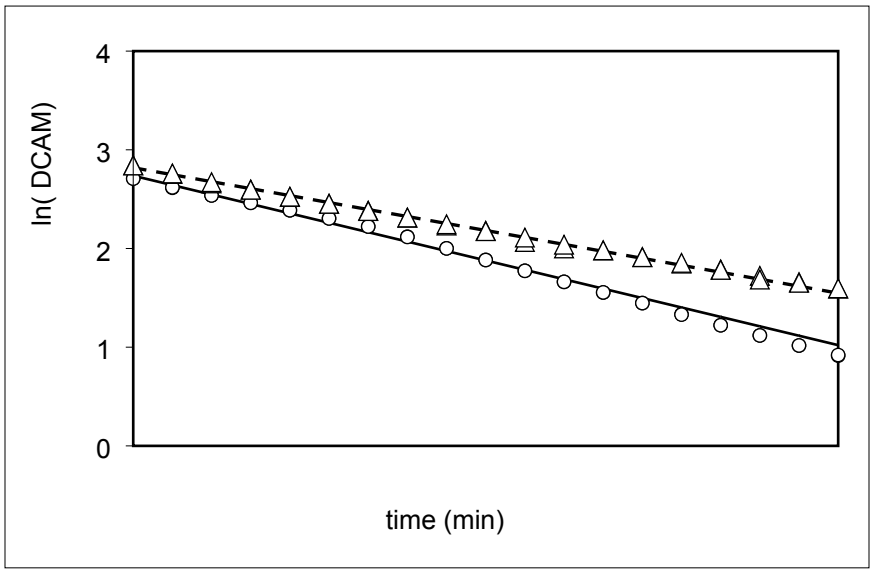

Figure S-9: Irradiation of 15 mg/L dicamba at pH 7 with 5 mg/L DA-6 adjuvant with 1% isopropanol as a hydroxyl radical quencher at 310 nm. Two experiments with average k = 0.017 ± 0.004 min^{-1}. Circle data points and solid linear regression line from experiment on 6-30-2020 and triangle data points and dashed linear regression line from experiment on 7-12-2019.

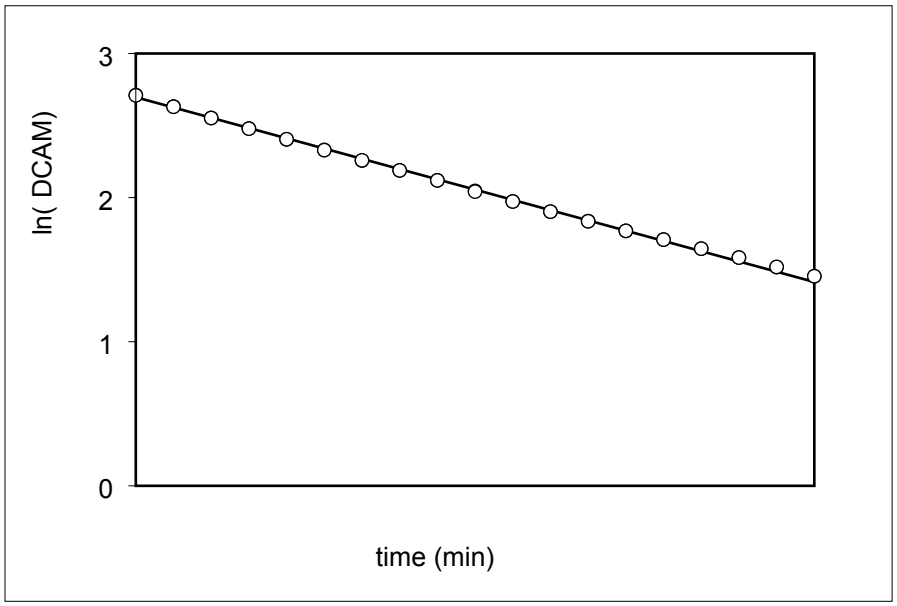

Figure S-10: Irradiation of 15 mg/L dicamba at pH 7 with 5 mg/L DA-6 adjuvant with 5 mM l-histidine at 310 nm. k = 0.014 ± 0.002 min^{-1}.

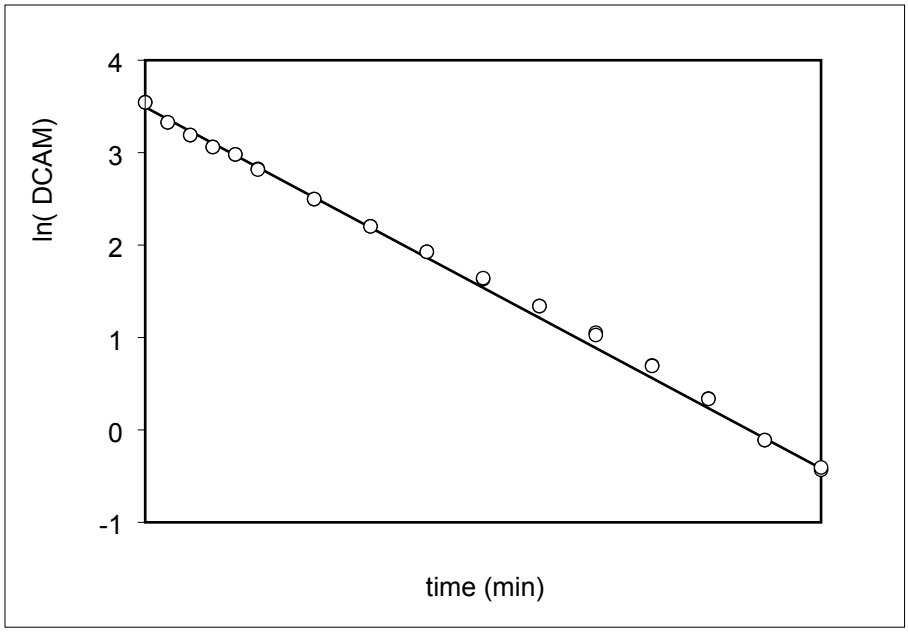

Figure S-11: Irradiation of 15 mg/L dicamba at pH 7 with 5 mM H_2O_2 as hydroxyl radical source at 310 nm. $k = 0.065 \pm 0.002$ min^{-1}.

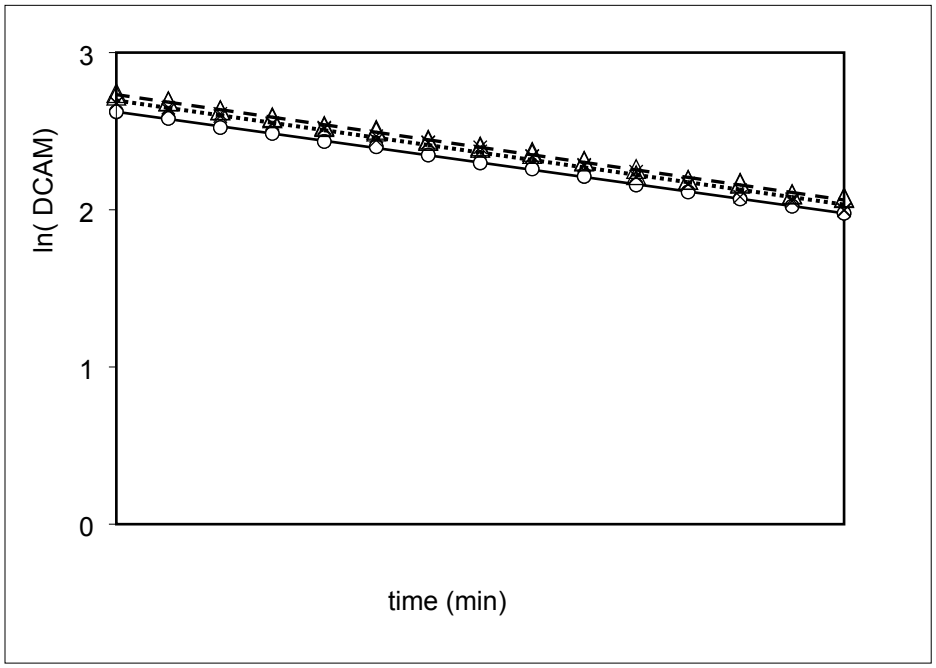

Figure S-12: Irradiation of 15 mg/L dicamba with 10 mg/L NOM at 310 nm. Three experiments with average $k = 0.009 \pm 0.001$ min^{-1}. Circle data points and solid linear regression line from experiment on 4-18-2018, triangle data points and dashed linear regression line from experiment on 7-21-2017, and X data points and dotted regression line from experiment on 8-3-2017.

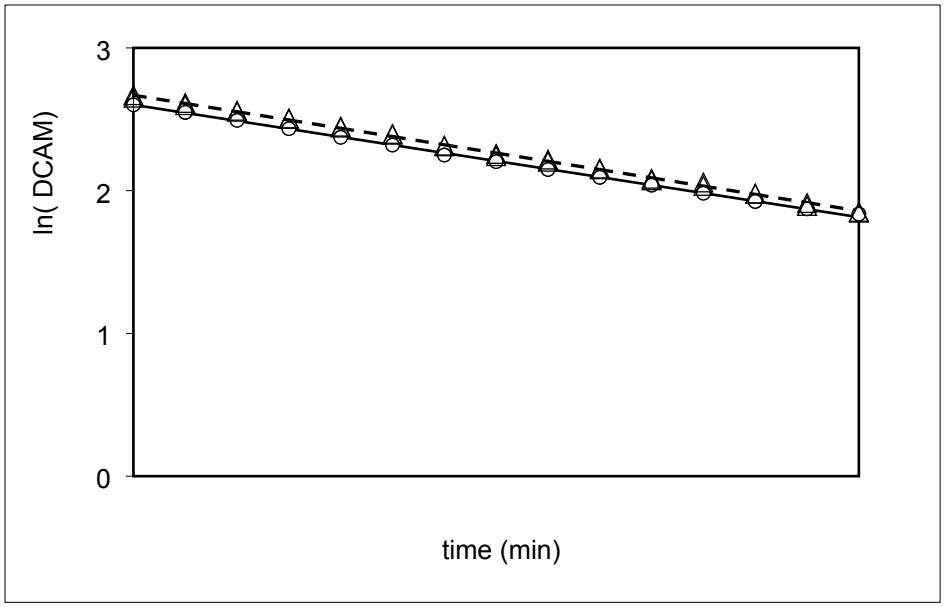

Figure S-13: Irradiation of 15 mg/L dicamba with 5.2 mg/L NOM at 310 nm. Two experiments with average k = 0.011 ± 0.001 min^{-1}. Circle data points and solid linear regression line from experiment on 4-18-2018, triangle data points and dashed linear regression line from experiment on 8-1-2017.

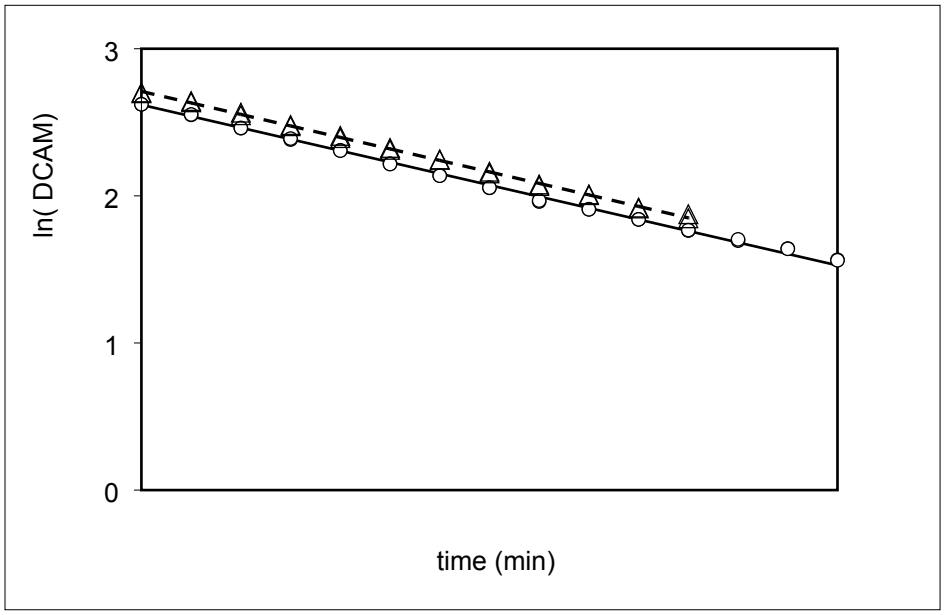

Figure S-14: Irradiation of 15 mg/L dicamba with 1.2 mg/L NOM at 310 nm. Two experiments with average k = 0.016 ± 0.001 min^{-1}. Circle data points and solid linear regression line from experiment on 4-18-2018, and triangle data points and dashed linear regression line from experiment on 8-2-2017.

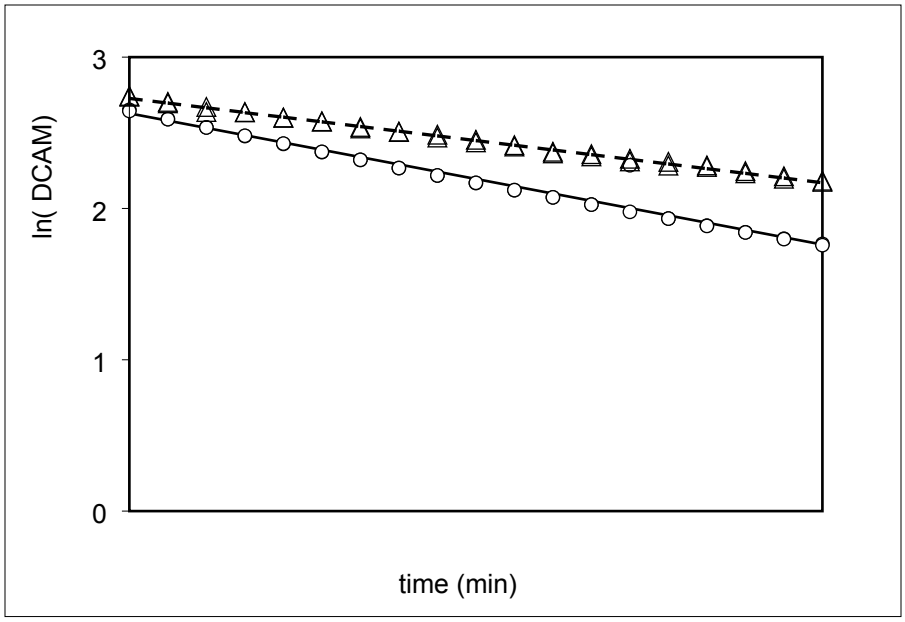

Figure S-15: Comparison of irradiation of 15 mg/L dicamba in Minnesota River water. Circle data points and solid linear regression from experiment on 6/22/2019, and triangles and dotted linear regression line from experiment on 6/22/2020.

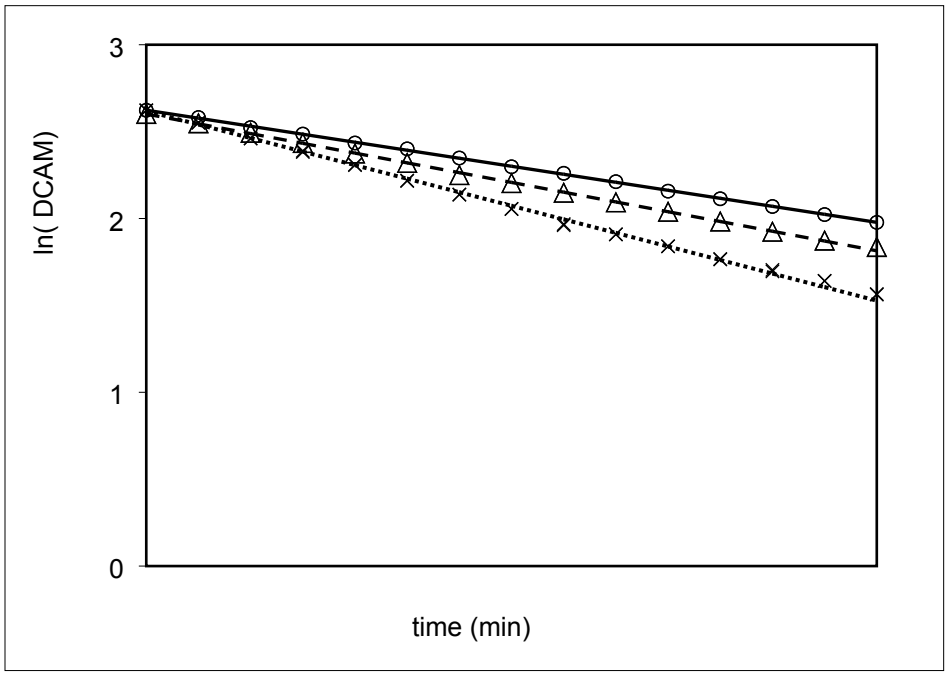

Figure S-16: Comparison of irradiation of 15 mg/L dicamba with 1.2 mg/L NOM (circles), 5.2 mg/L NOM (triangles), and 10.0 mg/L NOM (X). All lines are weighted linear regression lines. All data taken from 4-18 and 4-19-2018.

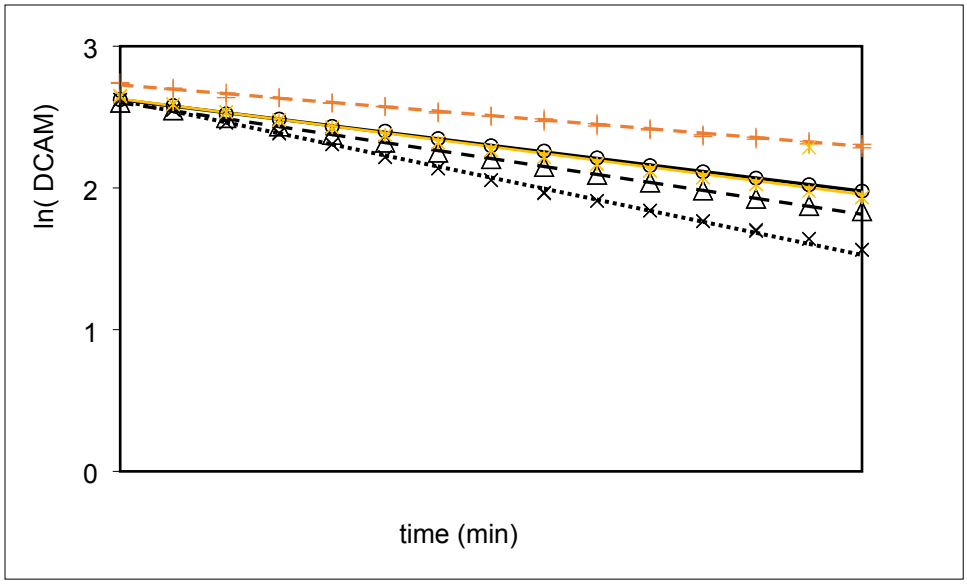

Figure S-17: Comparison of irradiation of 15 mg/L dicamba with 1.2 mg/L NOM (circles), 5.2 mg/L NOM (triangles), and 10.0 mg/L NOM (X). All lines are weighted linear regression lines. All data taken from 4-18 and 4-19-2018. Also overlaid is the data from irradiating 15 mg/L dicamba spiked into Minnesota River water (yellow = 2020 and orange = 2019).

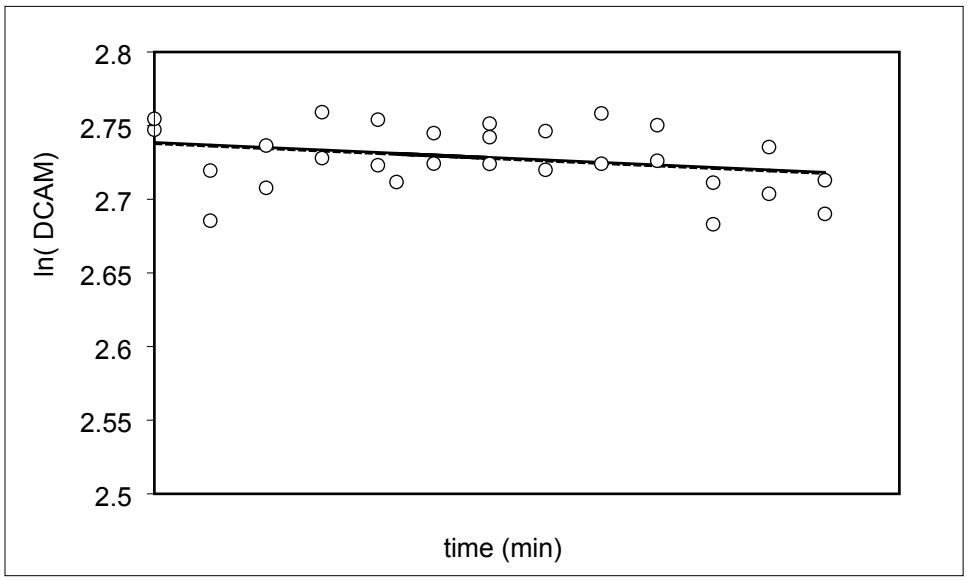

Figure S-18: Irradiation of 15 mg/L dicamba at pH 7 in St. Peter, MN on the Gustavus Adolphus College campus (44° 20' 0" N, 93° 58' 0" W) on June 12-13, 2019, from 11:10 am – 5:10 pm each day. $k = 3\times10^{-5} \pm 2\times10^{-5}$ min^{-1}.

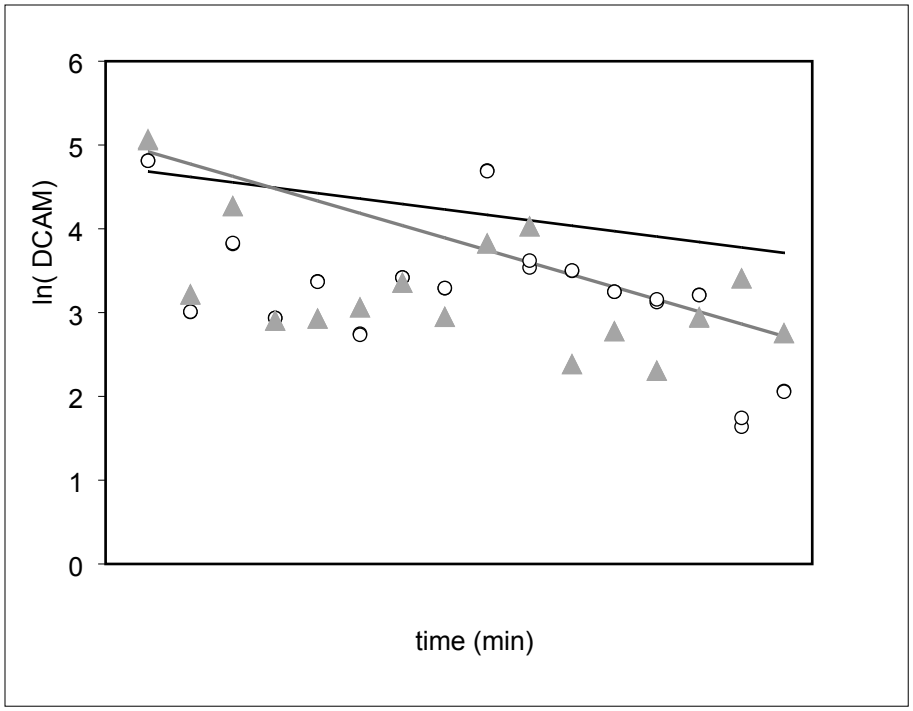

Figure S-19: Irradiation of 15 mg/L dicamba in aqueous solution at pH 7 in a Q-Sun solar simulator with Xe lamp and Daylight-Q filter. Two plates were irradiated simultaneously giving two data sets (circles and triangles). The lines are the weighted linear regression fits to the two data sets. The average rate constant is $k = 9\times10^{-4} \pm 5\times10^{-4}$ min^{-1}.

Section 2:

UV-Vis spectra and Irradiance plots

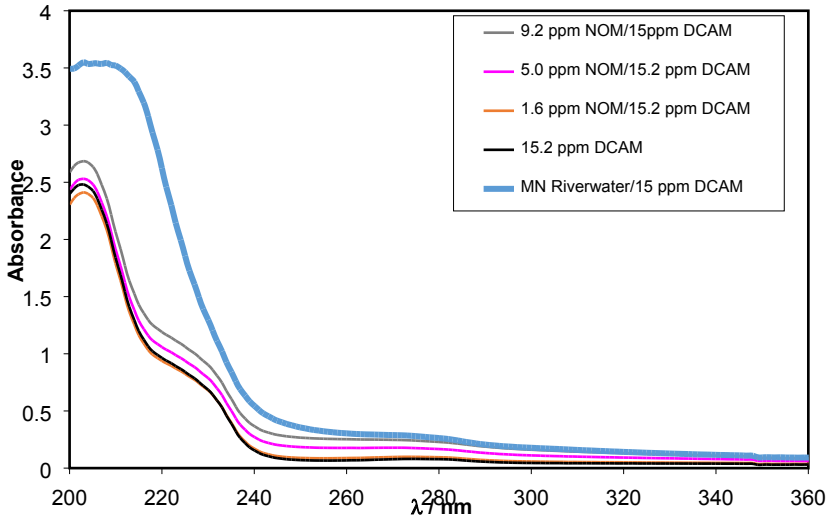

Figure S-20: UV-Vis spectra of 15.2 ppm dicamba in a) pH 7 phosphate buffer (black), b) pH 7 phosphate buffer with 1.6 mg/L NOM (green), c) pH 7 phosphate buffer with 5.0 mg/L NOM (pink), d) pH 7 phosphate buffer with 9.2 mg/L NOM (dark blue), and e) MN River water collected in 2019 (light blue).

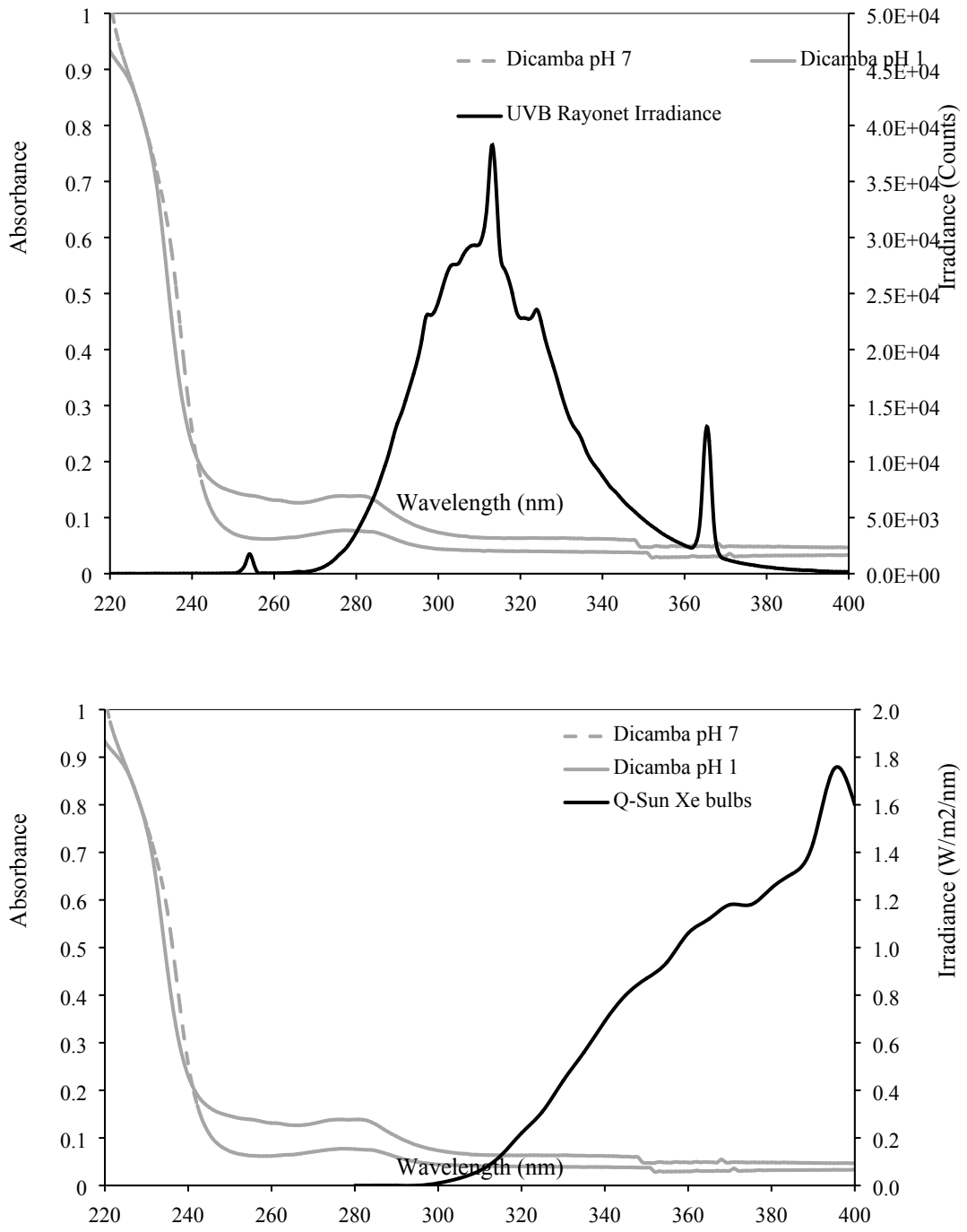

Figure S-21: (A) Absorbance spectra of 15 ppm dicamba buffered at pH 7 (dashed line) and pH 1 (solid line) and the irradiance spectrum of the Rayonet 310 nm bulbs used for all aqueous experiments. (B) Absorbance spectra of 15 ppm dicamba buffered at pH 7 (dashed line) and pH 1 (solid line) and the irradiance spectrum of the Q-sun Xenon lamps with daylight filter used for all wax experiments. Both the Rayonet and Q-sun spectra are estimated from product brochures.

Table S-1: Molar Extinction Coefficients for dicamba in solutions at pH 7 and pH 1

Dicamba	pH 7	pH 1
Wavelength nm	Molar Extinction 1/(M cm)	Molar Extinction 1/(M cm)
270	896.8	1313.6
271	874.7	1339.9
272	866.3	1367.2
273	871.5	1399.6
274	864.6	1424.1
275	858.7	1442.8
276	847.2	1445.5
277	840.6	1444.7
278	833.9	1442.2
279	824.3	1442.2
280	816.7	1441.8
281	812.8	1446.4
282	800.7	1449.3
283	781.6	1437.1
284	750.8	1404.5
285	700.9	1331.2
286	658.4	1255.8
287	619.6	1177.3
288	587.0	1109.4
289	545.0	1019.0
290	509.4	942.2
291	484.8	876.4
292	468.7	829.3
293	448.6	771.6
294	425.0	711.4
295	409.3	664.3
296	399.6	627.8
297	387.9	585.4
298	383.6	555.4
299	380.3	529.4
300	373.4	500.5
301	369.6	479.0
302	366.7	458.1
303	365.5	443.7
304	360.4	426.0
305	357.3	410.7
306	354.2	400.6
307	352.6	390.9
308	348.7	382.4
309	344.1	373.6

Dicamba	pH 7	pH 1
Wavelength nm	Molar Extinction 1/(M cm)	Molar Extinction 1/(M cm)
310	340.8	368.8
311	337.9	360.9
312	332.0	355.8
313	328.7	350.7
314	322.6	345.8
315	312.1	337.4
316	311.7	338.5
317	305.8	334.7
318	297.9	328.6
319	290.8	324.2
320	283.7	323.3
321	281.5	322.1
322	274.1	317.9
323	267.5	312.4
324	262.3	311.7
325	262.5	314.6
326	259.3	315.1
327	255.8	312.0
328	255.9	313.7
329	249.6	312.4
330	245.8	309.6
331	247.3	310.1
332	246.2	311.1
333	241.7	311.8
334	246.2	316.2
335	248.2	316.5
336	245.8	315.7
337	245.8	316.4
338	245.6	314.7
339	244.7	313.6
340	245.9	316.1
341	245.5	316.3
342	244.0	314.5
343	246.8	313.4
344	245.7	311.2
345	244.0	309.5
346	246.8	311.5
347	248.7	307.8
348	247.4	307.2
349	248.2	301.2
350	246.7	300.0

Section 3: Micelle Formation

Using the methods from Ross and Olivier,[1] we tested for the formation of micelles by examining the UV-Vis spectra of iodine (40 ppm) in a series of DA-6 solutions in Milli-Q water ranging from 0.5 to 5000 ppm. At low concentrations of DA-6 (below 550 ppm), the UV-Vis spectra of the I_2/DA-6 solutions were identical. At concentrations of DA-6 above 1000 ppm, the UV-Vis spectra showed higher absorbance and more structure between 250-400 nm (see Figure S_22). This change in absorbance is evidence for the formation of micelles, suggesting that the cmc for DA-6 is above 550 ppm. This is in accordance with the estimated value of 400 ppm taken from Mukerjee and Mysels,[2] and supports the conclusion that no micelles are formed in the photolysis experiments presented in this paper. The conclusion is photosensitization observed with the DA-6 solutions is not caused from the change in environment present in solutions containing micelles.

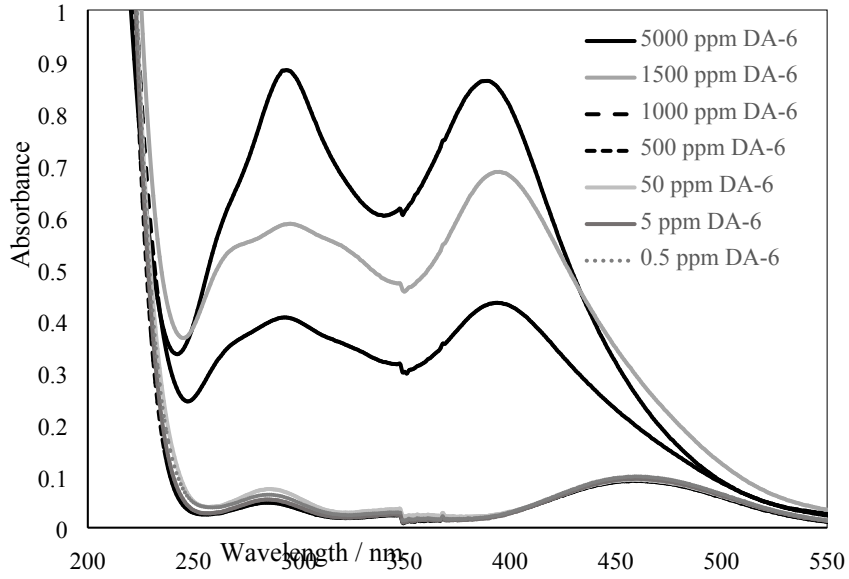

Figure S-22: UV-Vis spectra of 40 ppm I_2 (aq) with differing amounts of surfactant DA-6. At concentrations at 500 ppm or below, the UV-Vis spectra of I_2 (aq) are identical, but at 1000 ppm DA-6 or above, the spectra increase in intensity. This suggests the formation of micelles in solutions with concentrations above 1000 ppm DA-6. Photolysis experiments were conducted at 5 ppm DA-6 which is well below the critical micelle concentration.

References

1 S. Ross and J. P. Olivier, *The Journal of Physical Chemistry*, 1959, **63**, 1671–1674.

2 P. Mukerjee and K. Mysels, *Critical Micelle Concentrations of Aqueous Surfactant Systems*, Office of Standard Reference Data, National Bureau of Standards, 1971.

Section 4:

Chromatogram from LC-MS

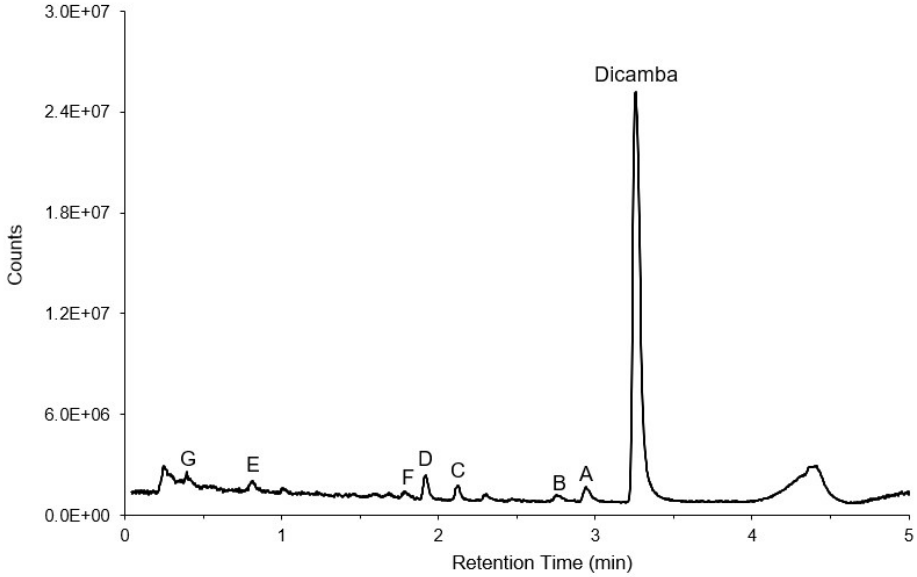

Figure S-23: LC-MS chromatogram obtained after 35 min of irradiation of 15.2 ppm dicamba with 310 nm light. The labels correspond to the photoproducts presented in Table 4. Because photoproduct G is so close the the solvent front, it was not explored further.

Section 5: Computational Data:

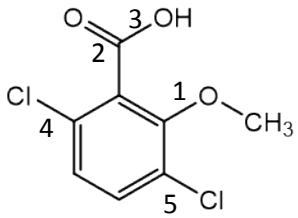

Table S-2: Bond lengths obtained from B3LYP/6-311G+(2d,p) calculations for dicamba in the ground (singlet) and excited (triplet) states. The most significant changes are reported.

Bond	Bond Length in Singlet State (Å)	Bond length in Triplet State (Å)	Difference (Å)
1	1.50	1.36	-0.14
2	1.50	1.39	-0.11
3	1.05	0.98	-0.07
4	1.76	1.82	0.06
5	1.76	1.83	0.07

Table S-3: Energies of possible structures of photoproducts B, C and D

Photoproduct	Enthalpy of Formation (Hartree)
B1	-1030.956771
B2	-1030.957517
C1	-1529.841444
C2	-1529.841286
D1	-1070.215545
D2	-1070.217382