Supporting Information

Combined effects of pH and borohydride reduction on the optical properties of humic substances (HS): A comparison of optical models

Authors

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Table S1. Optical properties and carbon content of HS at pH 7.

HS	Cat. No.	Mass (mg/L)	DOC (this lab) %(w/w)	C (IHSS) %(w/w)	A_{300} (OD) unt/red	A_{300}/Mass (OD) unt/red	$S_{300-700}$ (nm^{-1}) unt/red	λ_{max} λ_{ex}=300nm (nm) unt/red	Φ λ_{ex}=400 unt/red
SRFA	2S101F	50	52	52	0.683/0.477	0.0137/0.0095	0.0152/0.0182	444/424	0.0082/0.0158
SRHA	2S101H	50		52	0.888/0.672	0.0178/0.0134	0.0128/0.0157	465/434	0.0034/0.0102
LAC	19714 DS	44	22		0.279/0.163	0.0063/0.0037	0.0164/0.0214	422/419	0.0023/0.0072
LHA	1S104H-5	25	49	63	0.607/0.485	0.0243/0.0194	0.0096/0.0110	520/491	0.0030/0.0102
ESHA	1S102H	25	52	58	0.687/0.581	0.0275/0.0232	0.0076/0.0083	533/521	0.0030/0.0121
PLFA	1R109F	43	52	52	0.319/0.201	0.0074/0.0047	0.0160/0.0180	422/410	0.0120/0.0320

unt/red defined as untreated and reduced, respectively

Table S2. Changes in spectral slopes S (nm^{-1}) as function of pH, for untreated (top) and reduced (bottom) HS: changes in S over different pH ranges were calculated employing Eq. 4 relative to the S value at pH 2 or 7, as indicated.

Untreated - spectral slope, S												% S (decrease) over pH ranges		
	pH 2	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10	pH 11	pH 12	2-12	2-6	7-12
SRFA	0.0161	0.0161	0.0160	0.0158	0.0156	0.0152	0.0147	0.0136	0.0133	0.0126	0.0123	24	3	19
SRHA	0.0136	0.0137	0.0135	0.0134	0.0132	0.0128	0.0122	0.0115	0.0113	0.0107	0.0105	23	3	18
LAC	0.0172	0.0170	0.0170	0.0171	0.0170	0.0164	0.0160	0.0153	0.0149	0.0144	0.0142	17	1	13
LHA	0.0099	0.0100	0.0100	0.0100	0.0098	0.0096	0.0095	0.0091	0.0089	0.0085	0.0084	15	1	13
ESHA	0.0078	0.0078	0.0078	0.0078	0.0077	0.0076	0.0076	0.0074	0.0074	0.0072	0.0071	9	1	7
PLFA	0.0163	0.0164	0.0164	0.0163	0.0161	0.0160	0.0158	0.0153	0.0153	0.0149	0.0147	10	1	8

Reduced - spectral slope, S												% S (decrease) over pH ranges		
	2-12	2-12	2-12	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10	pH 11	pH 12	2-12	2-6	7-12
SRFA	0.0186	0.0188	0.0189	0.0189	0.0187	0.0182	0.0181	0.0169	0.0160	0.0158	0.0155	17	-1	15
SRHA	0.0159	0.0160	0.0160	0.0160	0.0159	0.0157	0.0151	0.0143	0.0136	0.0135	0.0133	16	0	15
LAC	0.0220	0.0219	0.0221	0.0220	0.0221	0.0214	0.0205	0.0195	0.0192	0.0190	0.0187	15	-1	13
LHA	0.0108	0.0109	0.0110	0.0110	0.110	0.0110	0.0107	0.0104	0.0102	0.0099	0.0098	10	-2	11
ESHA	0.0082	0.0082	0.0083	0.0083	0.0083	0.0083	0.0082	0.0082	0.0081	0.0080	0.0080	3	-1	4
PLFA	0.0180	0.0183	0.0183	0.0184	0.0181	0.0180	0.0180	0.0177	0.0176	0.0176	0.0175	3	0	3

Table S3. Chemical properties of HS (from IHSS).

HS	Cat. No.	C content (IHSS) %(w/w)	Carbon distribution (IHSS) ^{13}C NMR % peak area				Acidic Functional groups (IHSS) pH titrations (meq/g C)	
			Carbonyl	Carboxyl	Aromatic	Aliphatic	Carboxyl	Phenolic
SRFA	2S101F	52	5	17	22	35	11.17	2.84
SRHA	2S101H	52	6	15	31	29	9.13	3.72
LAC	19714 DS	na	na	na	na	na	Na	na
LHA	1S104H-5	63	8	15	58	14	7.46	2.31
ESHA	1S102H	58	6	18	50	16	8.28	1.87
PLFA	1R109F	52	1.2	17	12	61	7.09	1.75

na: not available

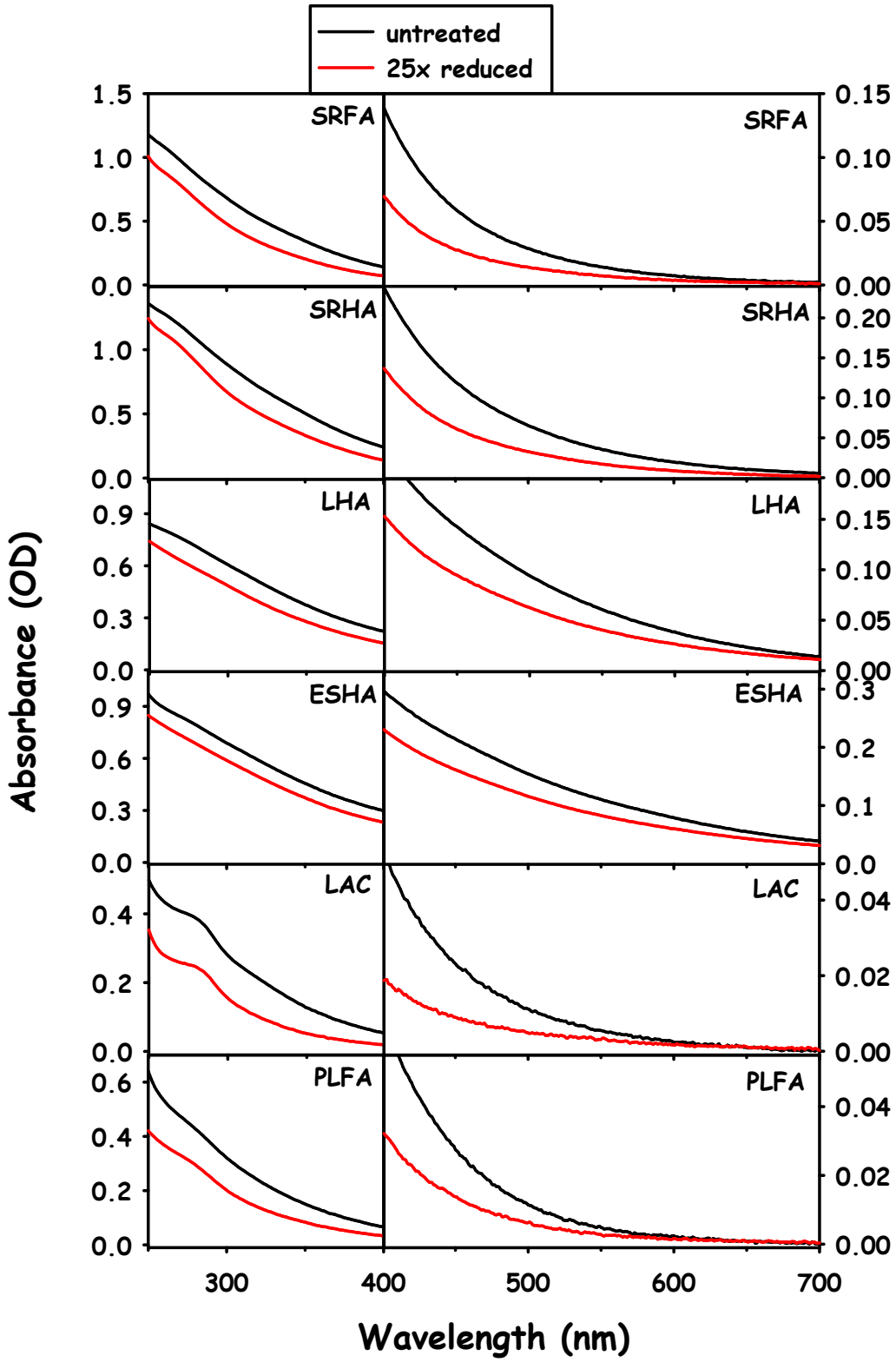

Figure S1. Absorption spectra at pH ~7 for HS untreated (Black lines) and reduced (Red lines). Right figures-same as left, zoomed in. HS concentrations are as follow: SRFA and SRHA, 50 mg/L; LAC, 43 mg/L; PLFA, 44 mg/L; LHA and ESHA, 25 mg/L.

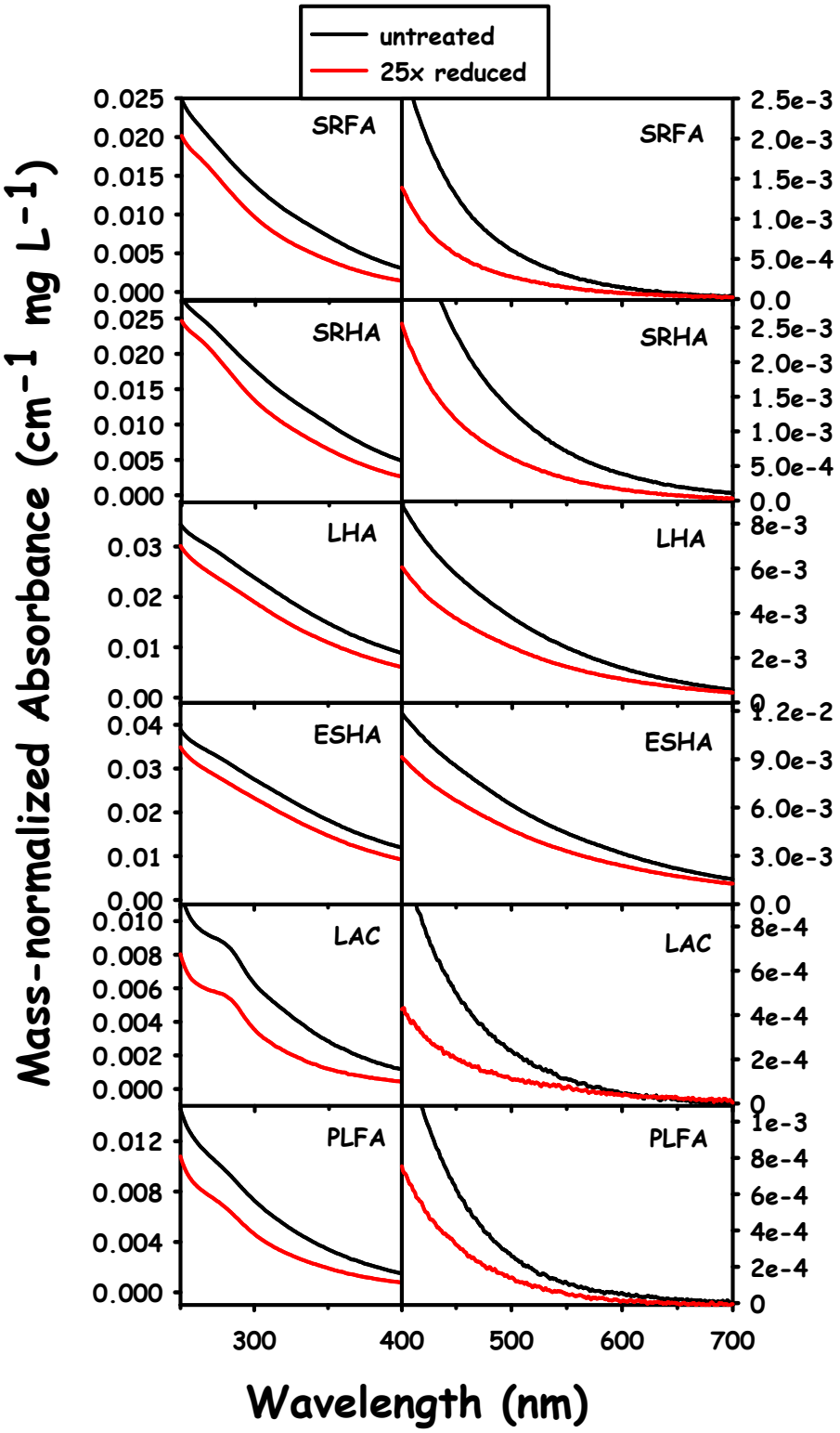

Figure S2. Mass-normalized absorption spectra at pH 7 for HS untreated (Black lines) and reduced (Red lines). Right figures-same as left, zoomed in. HS concentrations as in Fig. S1.

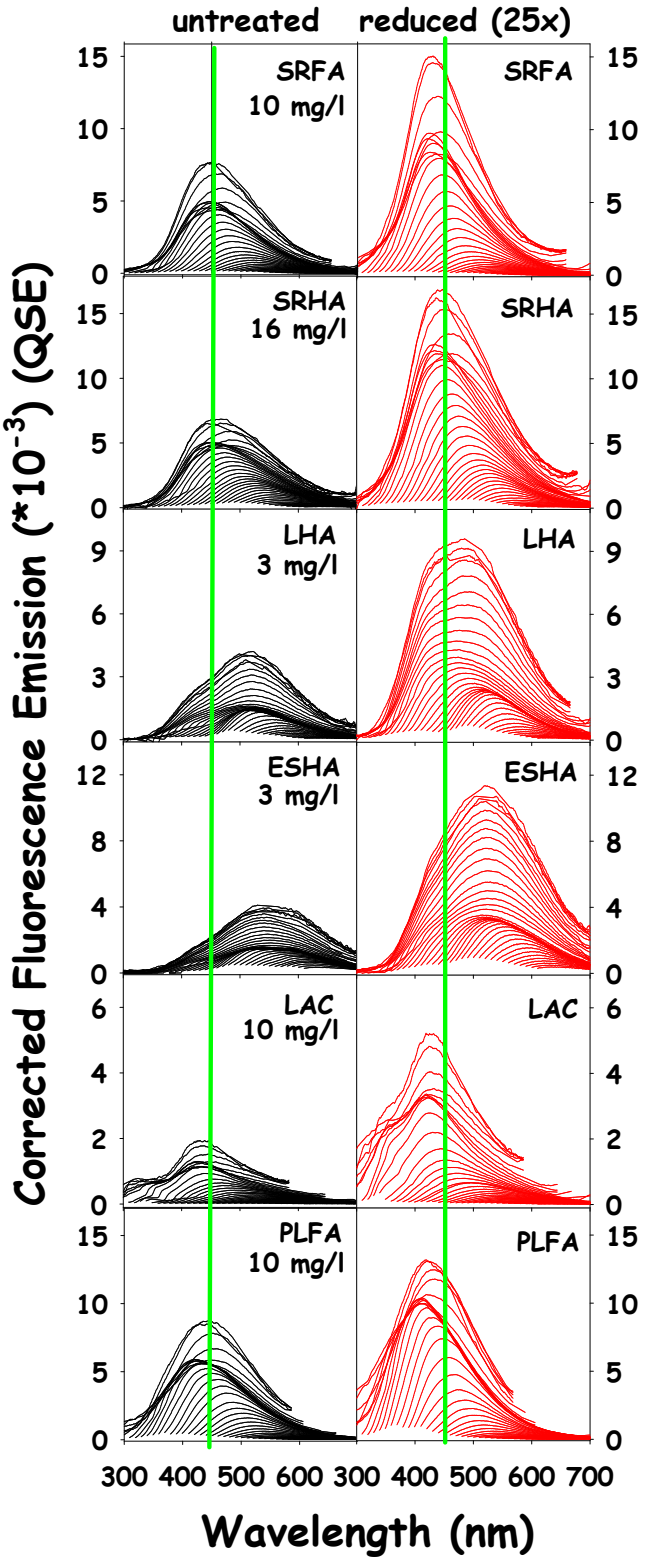

Figure S3. Corrected fluorescence emission spectra (QSE units) at pH 7 for HS untreated (Black-Left panel) and reduced (25x) (Red-Right panel). Emission spectra were collected at increasing concentrations with increasing excitation wavelengths; afterward, spectra were normalized to the lower concentration (as reported in figures) and merged into a single EEMs (see Methods Section). Green lines represent the 450 nm mark.

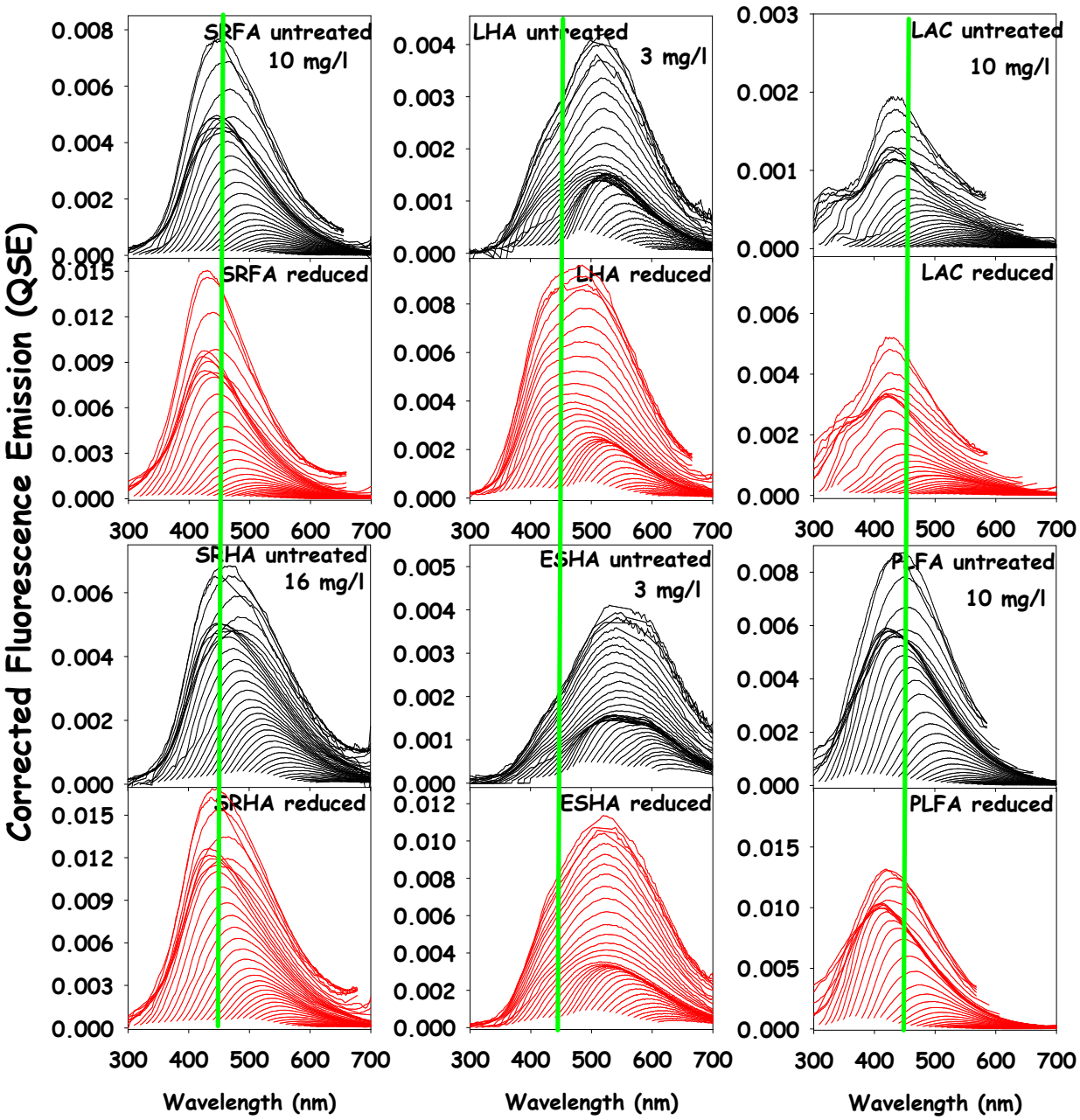

Figure S4. Corrected fluorescence emission spectra (QSE units) at pH 7 for HS untreated (Black) and reduced (25x) (Red-Right) (top and bottom panels in each group, respectively). Emission spectra were collected at increasing concentrations with increasing excitation wavelengths; afterward, spectra were normalized to the lower concentration (as reported in figures) and merged into a single EEMs (see Methods Section). Green lines represent the 450 nm mark.

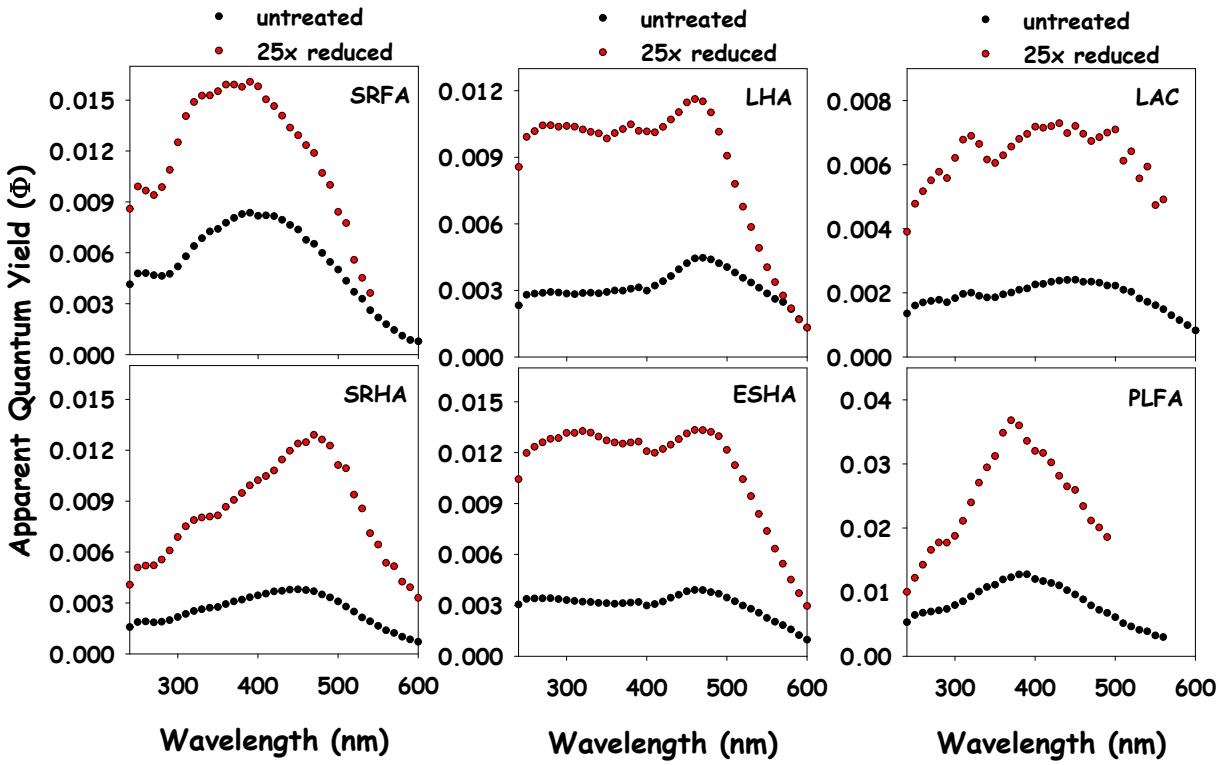

Figure S5. Wavelength dependence of the Apparent Quantum Yields (Φ) at pH ~7 for HS untreated (Black symbols) and reduced (Red symbols) HS.

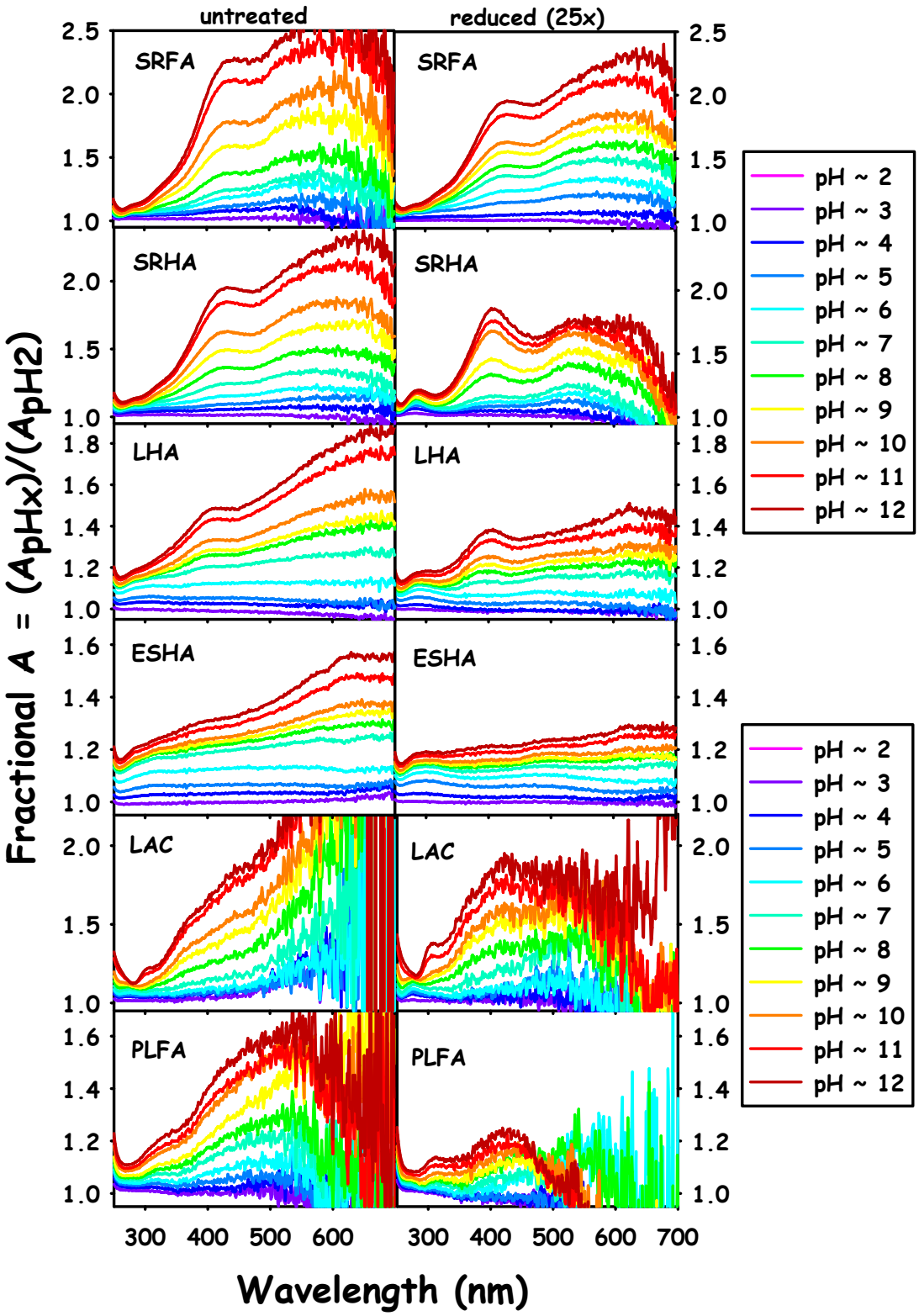

Figure S6. pH dependence of the fractional gain in absorption (Fractional A) relative to pH 2 for HS untreated (left) and reduced (right). HS concentrations as in Fig.S1.

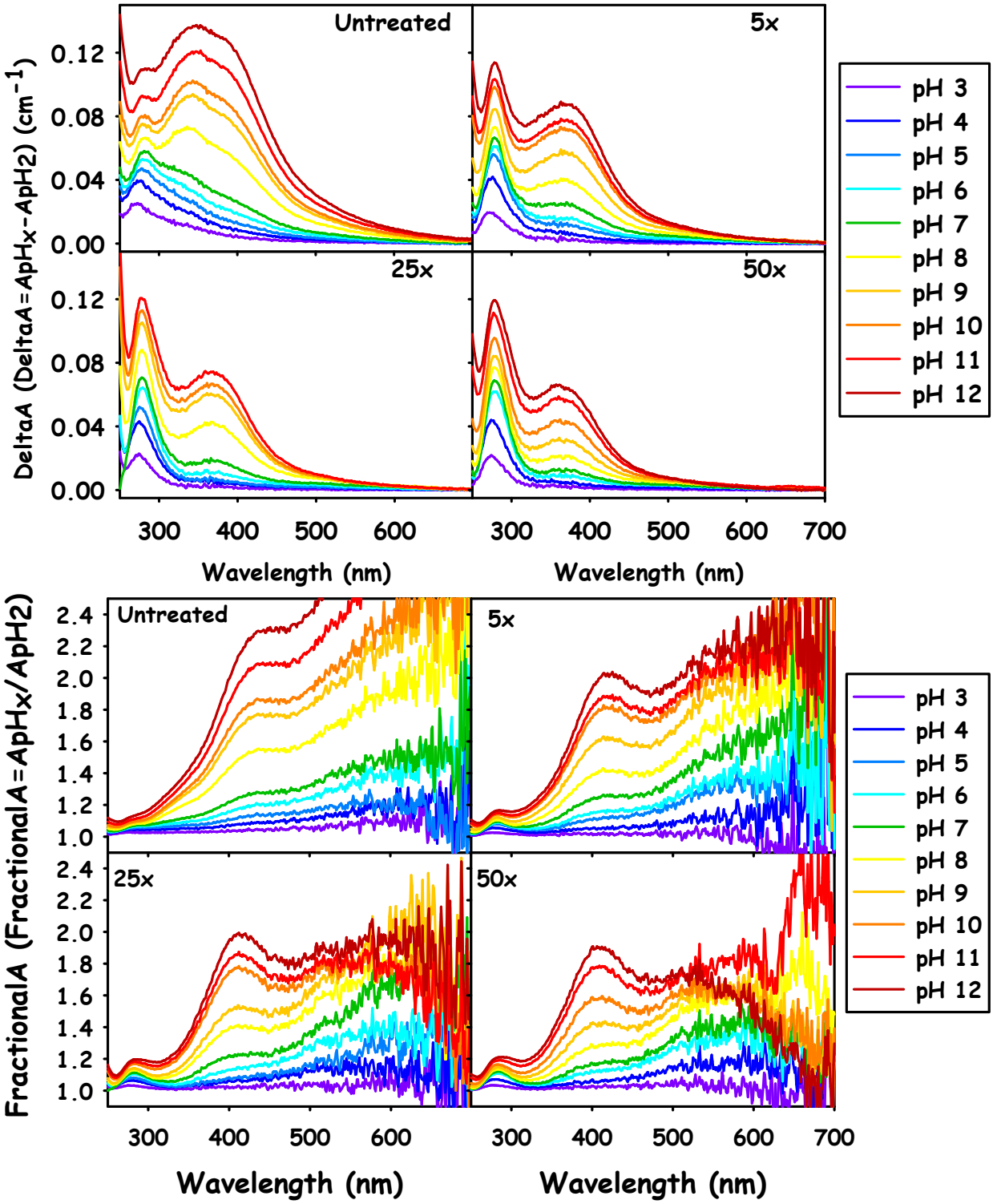

Figure S7. pH dependence of the difference spectra, DeltaA, (defined as DeltaA = ApH_x - ApH_2) (top) and of the fractional gain in absorption, Fractional A, (defined as Fractional A = ApH_x / ApH_2) (bottom) for SRFA (50 mg/L) untreated and 5-25-50-fold mass excess borohydride reduced (5x, 25x, 50x, respectively) referenced to the pH 2 spectrum.

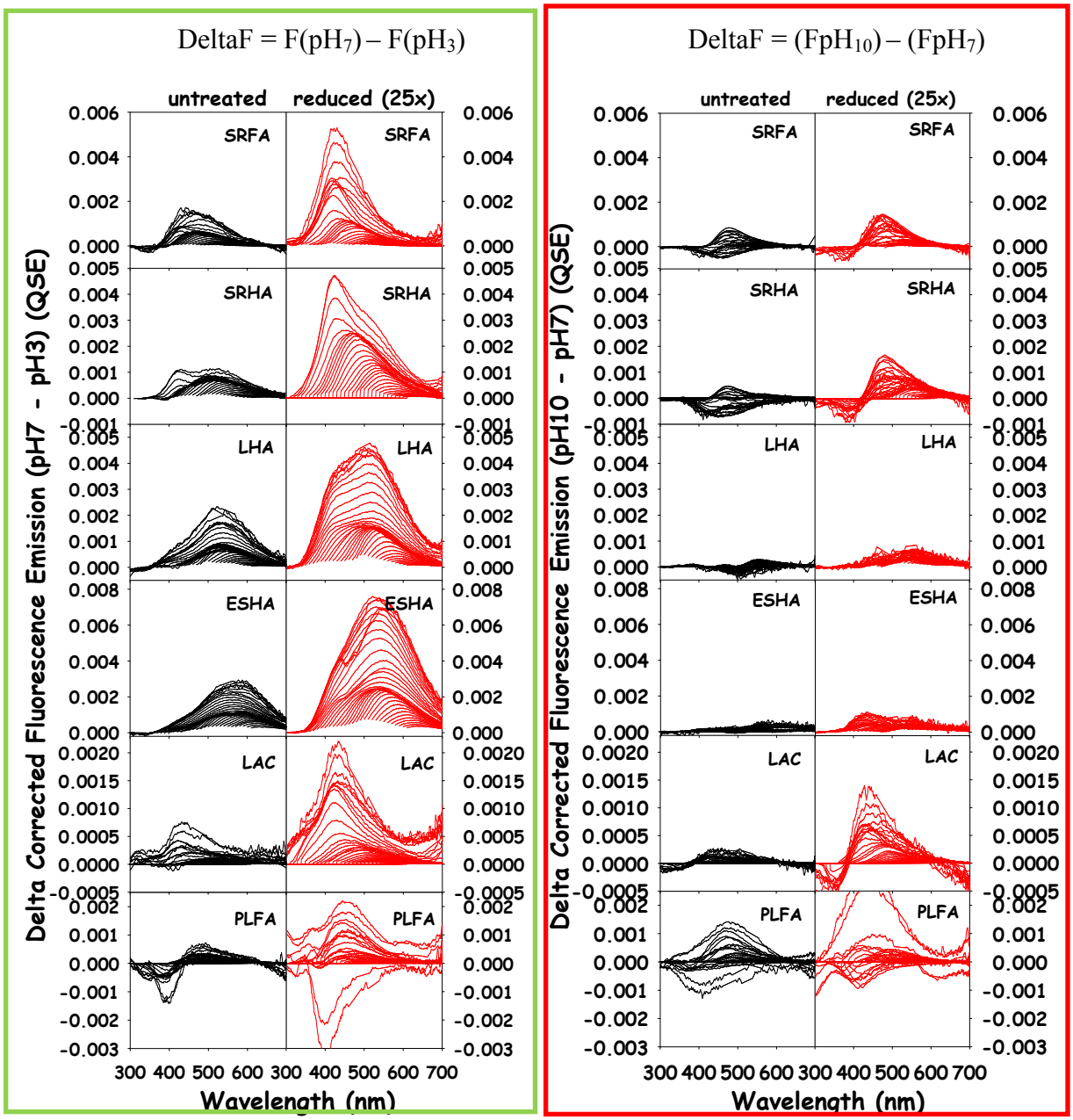

Figure S8. Difference fluorescence emission spectra, DeltaF, (defined as DeltaF = FpH_x – FpH_y where x and y are defined in each panel) for HS untreated (Black lines) and reduced (25x) (Red lines). Emission spectra were collected at increasing concentrations with increasing excitation wavelengths, normalized to the lowerer concentration (as reported in the figures) and merged into a single EEMs (see Methods Section).