Supporting Information

Photometric Hydroxyl Radical Scavenging Analysis of Standard Natural Organic Matter Isolates

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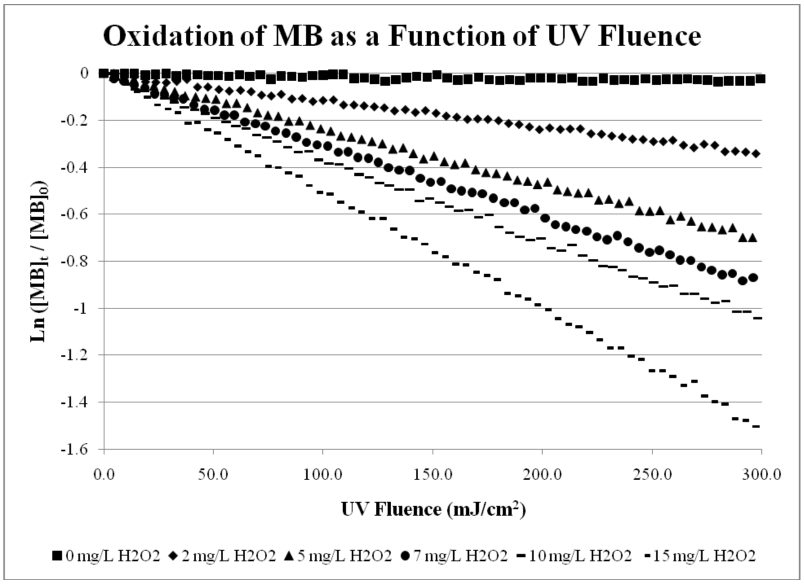

Fig. SI-1: Consistant second order degradation of MB to 80% decay. Minimal photodecay (at 0 mg/L H_2O_2) indicates resistance to UV_{254}. Linear decay curves at higher H_2O_2 concentrations indicates predicatable second order behavior when reacitng with •OH, and limited generation of •OH scavenging byproducts.

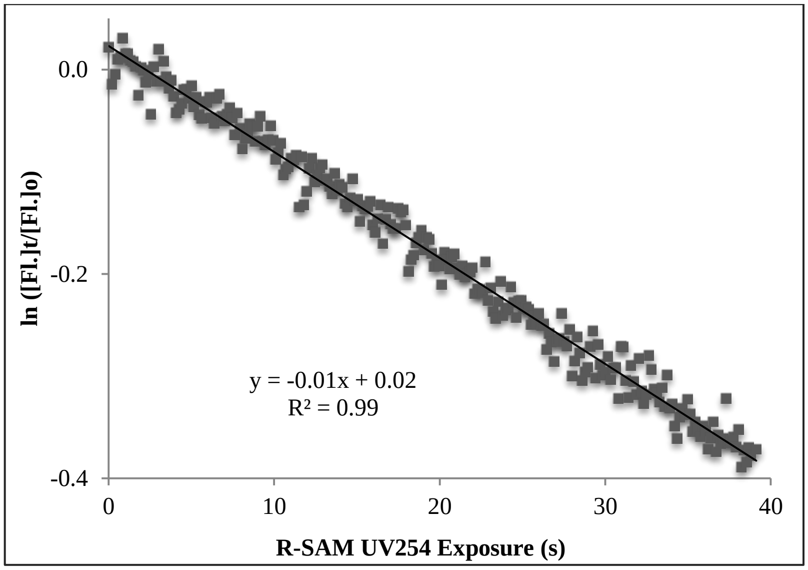

Fig. SI-2: Consistant second order degradation of fluorescein (Fl.) to 30% decay. Indicates predicatable second order behavior when reacting with •OH, and limited generation of •OH scavenging byproducts.

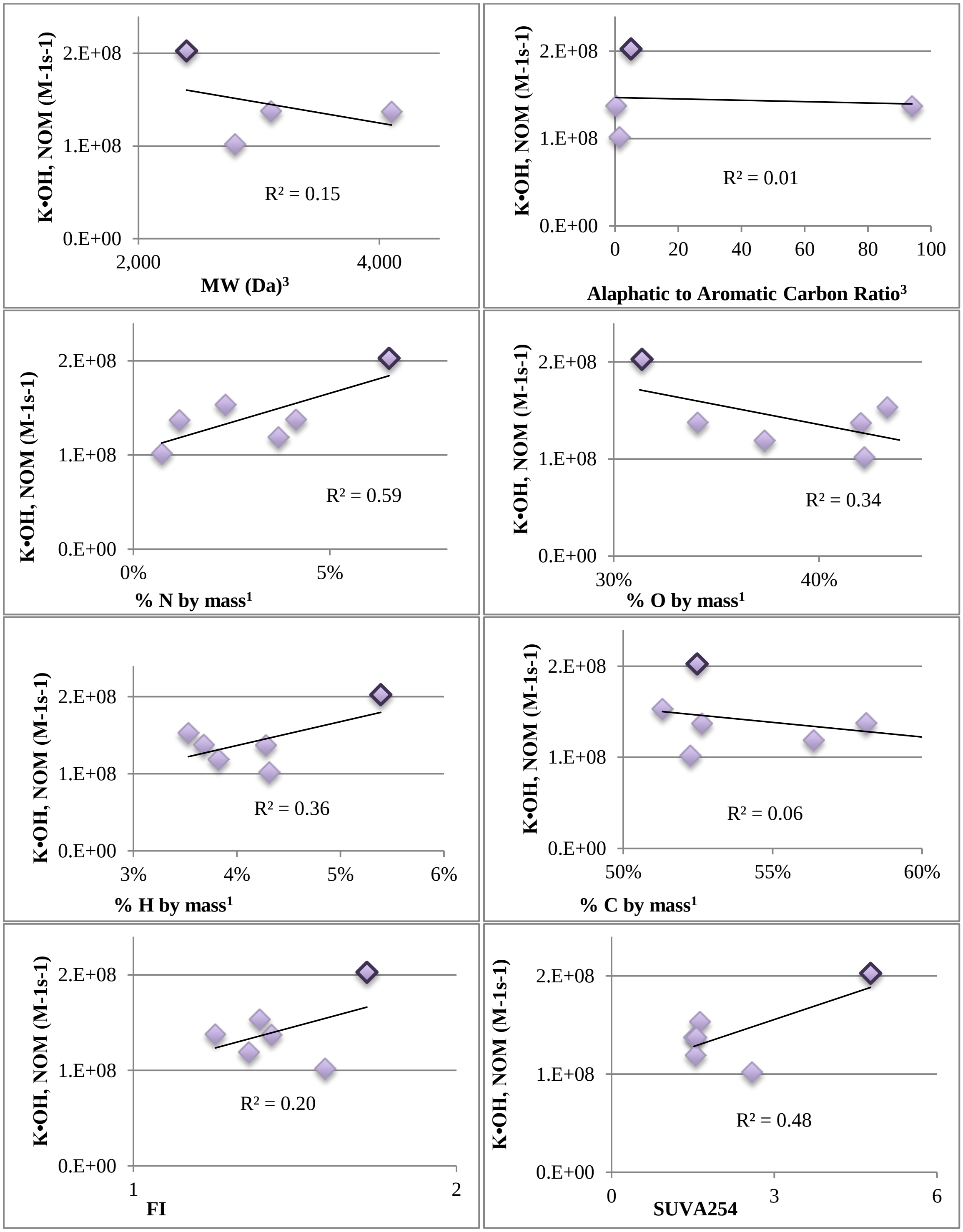

Fig. SI-3: Correlation of NOM characteristics with •OH scavenging rate constants. ◇: PLFA-R NOM. Apparent relationship between the NOM characteristic shown and the molar-carbon •OH scavenging rate were only due to inclusion of the PLFA-R outlier, and were thus not statistically significant.

1 IHHS, in *Elemental Compositions and Stable Isotopic Ratios of IHSS Samples*. *International Humic Substances Society Website*, 2013. Retrieved 6/26/2013 from <http://www.humicsubstances.org/sources%20-%20PonyLake.html>.

2 G. McKay, J. L. Kleinman, K. M. Johnston, M. M. Dong, F. L. Rosario-Ortiz, and S. P. Mezyk, *J Soils Sediments*, 2013, 1.

3 Thorn, K.A., Folan, D.W., MacCarthy, P., 1989. Characterization of the international humic substances society standard and reference fulvic and humic acids by solution state carbon-13 (^{13}C) and hydrogen-1 (^{1}H) nuclear magnetic resonance spectrometry.

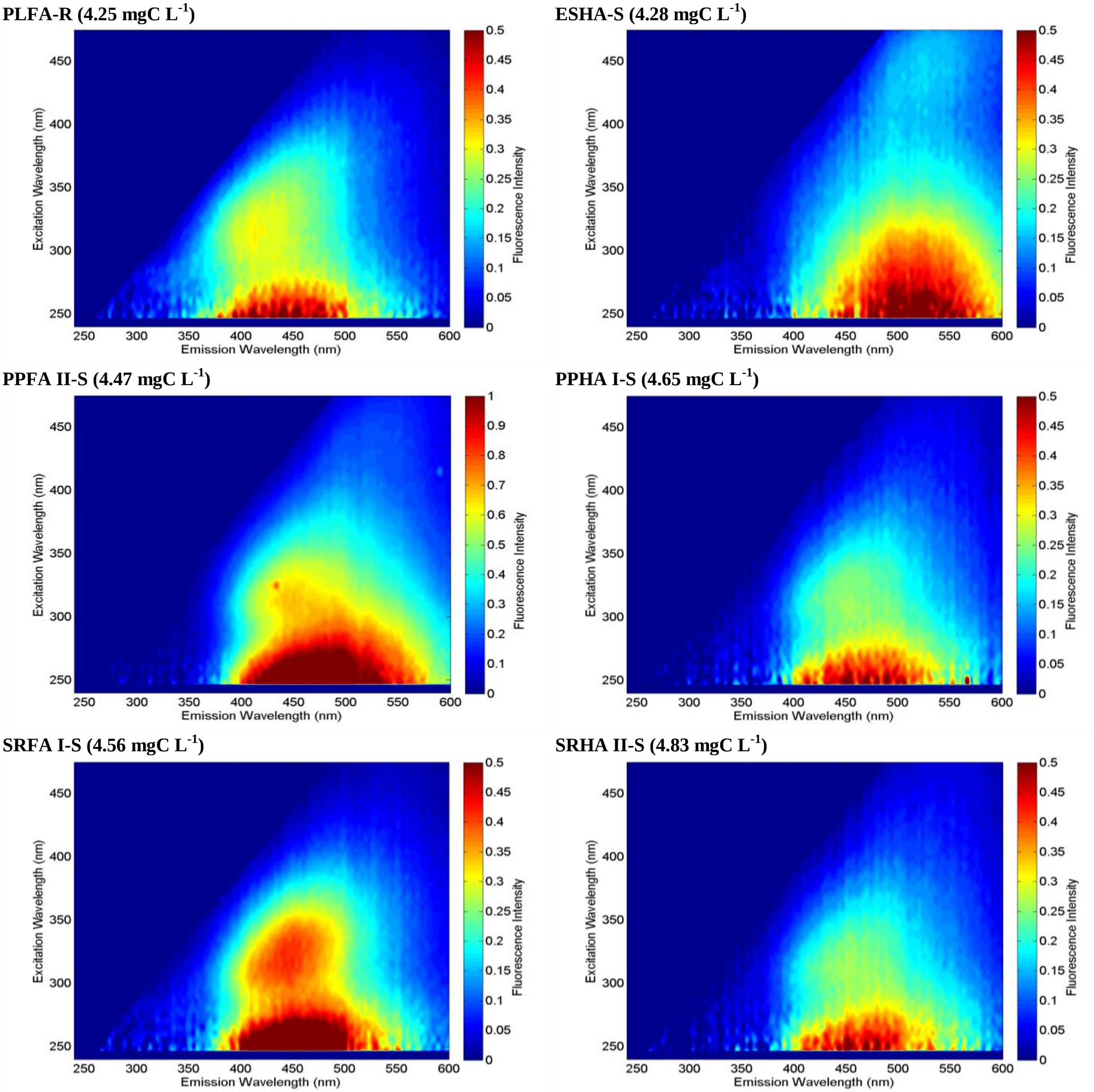

Fig. SI-4: EEMs for NOM isolates.

Derivation of Equation 2

The steady state hydroxyl radical equation (Equation a) models the chemistry of the R-SAM when measuring scavenging rates of NOM.

$$\alpha_{\bullet OH} = \left([NOM]k_{\bullet OH,NOM} + [t-BuOH]k_{\bullet OH,t-BuOH} + [P]k_{\bullet OH,P} + [H_2O_2]k_{\bullet OH,H_2O_2}\right)[\bullet OH]_{ss} \qquad (a)$$

where $\alpha_{\bullet OH}$, the production rate of •OH, is set equal to the consumption of •OH by all scavenging species in solution, including NOM, test concentrations of t-BuOH, the probe dye (P), and unphotolyzed H_2O_2, which also scavenges •OH. $[\bullet OH]_{ss}$ is the steady state concentration of •OH, $k_{\bullet OH,X}$ is the reaction rate constant of •OH with a species X present in the test water.

To perform the R-SAM analysis, solutions of probe dye and H_2O_2 were added to the sample waters to yeild concentrations of 1 or 5 µM (depending on the dye) and 0.59 mM (20 mg/L), respectively. 40 ml aliquots were spiked with t-BuOH to concentrations ranging from 0 to 1,000 µM. Probe decay rates (k^{app}_P) were measured under UV exposure for each t-BuOH concentration with the R-SAM spectrophotometer using Equation (b).

$$ln\left(\frac{abs(P)_t}{abs(P)_0}\right) = -k_P^{app} \times t \qquad (b)$$

where $abs(P)_t$ and $abs(P)_0$ are the absorbance-based concentration of the probe dye at times t and zero respectively. k^{app}_P is then used to determine $[\bullet OH]_{ss}$ as in Equation (c) using the initial 20% of probe decay to minimize potential effects of oxidation byproducts.

$$k_P^{app} = k_{\bullet OH,P}[\bullet OH]_{ss} \qquad (c)$$

Combining Eqs. a-c generates Eq. 2; a relationship between k^{app}_P and [t-BuOH]:

$$k_P^{app} = \frac{k_{\bullet OH,P} \times \alpha_{\bullet OH}}{k_{\bullet OH,NOM}[NOM] + k_{\bullet OH,t-BuOH}[t-BuOH] + k_{\bullet OH,P}[P] + k_{\bullet OH,H_2O_2}[H_2O_2]} \qquad (2)$$

Table SI-1: Fitting statistics for R-SAM analyses of NOM Isolates

								$\alpha_{\bullet OH}$			$[NOM]k_{\bullet OH,NOM}$				$k_{\bullet OH,NOM}$			*Inverse Squared SE-Weighted Average* $k_{\bullet OH,NOM}$	
NOM	***[NOM] (μMC)***	***SE [NOM]***	***rep.***	***excluded***	***n***	***DF***	***r2***	***value***	***SE***	***95% CI***	***value***	***SE***	***Relative SE***	***95% CI***	***value***	***SE***	***95% CI***	***Value***	***SE***
PLFA-R	467	1.7%	1	0	11	9	0.994	2.23E-07	7.28E-09	2.07E-07 to 2.40E-07	111,176	8,860	8.2%	9.11E+04 to 1.31E+05	2.38E+08	1.94E+07	*1.94E+08 to 2.82E+08*	***2.03E+08***	***1.2E+07***
PLFA-R	300	1.7%	2	0	20	18	0.989	1.38E-07	4.28E-09	1.29E-07 to 1.47E-07	53,335	4,790	9.1%	4.33E+04 to 6.34E+04	1.78E+08	1.63E+07	*1.44E+08 to 2.12E+08*		
PPFA II-1	273	0.5%	1	0	17	15	0.981	9.80E-08	4.39E-09	8.86E-08 to 1.07E-07	31,593	5,677	18.0%	1.95E+04 to 4.37E+04	1.16E+08	2.08E+07	*7.15E+07 to 1.60E+08*	***1.53E+08***	***1.3E+07***
PPFA II-1	273	0.5%	2	2	21	19	0.988	1.06E-07	3.27E-09	9.94E-08 to 1.13E-07	48,694	4,658	9.6%	3.89E+04 to 5.84E+04	1.79E+08	1.71E+07	*1.43E+08 to 2.14E+08*		
ESHA-S	417	3.5%	1	0	10	8	0.998	1.20E-07	2.84E-09	1.13E-07 to 1.26E-07	59,350	4,152	7.8%	4.98E+04 to 6.89E+04	1.42E+08	1.11E+07	*1.17E+08 to 1.68E+08*	***1.38E+08***	***8.3E+06***
ESHA-S	300	3.5%	2	2	16	14	0.995	1.05E-07	2.46E-09	1.00E-07 to 1.11E-07	39,561	3,507	9.5%	3.21E+04 to 4.70E+04	1.32E+08	1.26E+07	*1.05E+08 to 1.58E+08*		
SRHA1I-S	287	0.2%	1	3	16	14	0.993	9.91E-08	2.68E-09	9.34E-08 to 1.05E-07	35,985	3,671	10.2%	2.81E+04 to 4.39E+04	1.25E+08	1.28E+07	*9.80E+07 to 1.53E+08*	***1.37E+08***	***1.0E+07***
SRHA1I-S	287	0.2%	2	0	18	16	0.989	1.09E-07	3.45E-09	1.02E-07 to 1.17E-07	44,843	4,666	10.4%	3.50E+04 to 5.47E+04	1.56E+08	1.63E+07	*1.22E+08 to 1.91E+08*		
PPHA I-S	280	0.3%	1	0	19	17	0.984	1.08E-07	4.25E-09	9.92E-08 to 1.17E-07	31,943	5,094	16.0%	2.12E+04 to 4.27E+04	1.14E+08	1.82E+07	*7.58E+07 to 1.53E+08*	***1.19E+08***	***1.2E+07***
PPHA I-S	280	0.3%	2	0	21	19	0.986	1.03E-07	3.42E-09	9.55E-08 to 1.10E-07	34,293	4,459	13.0%	2.50E+04 to 4.36E+04	1.23E+08	1.60E+07	*8.94E+07 to 1.56E+08*		
SRFA1-S	475	1.9%	1	0	11	9	0.993	1.50E-07	6.84E-09	1.35E-07 to 1.65E-07	46,604	6,659	14.4%	3.15E+04 to 6.17E+04	9.81E+07	1.41E+07	*6.63E+07 to 1.30E+08*	***1.02E+08***	***1.0E+07***
SRFA1-S	300	1.9%	2	0	13	11	0.991	1.08E-07	3.88E-09	9.97E-08 to 1.17E-07	31,988	4,634	14.6%	2.18E+04 to 4.22E+04	1.07E+08	1.56E+07	*7.23E+07 to 1.41E+08*		