Supporting Information

Use of Multiparametric Techniques to Quantify the Effects of Naturally Occurring Ligands on the Kinetics of Fe(II) Oxidation

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Supp. Table 1. Elemental Composition for All Organic Matter Used (Received from the IHSS)

Sample	Cat. No.	H_2O	Ash	C	H	O	N	S	P	$\delta^{13}C$	$\delta^{15}N$
Suwannee River-NOM	1R101N	8.15	7.0	52.47	4.19	42.69	1.10	0.65	0.02	nd	nd
Suwannee River-HA	2S101H	20.4	1.04	52.63	4.28	42.04	1.17	0.54	0.013	nd	nd
Suwannee River-FA	2S101F	16.9	0.58	52.34	4.36	42.98	0.67	0.46	0.004	nd	nd
Nordic Reservoir - NOM	1R108N	nd	41.4	53.17	5.67	nd	1.10	nd	nd	nd	nd
Nordic Reservoir - HA	1R105H	9.1	0.31	53.33	3.97	43.09	1.16	0.58	0.01	-27.8	-1.55
Nordic Reservoir - FA	1R105F	9.2	0.45	52.31	3.98	45.12	0.68	0.46	<0.01	-27.8	-3.19
Pony Lake - FA	1R109F	4.32	1.25	52.47	5.39	31.38	6.51	3.03	0.55	nd	nd

Source: Elemental analyses by Huffman Laboratories, Wheat Ridge, CO, USA; Isotopic analyses by Soil Biochemistry Laboratory, Dept. of Soil, Water, and Climate, University of Minnesota, St. Paul, MN, USA. H_2O content is the %(w/w) of H_2O in the air-equilibrated sample (a function of relative humidity). Ash is the %(w/w) of inorganic residue in a dry sample. C, H, O, N, S, and P are the elemental composition in %(w/w) of a dry, ash-free sample. $\delta^{13}C$ and $\delta^{15}N$ are the abundances of the respective stable isotopes in units of per mil, or o/oo . The data for bulk source materials are eported on an as-stored basis, except that %H and %O are corrected for water content. nd means that an item was not determined.

Supp. Table 2. Experimental parameters and average k_{obs} for each of the 43 experimental conditions for Fe(II) oxidation for each condition. N = 3 for experimental conditions #1-#42, N = 6 for the center point condition (#43), mean RSD 21.2%

Experimental parameters						Results		
Experimental Condition	Cl^- (mM)	SO_4^{2-} (mM)	HCO_3^- /CO_3^- (mM)	F- (µM)	NOM (mg/L)	Average R^2	Average k_{obs} (x10^{-4})	RSD (%)
1	316.4	16.4	1.41	38.9	8.7	0.973	64	13.9
2	777.5	16.4	1.41	38.9	8.7	0.997	158	32.9
3	316.4	40.1	1.41	38.9	8.7	0.992	69	13.8
4	777.5	40.1	1.41	38.9	8.7	0.989	56	16.8
5	316.4	16.4	3.14	38.9	8.7	0.978	218	31.9
6	777.5	16.4	3.14	38.9	8.7	0.996	248	8.5
7	316.4	40.1	3.14	38.9	8.7	0.997	195	19.7
8	777.5	40.1	3.14	38.9	8.7	0.954	242	19.8
9	316.4	16.4	1.41	95.8	8.7	0.998	87	14.1
10	777.5	16.4	1.41	95.8	8.7	0.995	68	26.8
11	316.4	40.1	1.41	95.8	8.7	0.984	34	22.2
12	777.5	40.1	1.41	95.8	8.7	0.994	67	16.5
13	316.4	16.4	3.14	95.8	8.7	0.984	189	20.1
14	777.5	16.4	3.14	95.8	8.7	0.992	218	30.5
15	316.4	40.1	3.14	95.8	8.7	0.992	130	27.8
16	777.5	40.1	3.14	95.8	8.7	0.998	213	19.0
17	316.4	16.4	1.41	38.9	21.3	0.990	86	20.1
18	777.5	16.4	1.41	38.9	21.3	0.997	102	33.0
19	316.4	40.1	1.41	38.9	21.3	0.968	90	22.9
20	777.5	40.1	1.41	38.9	21.3	0.998	142	32.9
21	316.4	16.4	3.14	38.9	21.3	0.996	206	18.9
22	777.5	16.4	3.14	38.9	21.3	0.998	266	29.9
23	316.4	40.1	3.14	38.9	21.3	0.994	234	29.4
24	777.5	40.1	3.14	38.9	21.3	0.999	184	8.2
25	316.4	16.4	1.41	95.8	21.3	0.993	111	18.7
26	777.5	16.4	1.41	95.8	21.3	0.996	91	20.0
27	316.4	40.1	1.41	95.8	21.3	0.990	85	18.5
28	777.5	40.1	1.41	95.8	21.3	0.995	101	25.6
29	316.4	16.4	3.14	95.8	21.3	0.993	278	16.6
30	777.5	16.4	3.14	95.8	21.3	0.995	303	12.9
31	316.4	40.1	3.14	95.8	21.3	0.997	206	27.3
32	777.5	40.1	3.14	95.8	21.3	0.995	163	11.6
33	0	28.2	2.28	67.4	15	0.993	172	33.6
34	1091.8	28.2	2.28	67.4	15	0.998	204	29.1
35	545.9	0	2.28	67.4	15	0.995	253	8.2
36	545.9	56.4	2.28	67.4	15	0.994	88	29.2
37	545.9	28.2	0.21	67.4	15	0.783	9	34.4
38	545.9	28.2	4.34	67.4	15	0.996	311	7.1
39	545.9	28.2	2.28	0	15	0.987	192	29.2
40	545.9	28.2	2.28	134.8	15	0.999	122	6.8
41	545.9	28.2	2.28	67.4	0	0.996	47	20.0
42	545.9	28.2	2.28	67.4	30	0.998	198	14.9
43	545.9	28.2	2.28	67.4	15	0.993	161	17.1

Supp. Table 3. Normalized rates for the 7 experimental conditions investigated for the other types of organic matter. Experimental condition #1 contains no NOM, so the normalized values are the same for all types of organic matter. The error values are one standard deviation. The error for the average values was calculated be pooling the standard deviation for the seven errors values in the associated column.

Exp. condition #	Coded HCO_3^- value	Coded NOM value	NLNOM	NLFA	NLHA	SRNOM	SRHA	SRFA	PLFA
7	+1	-1	1	0.9436	0.9128	0.7179	0.7231	0.8154	0.3795
			± 0.2756	±0.1896	±0.2286	±0.1705	±0.2242	±0.1618	±0.0767
11	-1	-1	1	1.5882	1.3824	1.5588	2.3529	1.5294	1.0294
			±0.3328	±0.4267	±0.3700	±0.3680	±0.7266	±0.4839	±0.2997
22	+1	+1	1	0.7256	0.5113	0.6429	1.1429	1.1842	0.5263
			±0.4200	±0.3092	±0.1595	±0.2454	±0.3532	±0.3717	±0.1570
26	-1	+1	1	1.0769	0.8791	0.8901	1.0220	0.6703	0.8242
			±0.2797	±0.2397	±0.1824	±0.2136	±0.2735	± 0.1366	±0.2168
41	0	-2	1	1	1	1	1	1	1
			±0.2708	±0.2708	±0.2708	±0.2780	±0.2708	±0.2708	±0.2708
42	0	+2	1	0.8990	0.5303	0.6616	0.6212	0.4343	0.3939
			±0.2143	±0.1491	±0.1006	±0.1423	±0.1093	±0.0666	±0.00721
43	0	0	1	0.6460	0.6398	0.8944	0.5963	0.4845	0.5217
			±0.2460	±0.1675	±0.1668	±0.1846	±0.1394	±0.0978	±0.1301
average			1	0.9828	0.8365	0.9094	1.0655	0.8740	0.6679
			±0.2894	±0.2513	±0.2172	±0.2298	±0.3277	±0.2471	±0.1841

Supp. Table 4. Experimental parameters obtained from field measurements of Pacific Ocean and Congaree River waters.

	Concentrations (mg/L)				
	Cl^- (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	F^- (mg/L)	NOM (mgC/L)
Pacific 3.2	17400	115.83	2440	0.6	0.972
Pacific 109	17400	102.79	2440	0.55	0.972
Congaree river	552	24.187	77.4	0.11	5.75
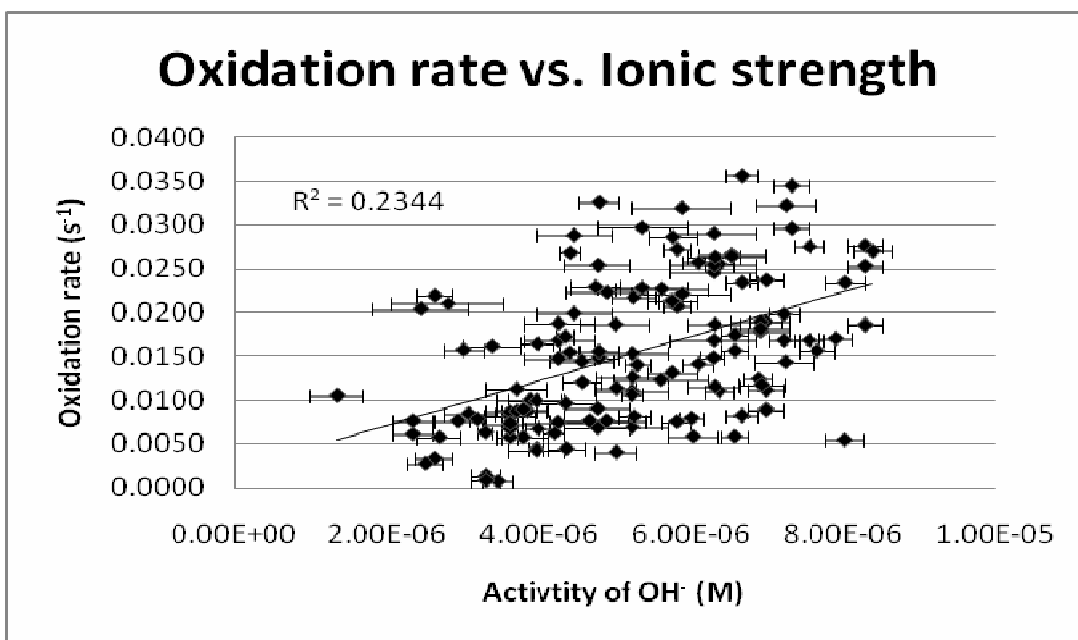
Supp. Figure 1. Rate of Fe(II) oxidation vs. the activity of HO⁻. The activity of HO⁻ did not correlate with k_{obs} over the pH range of these experiments (pH 8.34 ± 0.13). Activity of HO⁻ was calculated based on pH probe responses to the pH 8 NBS buffer against a range of ionic strengths. Ionic strength adjustment was achieved with NaCl addition. NaCl was chosen because it is the primary source of ionic strength for the experiments in the matrix. K_w for the HO⁻ activity estimations was obtained from Millero *et al*, *The oxidation kinetics of Fe(II) in seawater*, Geochimica et Cosmochimica Acta, (51), p 793-801, 1987.
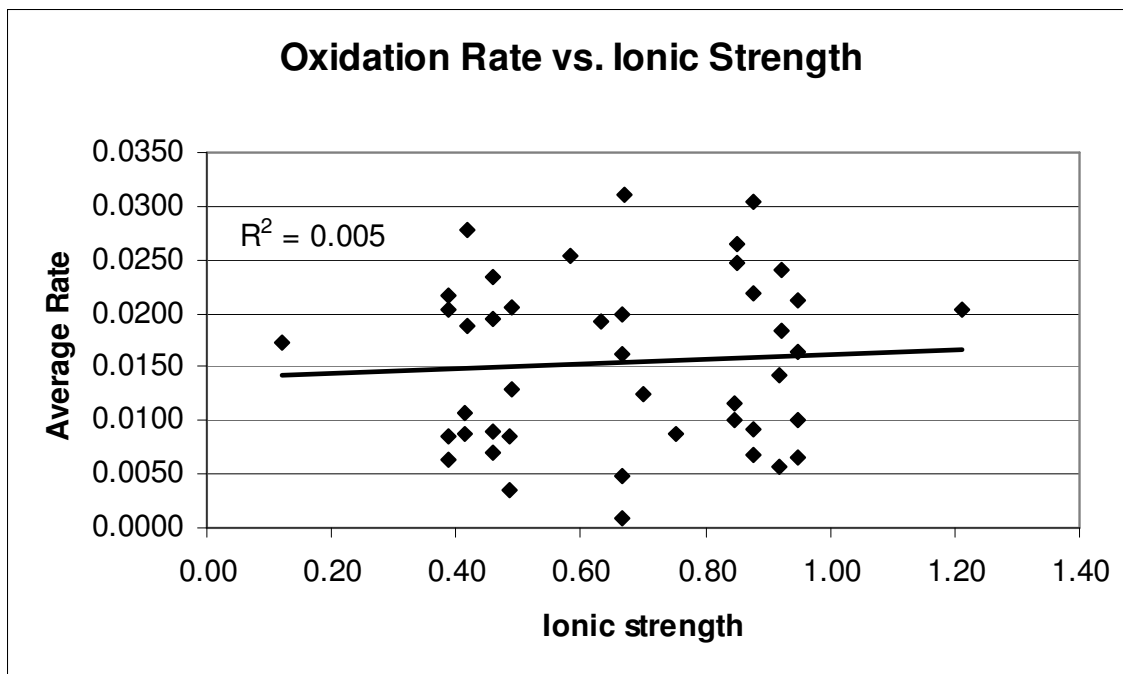
Supp. Figure 2. Plot of average Fe(II) oxidation rate vs. the ionic strength for each experimental condition. This plot show that there is no correlation between the Fe(II) oxidation rate and ionic strength.

General conditions for ^{13}C NMR Spectra (Supp. Figure 3; 1-7). Solid state ^{13}C NMR spectra for each type of natural organic matter studied in this work. [13]C CP-MAS spectra were collected on a Varian Unity Inova 500 MHz spectrometer fitted with a Doty 4mm XC MAS probe. The spectra were collected at ambient temperature with sample rotation rate of 6 kHz. TOSS sideband suppression was used as well as TPPM decoupling at a ^{1}H field strength of 64kHz (3.9μsec 90° pulse width) . A 1.5 msec contact time with a tangential amplitude ramped on the ^{13}C RF channel. Free induction decays were collected with a 40 msec acquisition time over a 400 ppm spectra width. The number of transients varied form 464 to 53520 and a 1.5 sec relaxation delay was used. The data was weighted with a 150 Hz line broadened function prior to Fourier transformation. Integrals for each functional group were assigned based those used by the IHSS.(K. A. Thorn, D. W. Folan, and P. MacCarthy (*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*, U.S. Geological Survey, Water-Resources Investigations Report 89-4196, Denver, CO, 93 pp.)
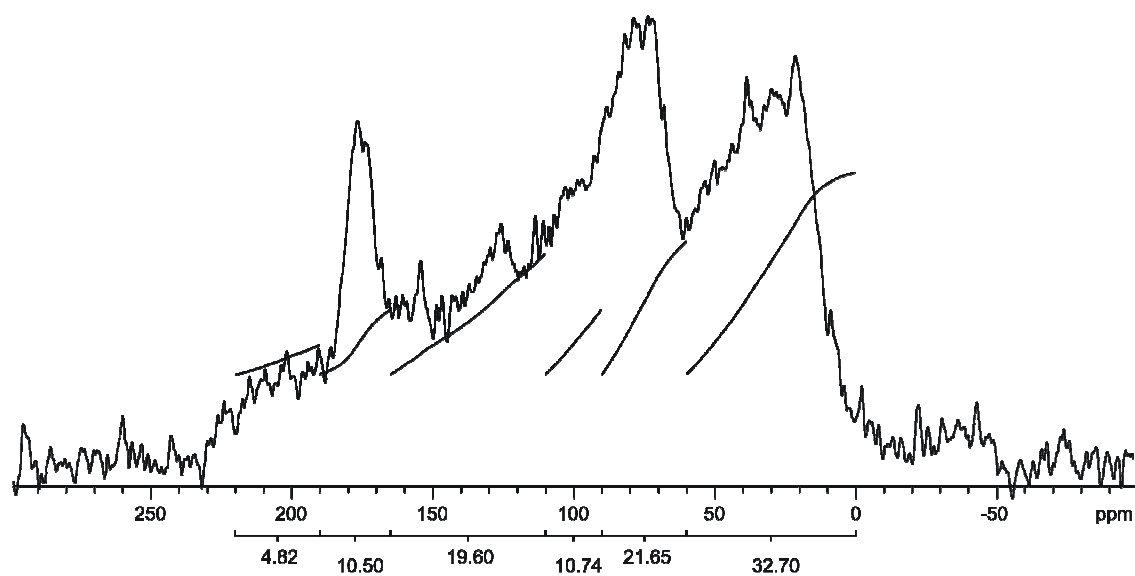
Supp. Figure 3.1 ^{13}C CP-MAS spectra for the Nordic reservoir natural organic matter used. % Carbonyl = 4.82, % Carboxyl = 10.50. % Aromatic = 19.60, % Acetal = 10.74, % Heteroaliphatic = 21.65, % Aliphatic = 32.70.
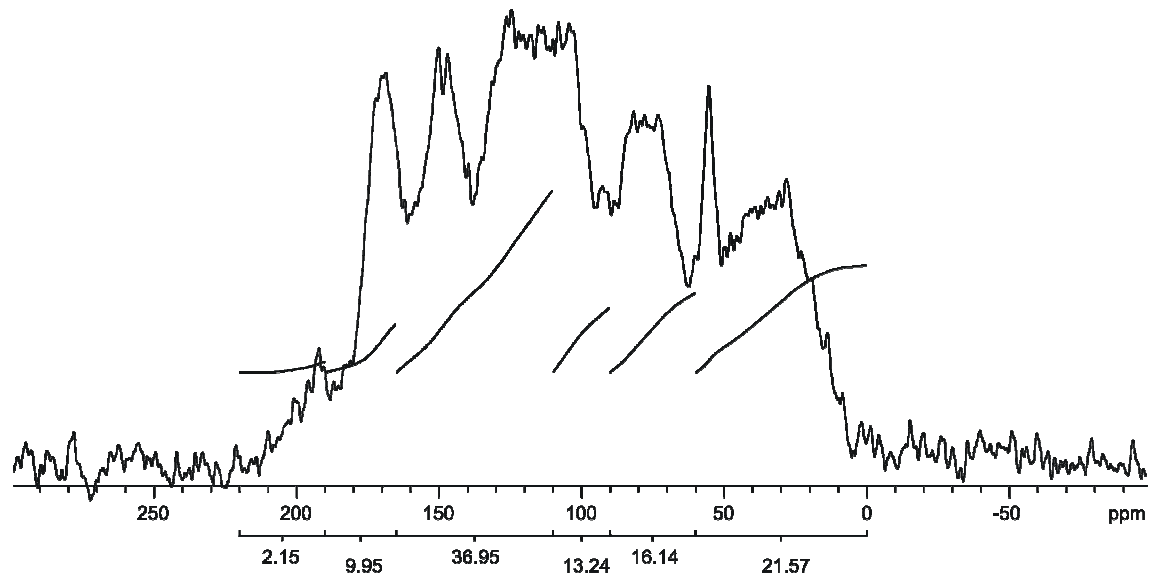
Supp. Figure 3.2 ^{13}C CP-MAS spectra for the Nordic reservoir humic acid used. % Carbonyl = 2.15, % Carboxyl = 9.95. % Aromatic = 36.95, % Acetal = 13.24, % Heteroaliphatic = 16.14, % Aliphatic = 21.57.
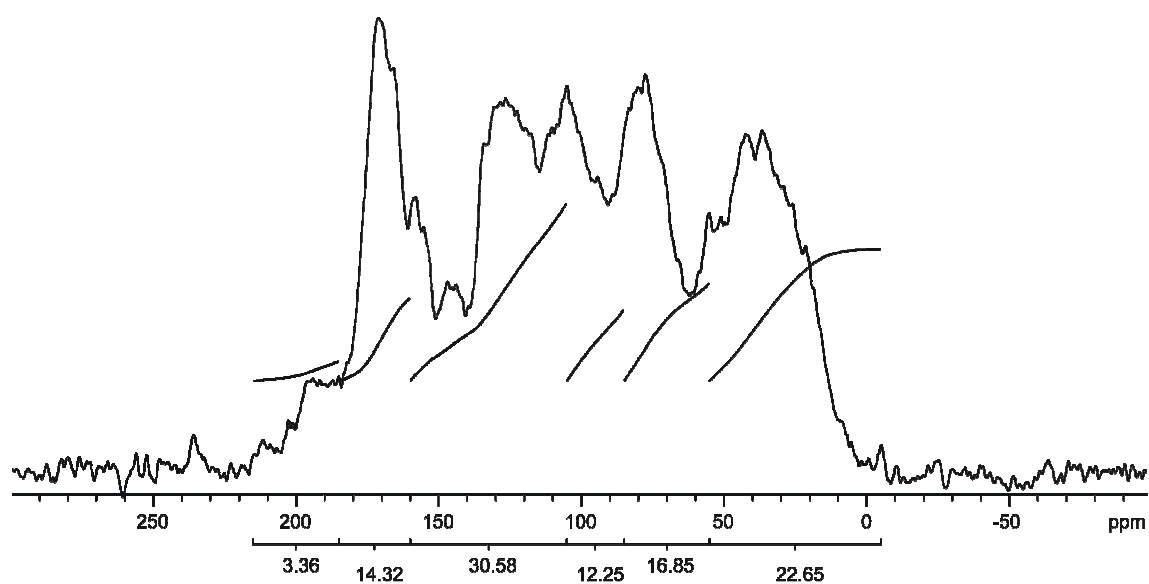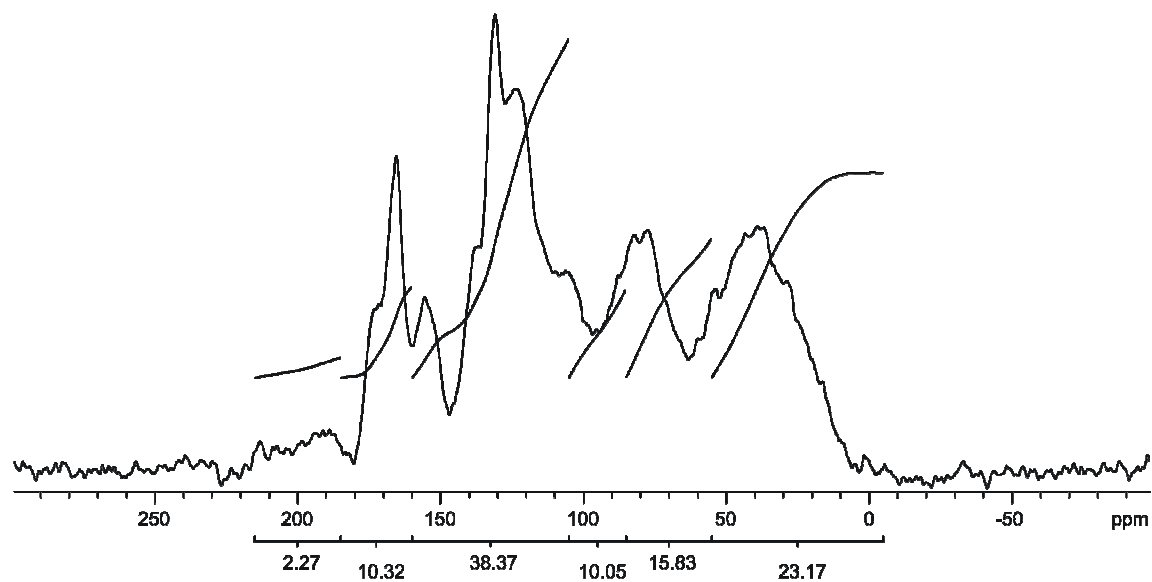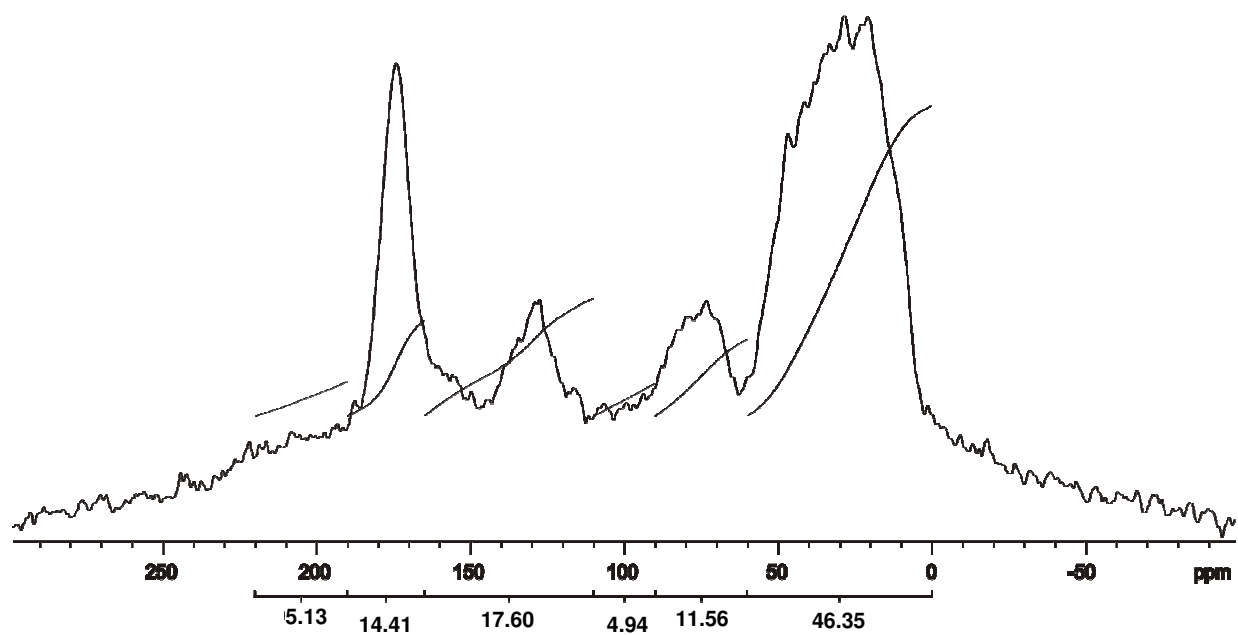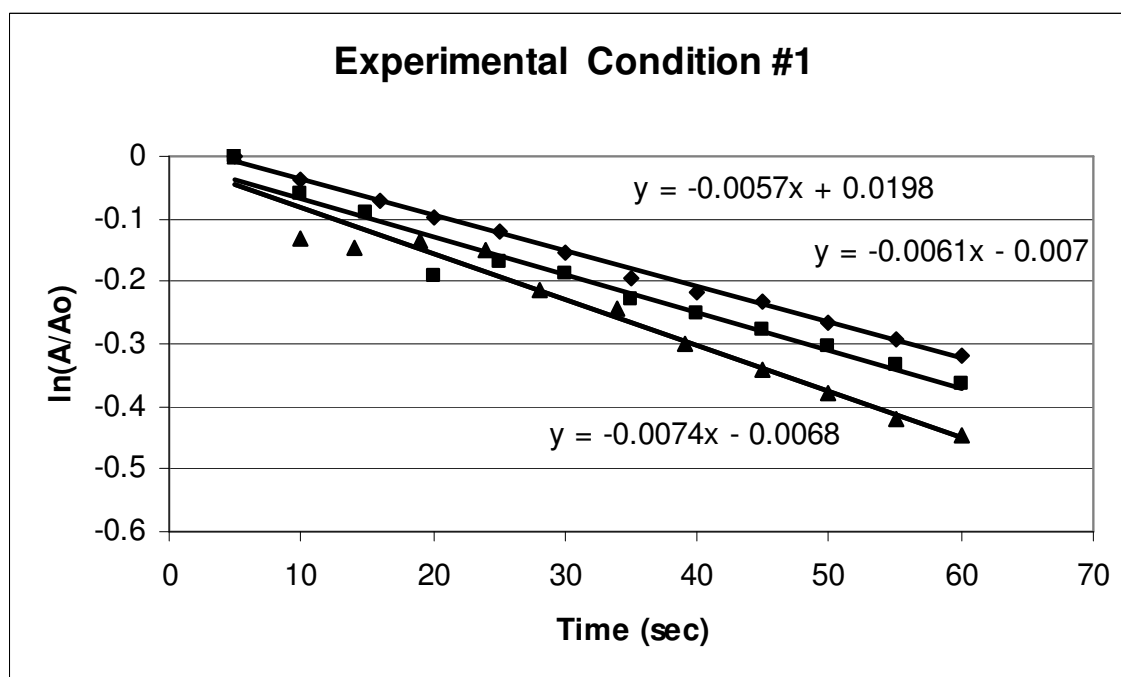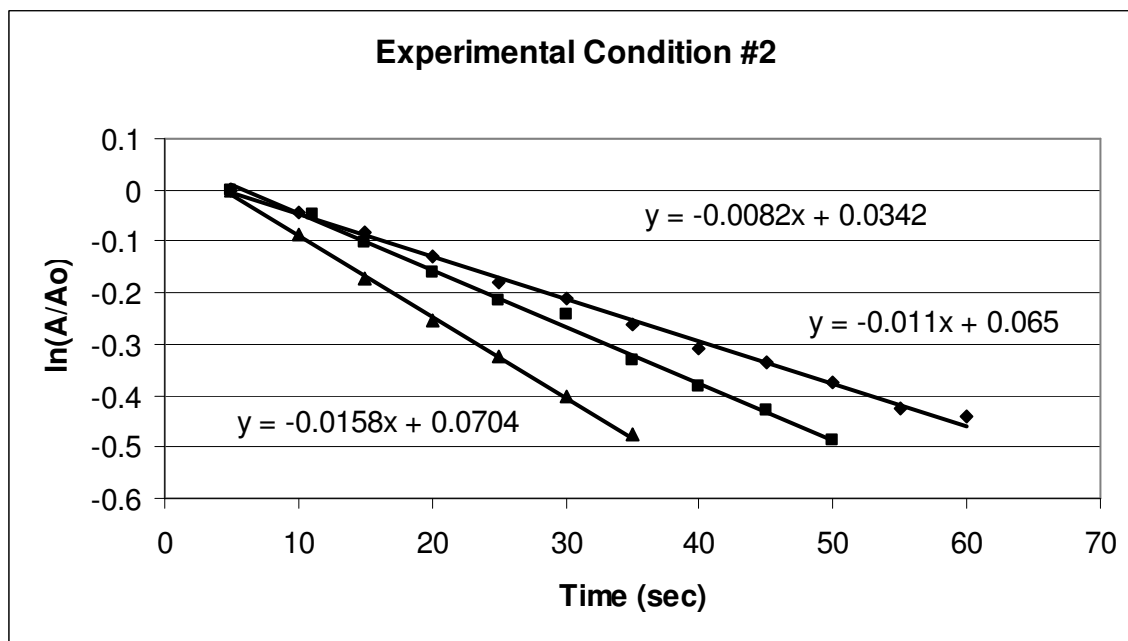
Supp. Figure 3.3 ^{13}C CP-MAS spectra for the Nordic reservoir fulvic used. % Carbonyl = 3.36, % Carboxyl = 14.32. % Aromatic = 30.58, % Acetal = 12.25, % Heteroaliphatic = 16.85, % Aliphatic = 22.65.
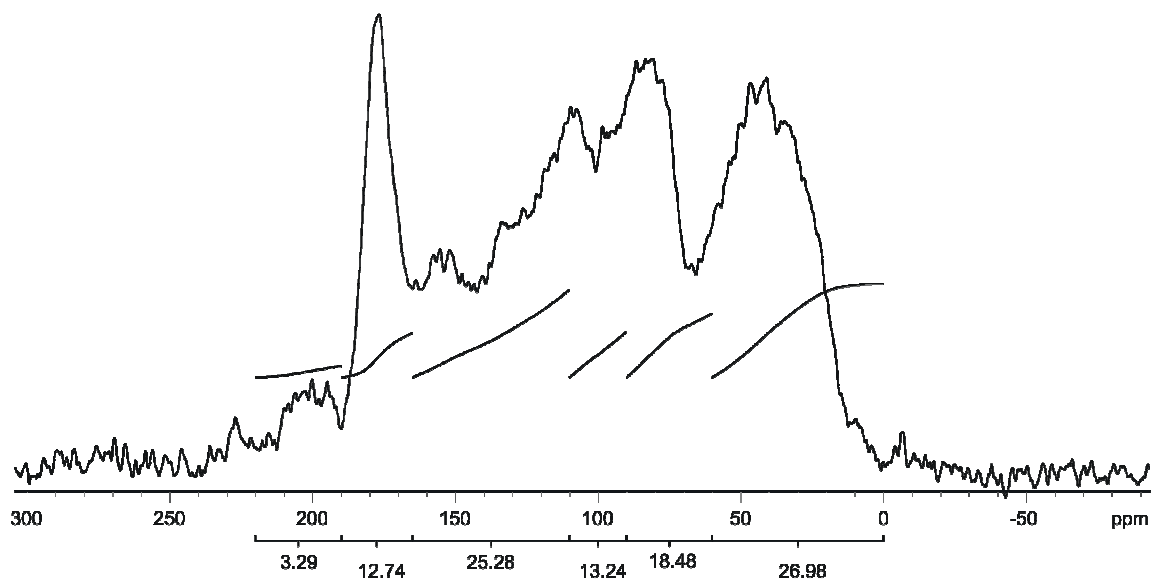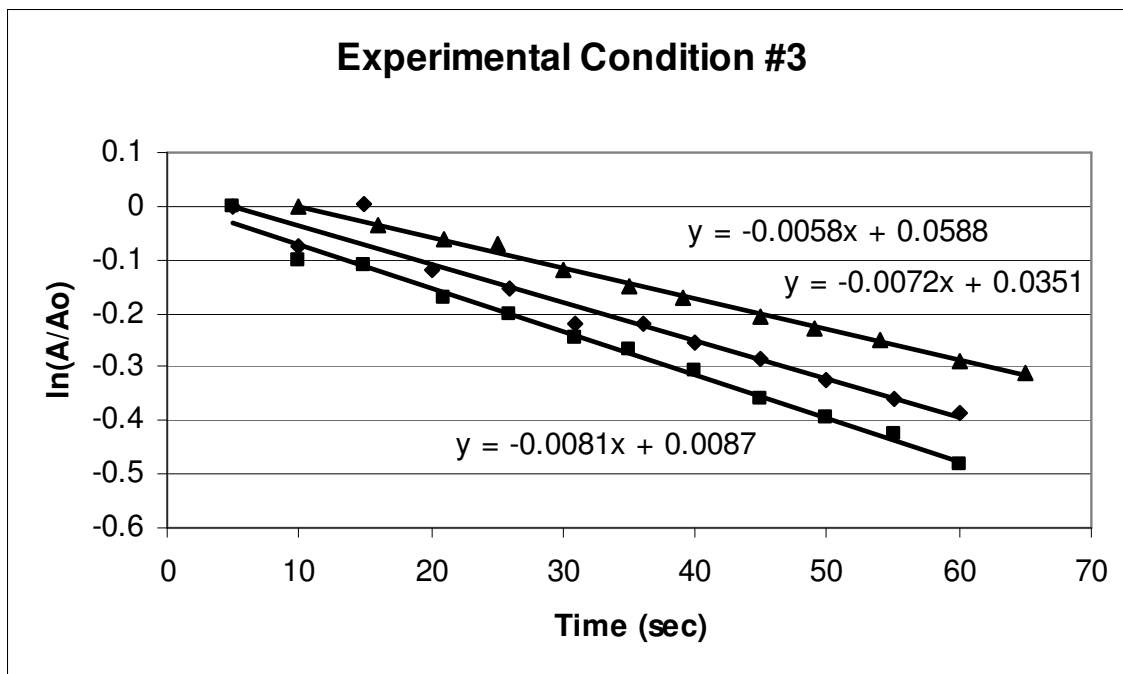
Supp. Figure 3.4 ^{13}C CP-MAS spectra for the Suwannee river natural organic matter used. % Carbonyl = 3.29, % Carboxyl = 12.74. % Aromatic = 25.28, % Acetal = 13.24, % Heteroaliphatic = 18.48, % Aliphatic = 26.96.
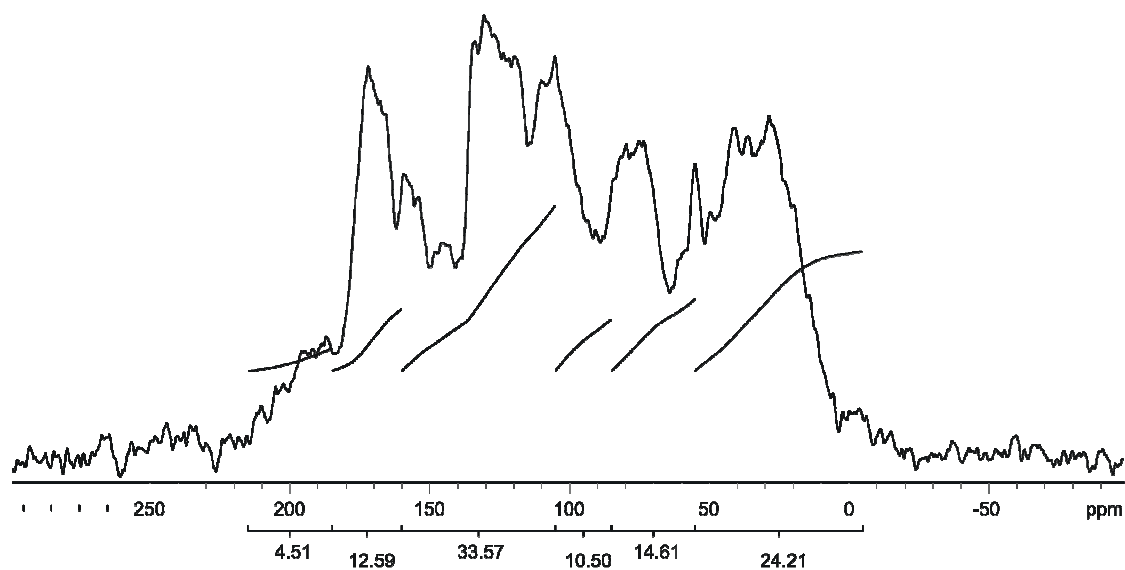
Supp. Figure 3.5 ^{13}C CP-MAS spectra for the Suwannee river humic acid used. % Carbonyl = 4.51, % Carboxyl = 12.59. % Aromatic = 33.57, % Acetal = 10.50, % Heteroaliphatic = 14.61, % Aliphatic = 24.21.

Supp. Figure 3.6 ^{13}C CP-MAS spectra for the Suwannee river fulvic acid used. % Carbonyl = 2.27, % Carboxyl = 10.32. % Aromatic = 38.37, % Acetal = 10.05, % Heteroaliphatic = 15.83, % Aliphatic = 23.17.

5.13 14.41 17.60 4.94 11.56 46.35

Supp. Figure 3.7 ^{13}C CP-MAS spectra for the Pony Lake fulvic acid used. % Carbonyl = 5.13, % Carboxyl = 14.41. % Aromatic = 17.60, % Acetal = 4.94, % Heteroaliphatic = 11.56, % Aliphatic = 46.35.

Experimental Condition #1

$y = -0.0057x + 0.0198$

$y = -0.0061x - 0.007$

$y = -0.0074x - 0.0068$

Supp. Figure 4.1 Experimental condition #1. $Cl^- = 316.4$ mM, $SO_4^{2-} = 16.4$ mM, HCO_3^- /$CO_3^{2-} = 1.41$, $F^- = 38.9$ μM, NOM = 8.7 mg/L, N = 3.

Experimental Condition #2

$y = -0.0082x + 0.0342$

$y = -0.011x + 0.065$

$y = -0.0158x + 0.0704$

Supp. Figure 4.2 Experimental condition #2. $Cl^- = 777.5$ mM, $SO_4^{2-} = 16.4$ mM, $HCO_3^-/CO_3^{2-} = 1.41$, $F^- = 38.9$ μM, NOM = 8.7 mg/L, N = 3.

Experimental Condition #3

$y = -0.0058x + 0.0588$

$y = -0.0072x + 0.0351$

$y = -0.0081x + 0.0087$

ln(A/Ao)

Time (sec)

Supp. Figure 4.3 Experimental condition #3. $Cl^- = 316.4$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 1.41$, $F^- = 38.9$ μM, NOM = 8.7 mg/L N = 3.

Experimental Condition #4

$y = -0.0044x + 0.0255$

$y = -0.0067x + 0.0522$

$y = -0.0058x + 0.0293$
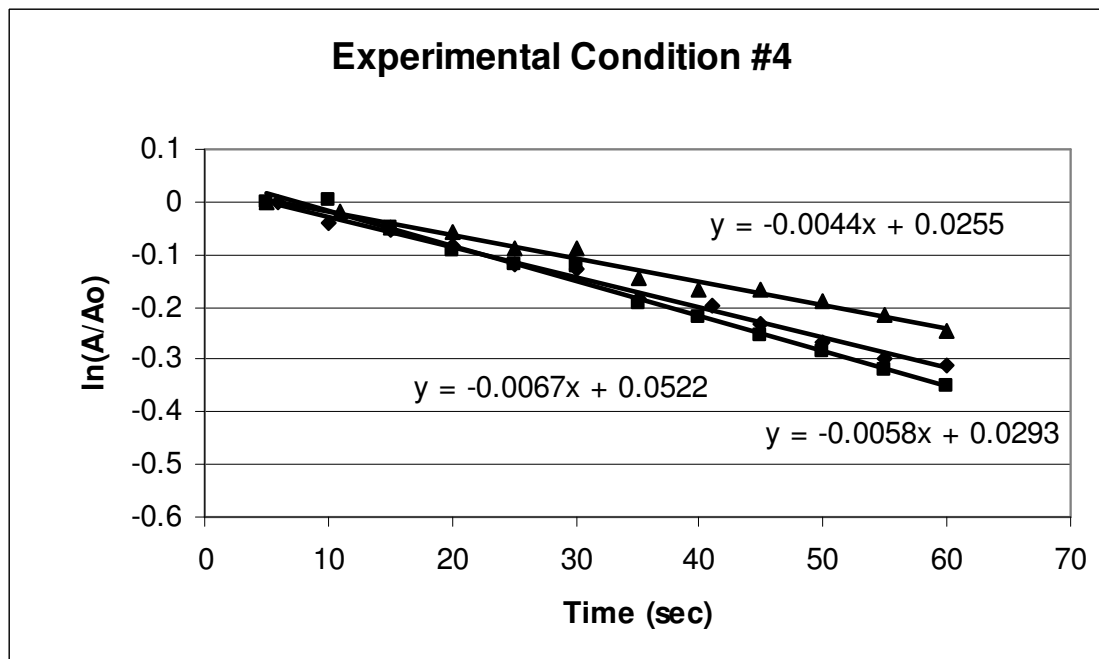
Supp. Figure 4.4 Experimental condition #4. $Cl^- = 777.5$ mM, $SO_4^{2-} = 40.1$ mM, HCO_3^- /$CO_3^{2-} = 1.41$, $F^- = 38.9$ µM, NOM = 8.7 mg/L, N = 3.

Experimental Condition #5

$y = -0.0168x + 0.1329$

$y = -0.0188x + 0.1039$

$y = -0.0297x + 0.1498$
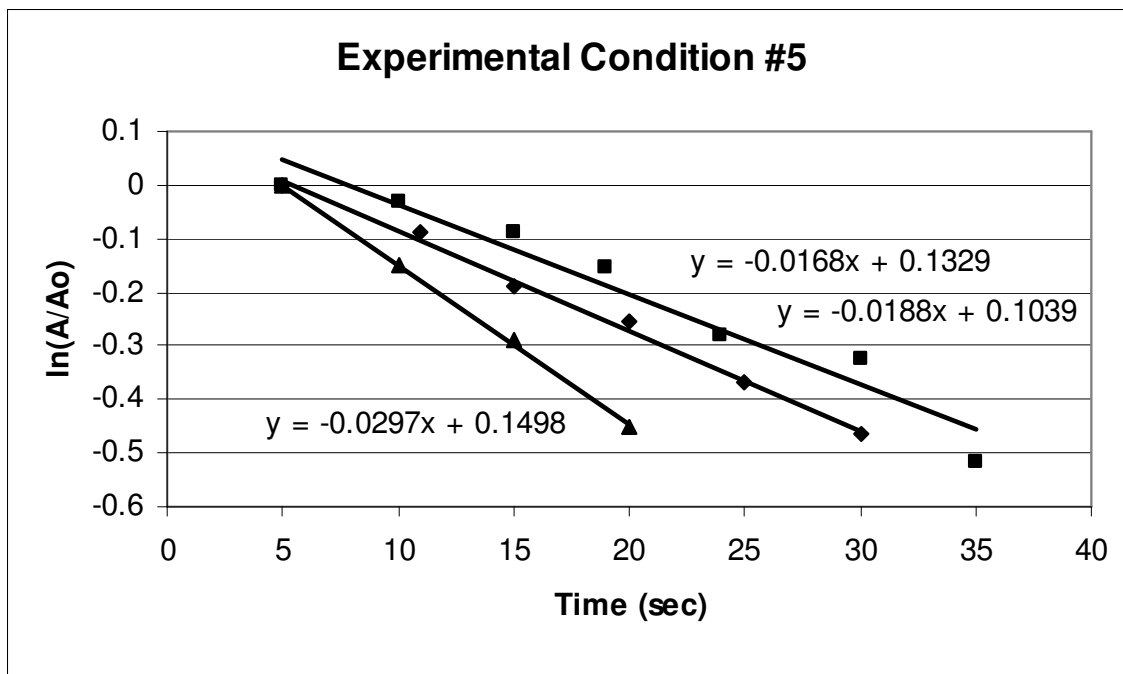
Supp. Figure 4.5 Experimental condition #5. $Cl^- = 316.4$ mM, $SO_4^{2-} = 16.4$ mM, HCO_3^- /$CO_3^{2-} = 3.14$, $F^- = 38.9$ μM, NOM = 8.7 mg/L, N = 3.

Experimental Condition #6

$y = -0.0234x + 0.1149$

$y = -0.0237x + 0.1327$

$y = -0.0272x + 0.124$
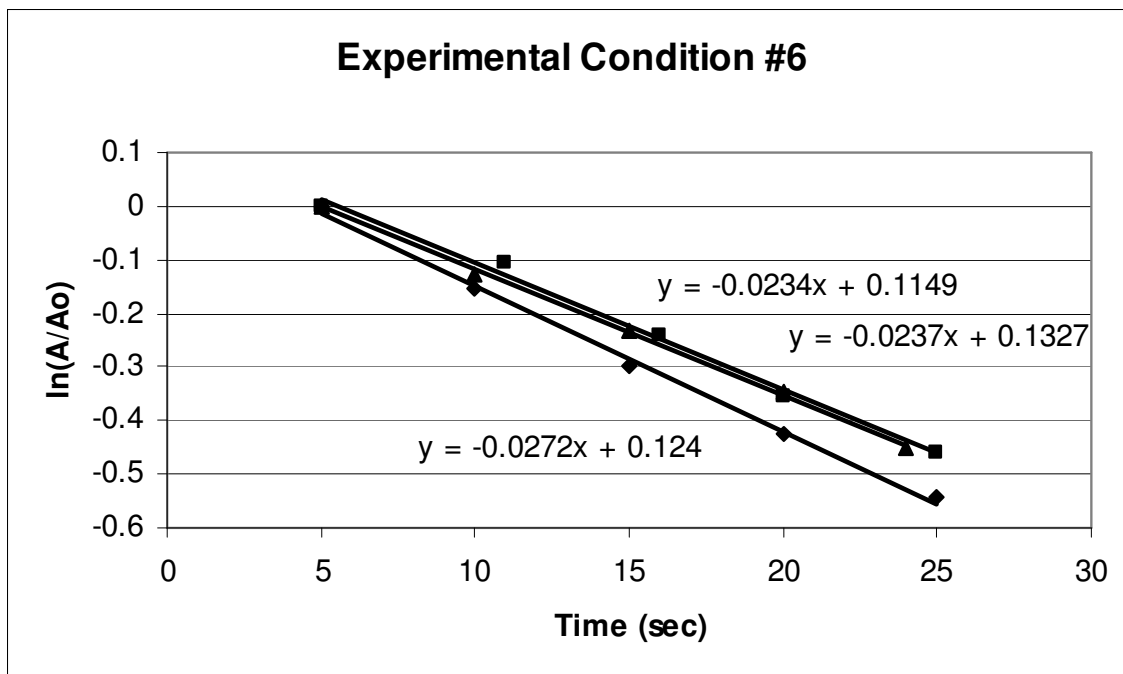
Supp. Figure 4.6 Experimental condition #6. $Cl^- = 777.5$ mM, $SO_4^{2-} = 16.4$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 38.9$ μM, NOM = 8.7 mg/L, N = 3.

Experimental Condition #7

$y = -0.0153x + 0.0696$

$y = -0.0186x + 0.1112$

$y = -0.0246x + 0.1181$
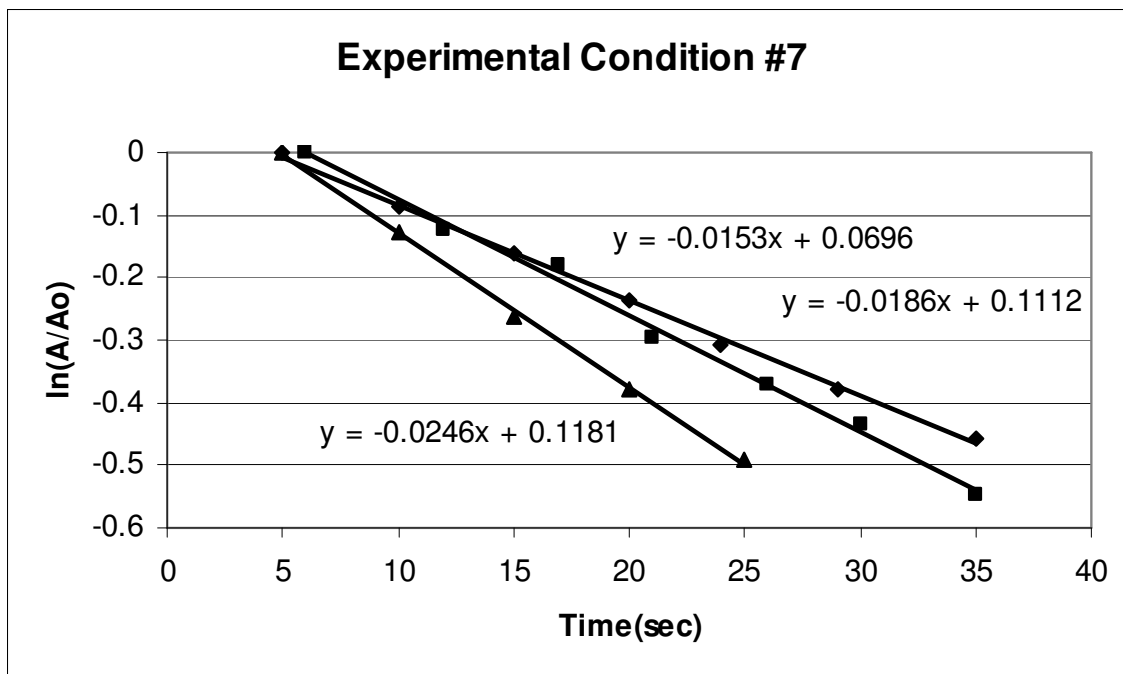
Supp. Figure 4.7 Experimental condition #7. $Cl^- = 316.4$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 38.9$ µM, NOM = 8.7 mg/L, N = 3.

Experimental Condition #8

$y = -0.0174x + 0.097$

$y = -0.0276x + 0.1283$

$y = -0.0275x + 0.1241$
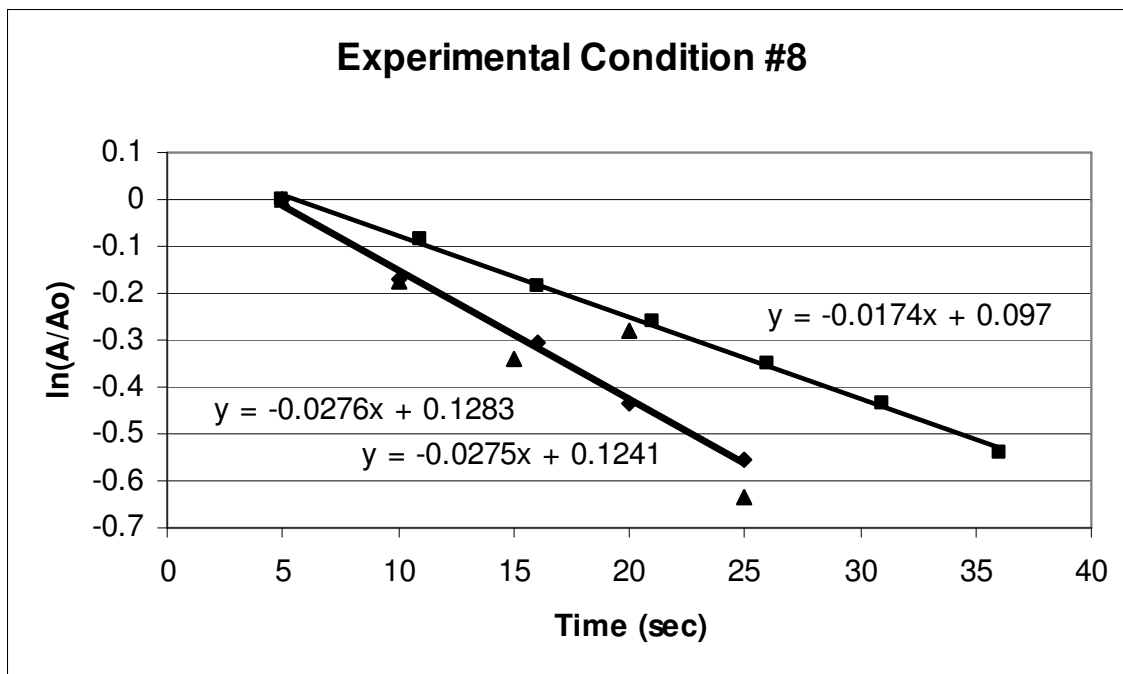
Supp. Figure 4.8 Experimental condition #8. $Cl^- = 777.5$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 38.9$ μM, NOM = 8.7 mg/L, N = 3.

Experimental Condition #9

$y = -0.0076x + 0.0357$

$y = -0.0084x + 0.0547$

$y = -0.01x + 0.0394$
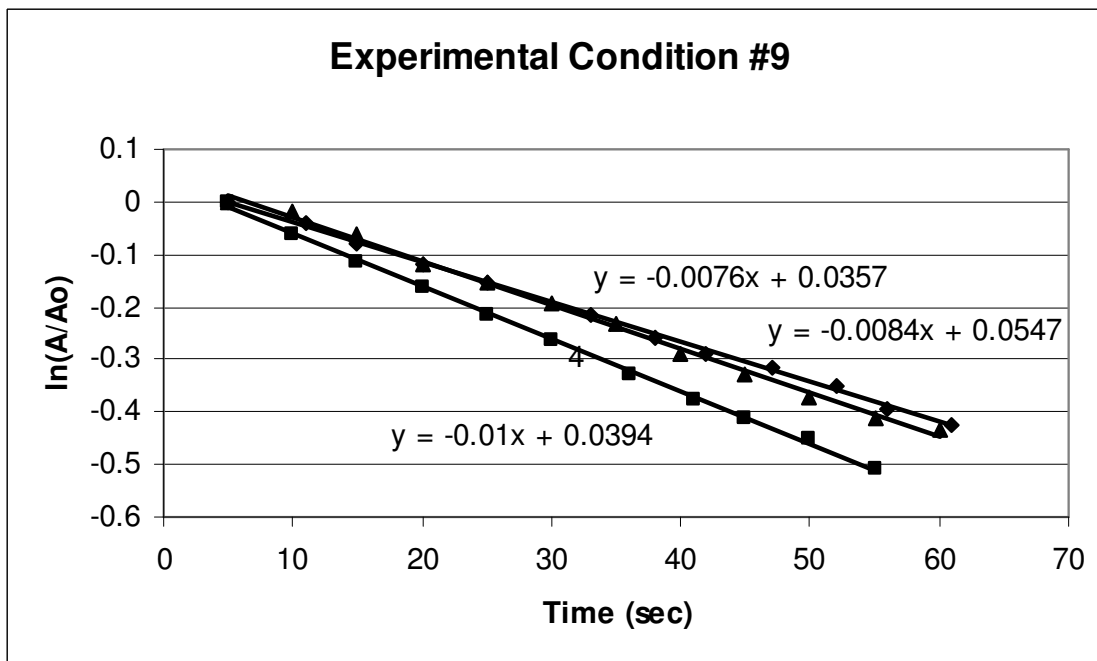
Supp. Figure 4.9 Experimental condition #9. $Cl^- = 316.4$ mM, $SO_4^{2-} = 16.4$ mM, HCO_3^- /$CO_3^{2-} = 1.41$, $F^- = 95.8$ µM, NOM = 8.7 mg/L, N = 3.

Experimenal Conditon #10

y = -0.0054x + 0.0204

y = -0.0062x + 0.0492

y = -0.0089x + 0.0225
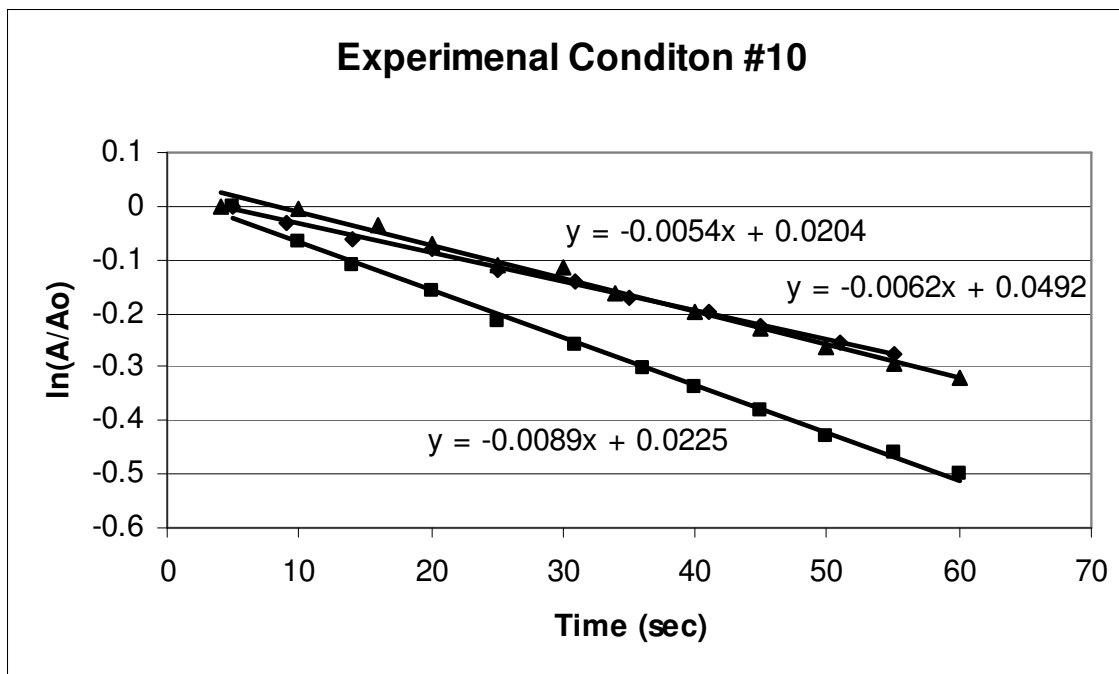
Supp. Figure 4.10 Experimental condition #10. $Cl^- = 777.5$ mM, $SO_4^{2-} = 16.4$ mM, $HCO_3^-/CO_3^{2-} = 1.41$, $F^- = 95.8$ µM, NOM = 8.7 mg/L, N = 3.

Experimental Condition #11

$y = -0.0027x + 0.0057$

$y = -0.0033x + 0.0255$

$y = -0.0042x + 0.014$
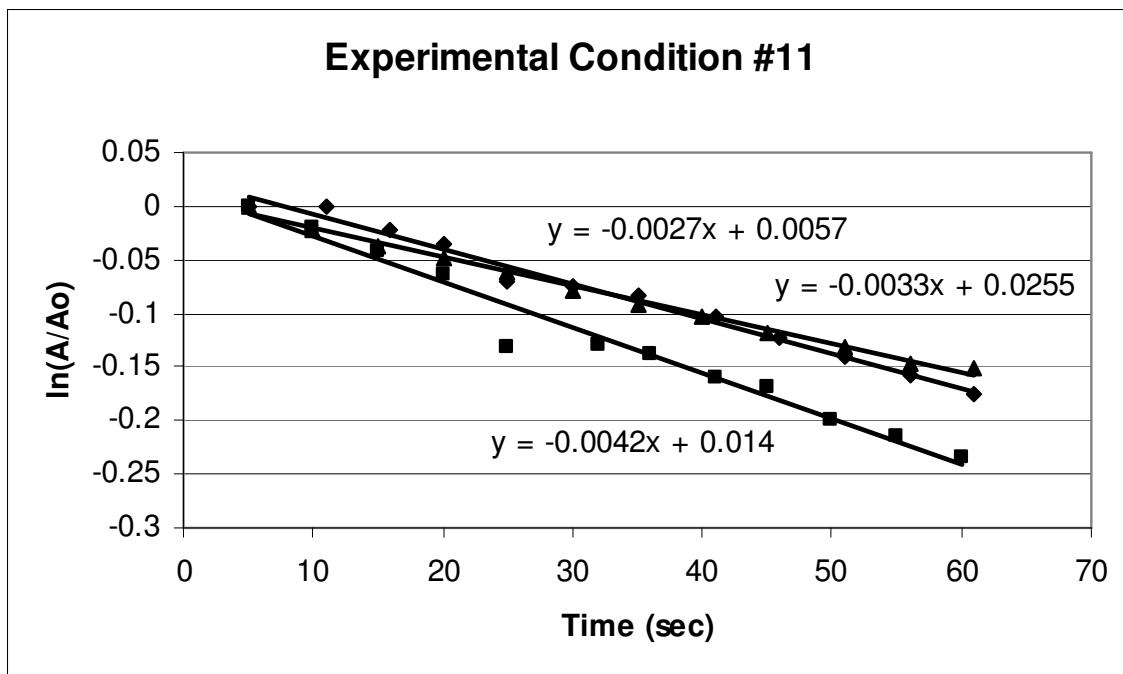
Supp. Figure 4.11 Experimental condition #11. $Cl^- = 316.4$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 1.41$, $F^- = 95.8$ µM, NOM = 8.7 mg/L, N = 3.

Experimental Conditon #12

$y = -0.0058x + 0.0546$

$y = -0.0063x + 0.0236$

$y = -0.0079x + 0.0509$

In(A/Ao)

Time (sec)
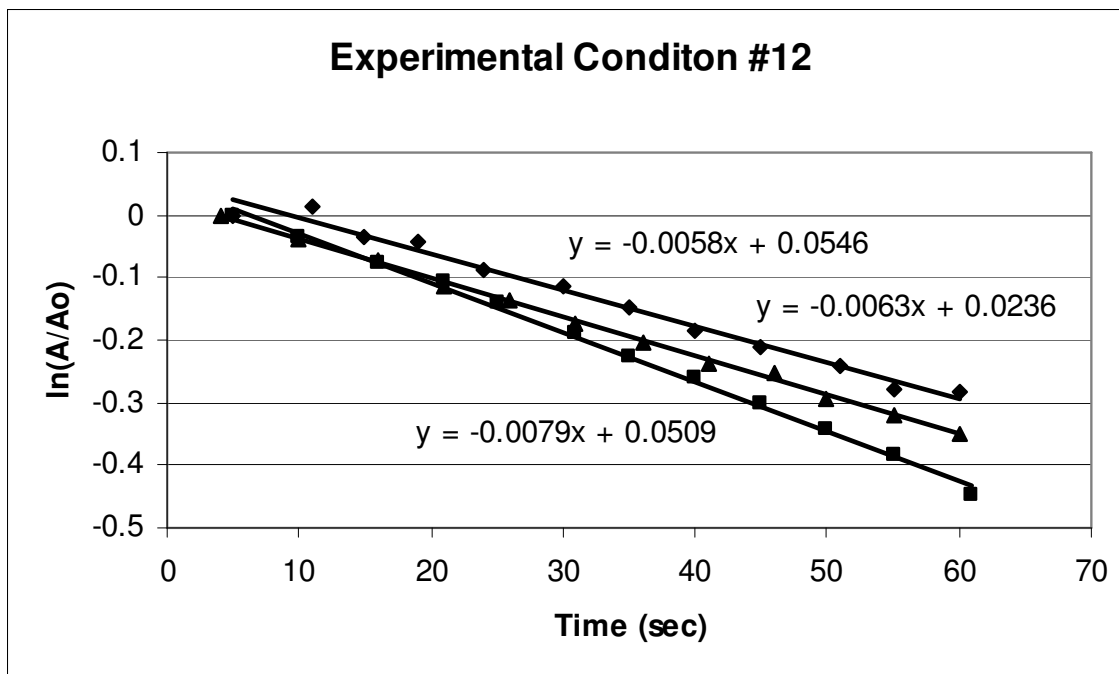
Supp. Figure 4.12 Experimental condition #12. $Cl^- = 777.5$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 1.41$, $F^- = 95.8$ μM, NOM = 8.7 mg/L, N = 3.

Experimental Condition #13

$y = -0.0147x + 0.0675$

$y = -0.0221x + 0.0892$

$y = -0.0199x + 0.1013$
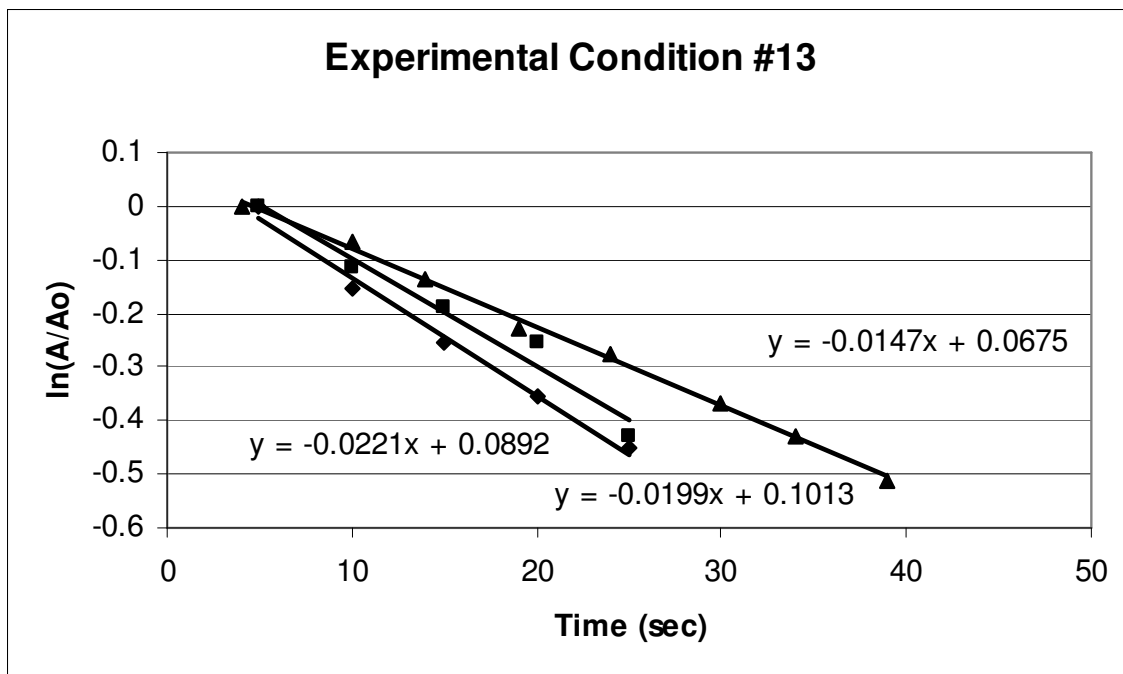
Supp. Figure 4.13 Experimental condition #13. $Cl^- = 316.4$ mM, $SO_4^{2-} = 16.4$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 95.8$ μM, NOM = 8.7 mg/L, N = 3.

Experimental Condition #14

$y = -0.0141x + 0.0988$

$y = -0.0257x + 0.1158$

$y = -0.0255x + 0.1872$
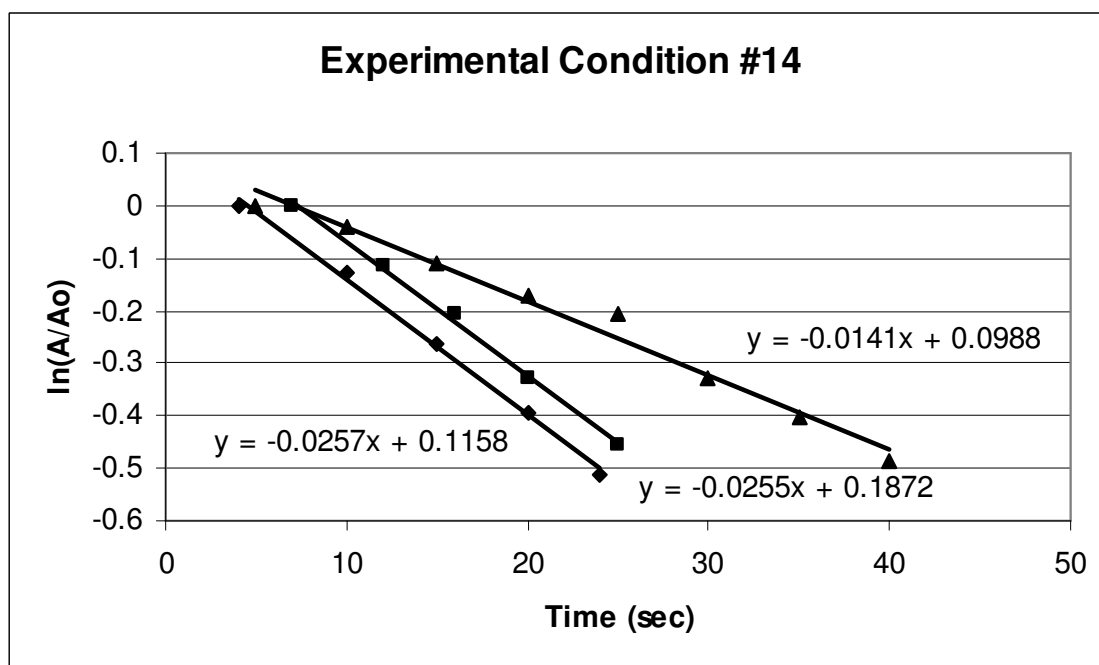
Supp. Figure 4.14 Experimental condition #14. $Cl^- = 777.5$ mM, $SO_4^{2-} = 16.4$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 95.8$ µM, NOM = 8.7 mg/L, N = 3.

Experimental Condition #15

$y = -0.0096x + 0.0546$

$y = -0.0126x + 0.0603$

$y = -0.0168x + 0.0863$
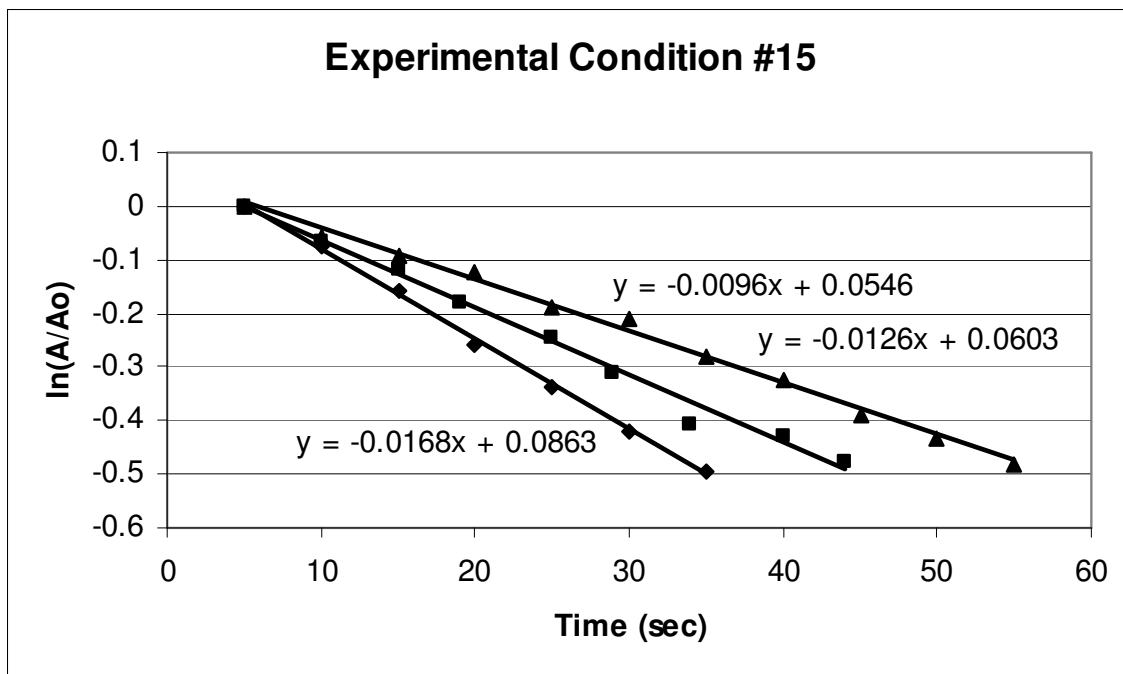
Supp. Figure 4.15 Experimental condition #15. $Cl^- = 316.4$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 95.8$ μM, NOM = 8.7 mg/L, N = 3.
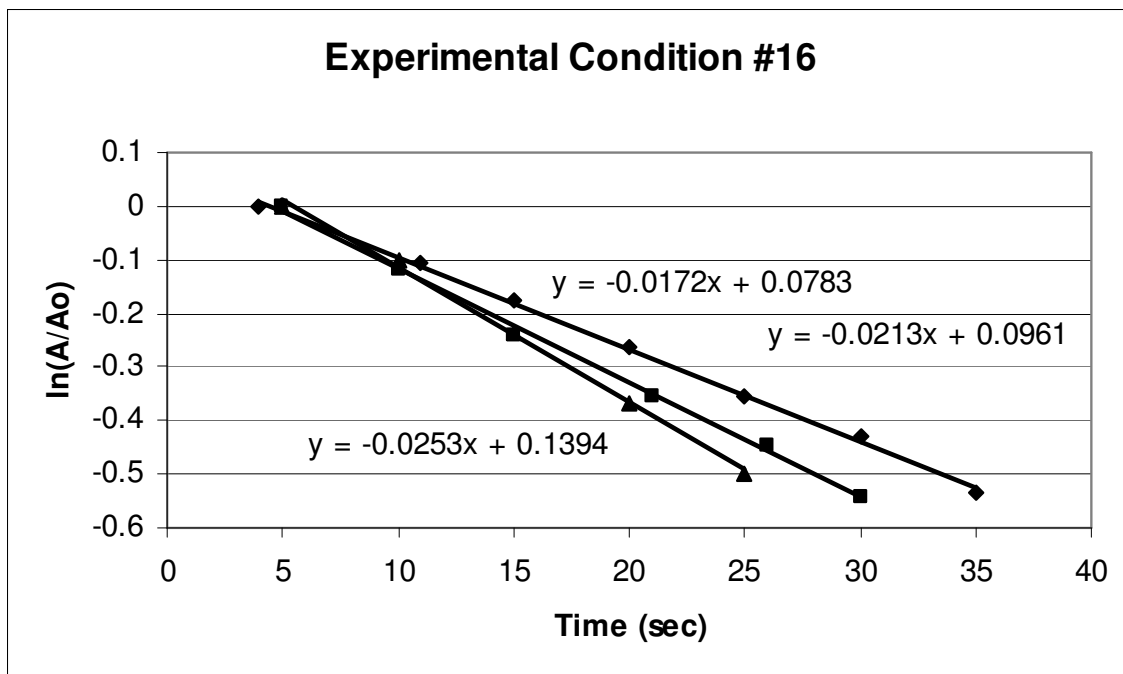
Supp. Figure 4.16 Experimental condition #16. $Cl^- = 777.5$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 98.5$ μM, NOM = 8.7 mg/L, N = 3.

Experimental Condition #17

$y = -0.0076x + 0.031$

$y = -0.0076x + 0.0218$

$y = -0.0106x + 0.0151$
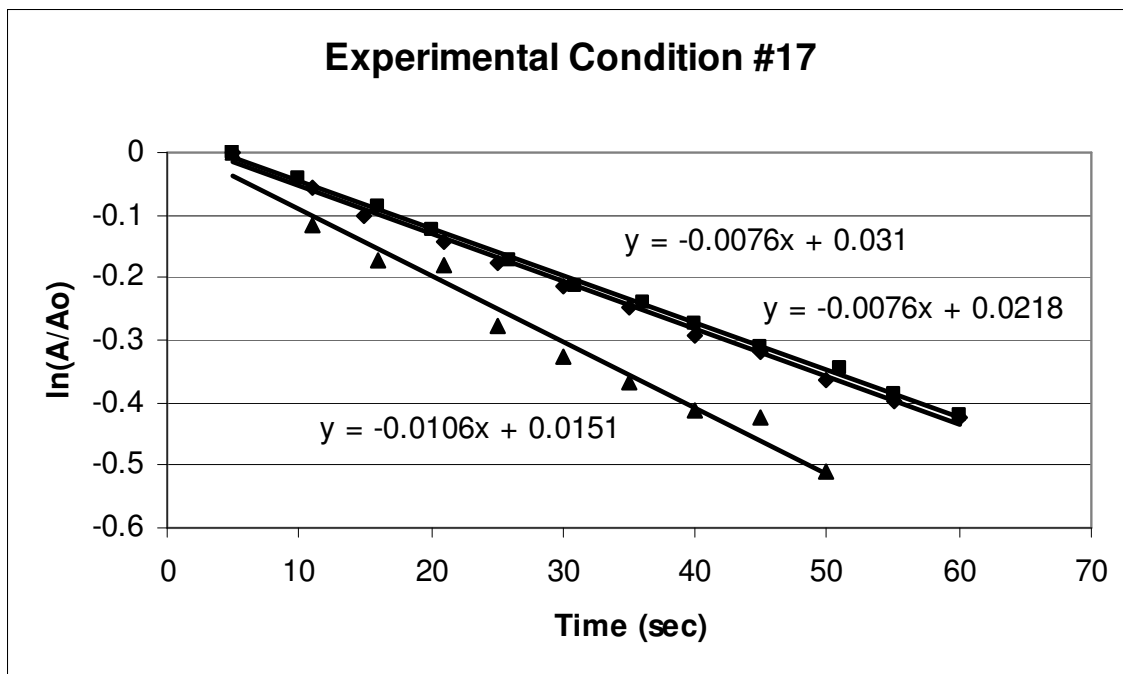
Supp. Figure 4.17 Experimental condition #17. $Cl^- = 316.4$ mM, $SO_4^{2-} = 16.4$ mM, $HCO_3^-/CO_3^{2-} = 1.41$, $F^- = 38.9$ μM, NOM = 21.3 mg/L, N = 3.

Experimental Condition #18

$y = -0.0078x + 0.0407$

$y = -0.0087x + 0.0347$

$y = -0.014x + 0.065$
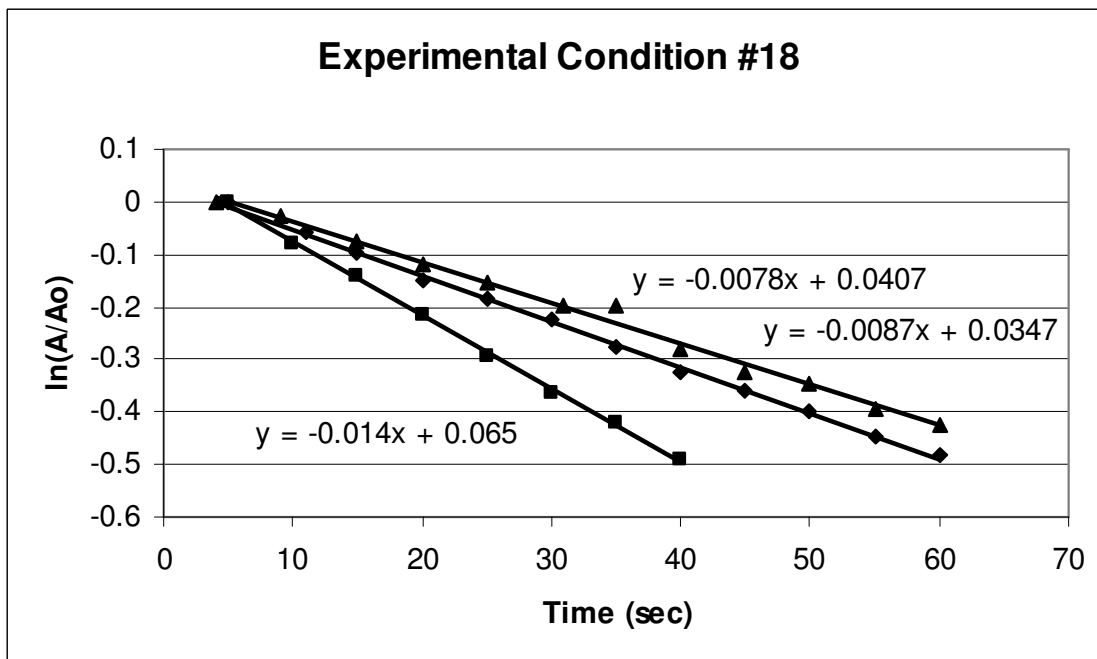
Supp. Figure 4.18 Experimental condition #18. $Cl^- = 777.5$ mM, $SO_4^{2-} = 16.4$ mM, $HCO_3^-/CO_3^{2-} = 1.41$, $F^- = 38.9$ μM, NOM = 21.3 mg/L, N = 3.

Experimental Condition #19

y = -0.0069x + 0.0353

y = -0.009x + 0.0414

y = -0.011x + 0.039

In(A/Ao)

Time (sec)
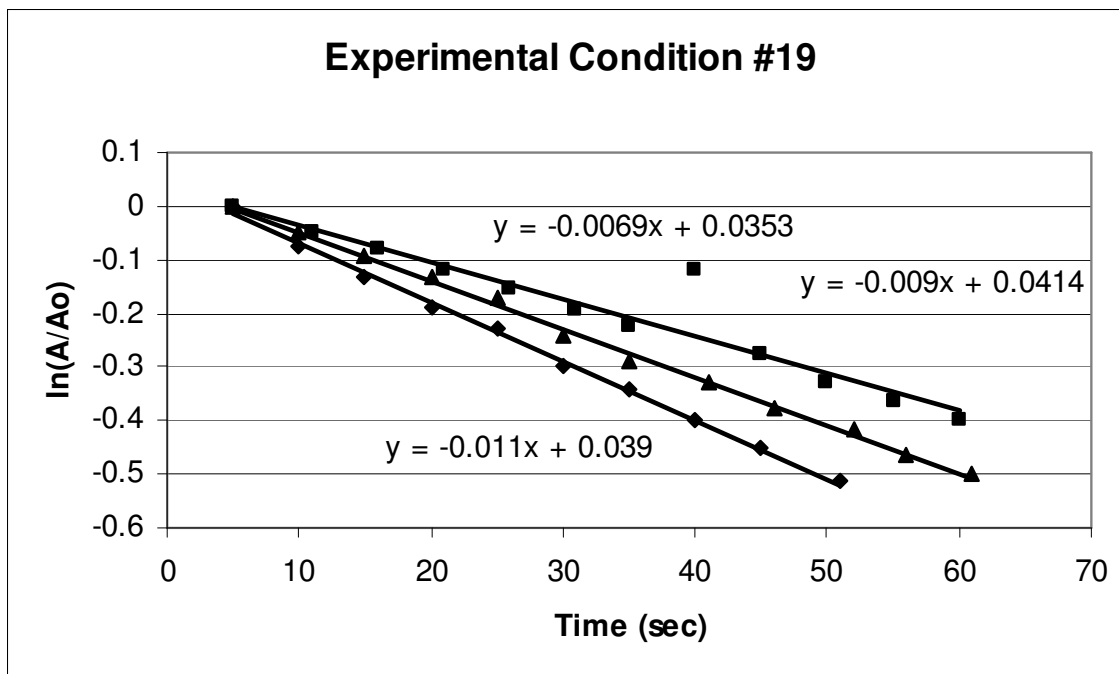
Supp. Figure 4.19 Experimental condition #19. $Cl^- = 316.4$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 1.41$, $F^- = 38.9$ μM, NOM = 21.3 mg/L, N = 3.

Experimental Condition #20

$y = -0.0088x + 0.0446$
$R^2 = 0.9995$

$y = -0.017x + 0.0904$
$R^2 = 0.9976$

$y = -0.0168x + 0.0875$
$R^2 = 0.9975$
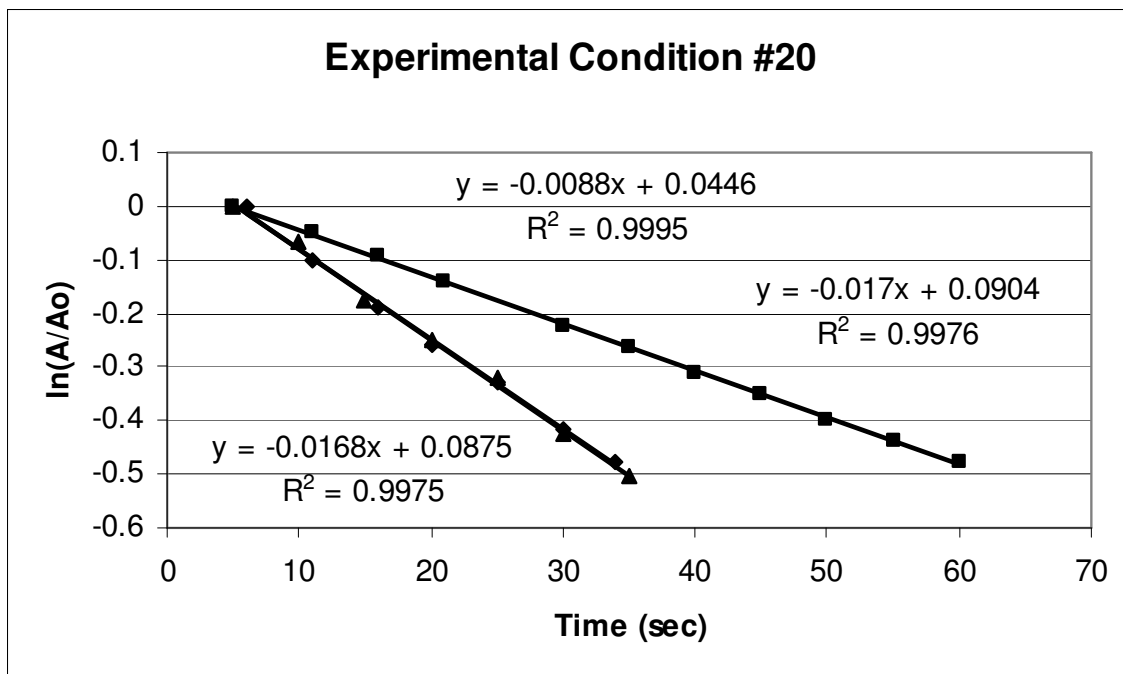
Supp. Figure 4.20 Experimental condition #20. $Cl^- = 777.5$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 1.41$, $F^- = 38.9$ μM, NOM = 21.3 mg/L, N = 3.

Experimental Condition #21

$y = -0.0161x + 0.0761$

$y = -0.023x + 0.1229$

$y = -0.0227x + 0.1113$
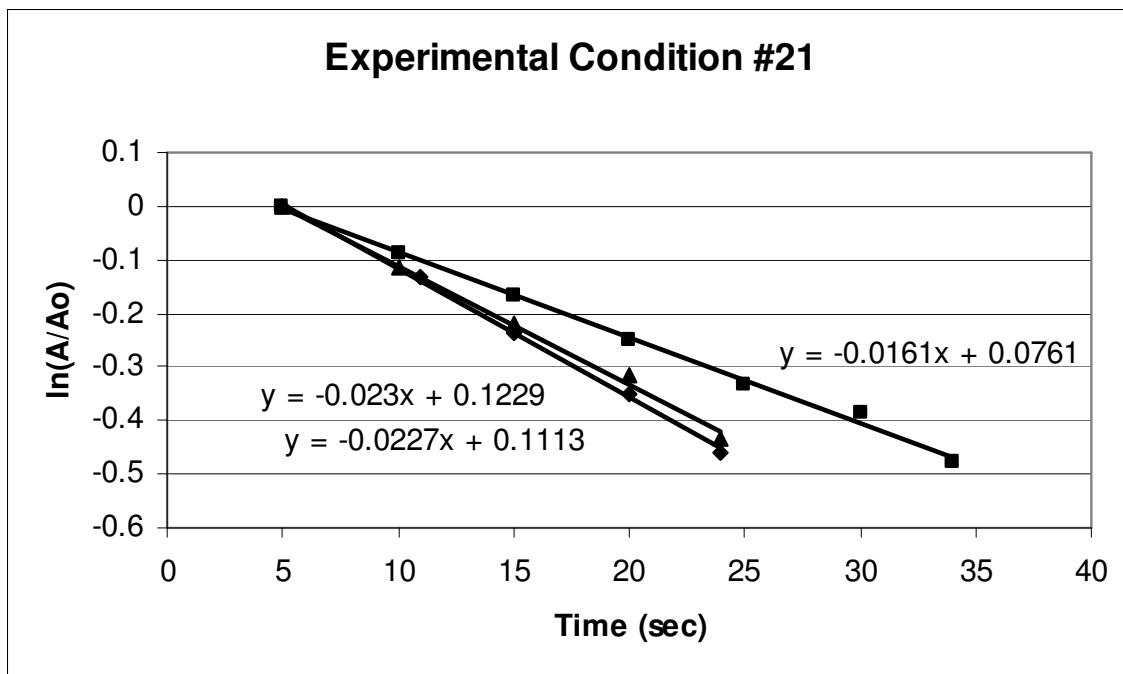
Supp. Figure 4.21 Experimental condition #21. $Cl^- = 316.4$ mM, $SO_4^{2-} = 16.4$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 38.9$ µM, NOM = 21.3 mg/L, N = 3.

Experimental Condition #22

y = -0.0207x + 0.1191

y = -0.0234x + 0.1421

y = -0.0356x + 0.1736
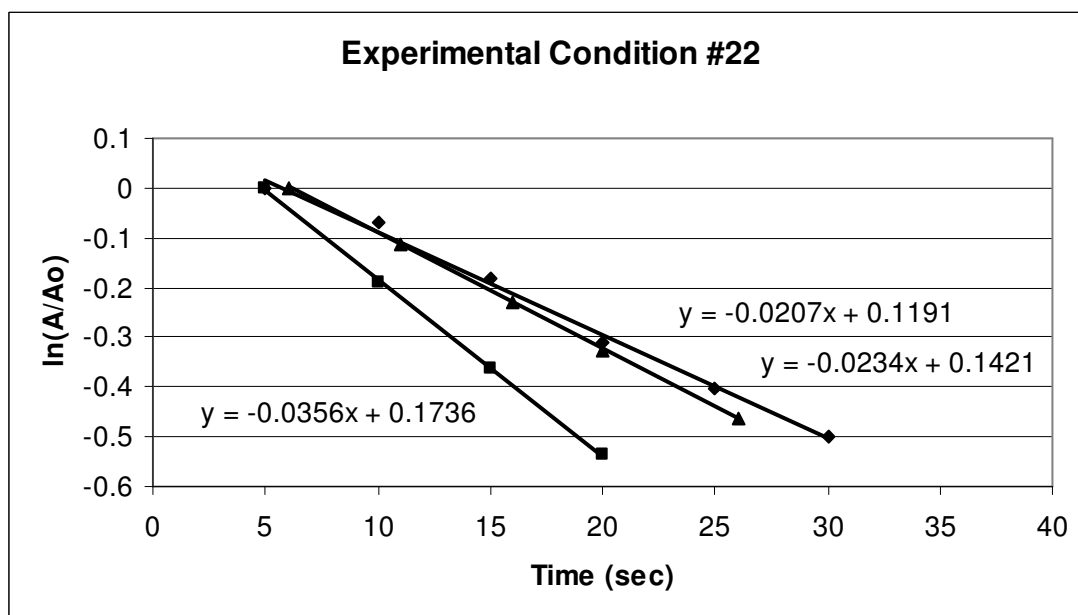
Supp. Figure 4.22 Experimental condition #22. $Cl^- = 777.5$ mM, $SO_4^{2-} = 16.4$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 38.9$ μM, NOM = 21.3 mg/L, N = 3.

Experimental Condition #23

$y = -0.0157x + 0.0848$

$y = -0.0254x + 0.1414$

$y = -0.029x + 0.1452$
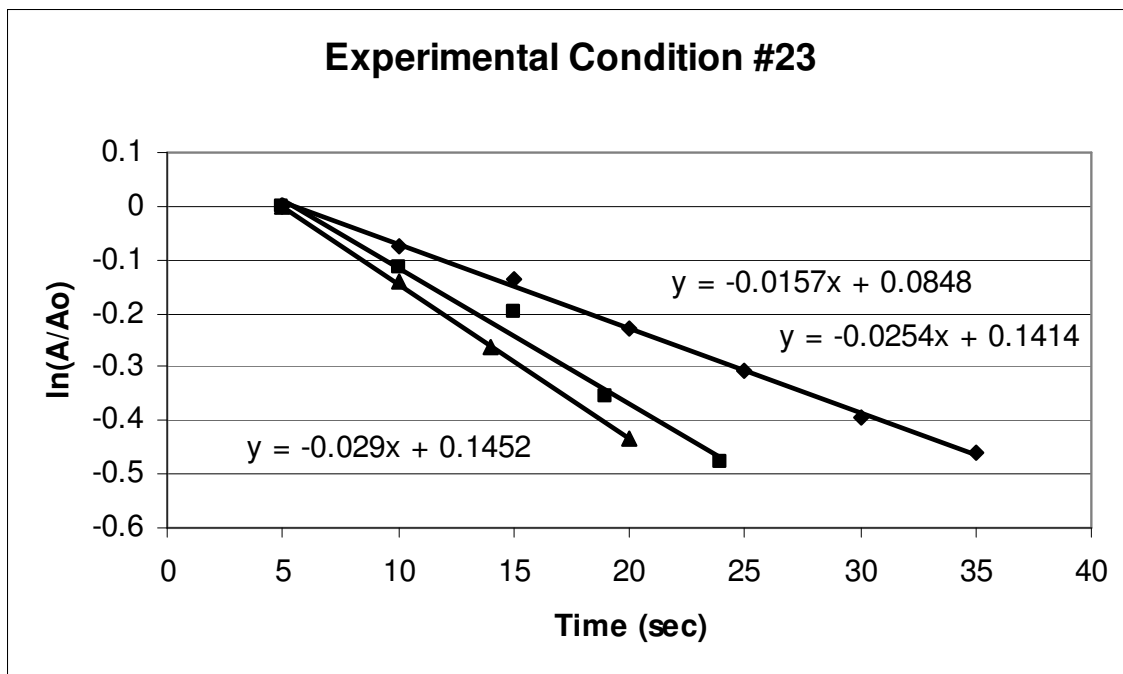
Supp. Figure 4.23 Experimental condition #23. $Cl^- = 316.4$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 38.9$ μM, NOM = 21.3 mg/L, N = 3.

Experimental Condition #24

$y = -0.0168x + 0.0855$

$y = -0.0186x + 0.0897$

$y = -0.0198x + 0.1076$
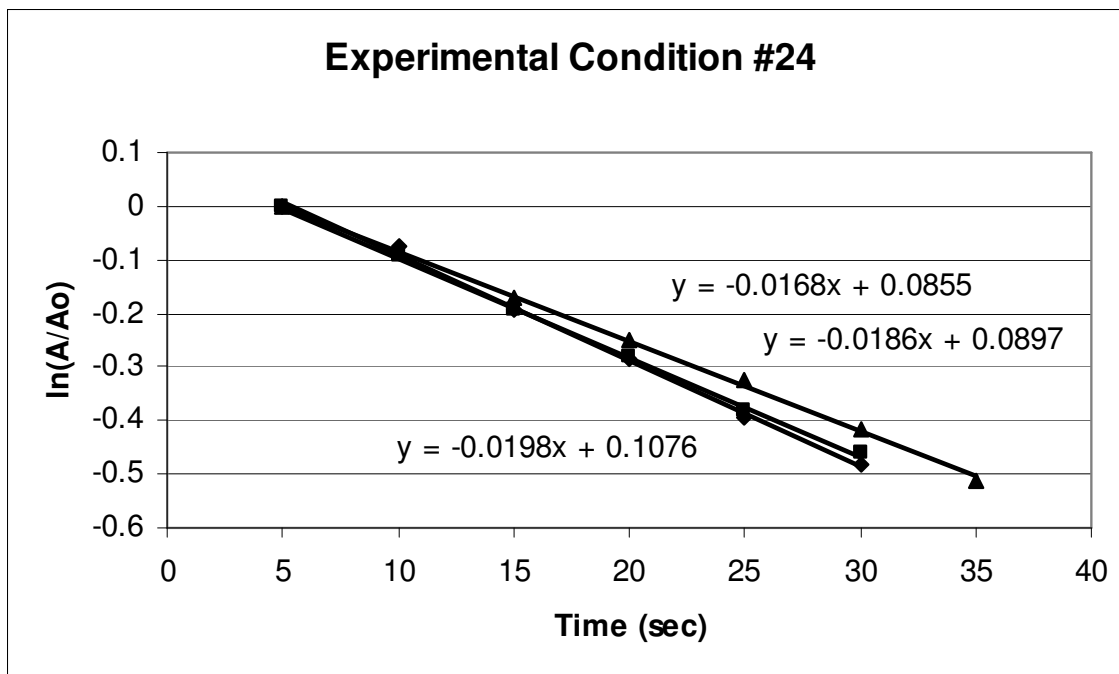
Supp. Figure 4.24 Experimental condition #24. $Cl^- = 777.5$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 38.9$ µM, NOM = 21.3 mg/L, N = 3.

Experimental Condition #25

$y = -0.0087x + 0.0023$

$y = -0.0123x + 0.0551$

$y = -0.0123x + 0.037$
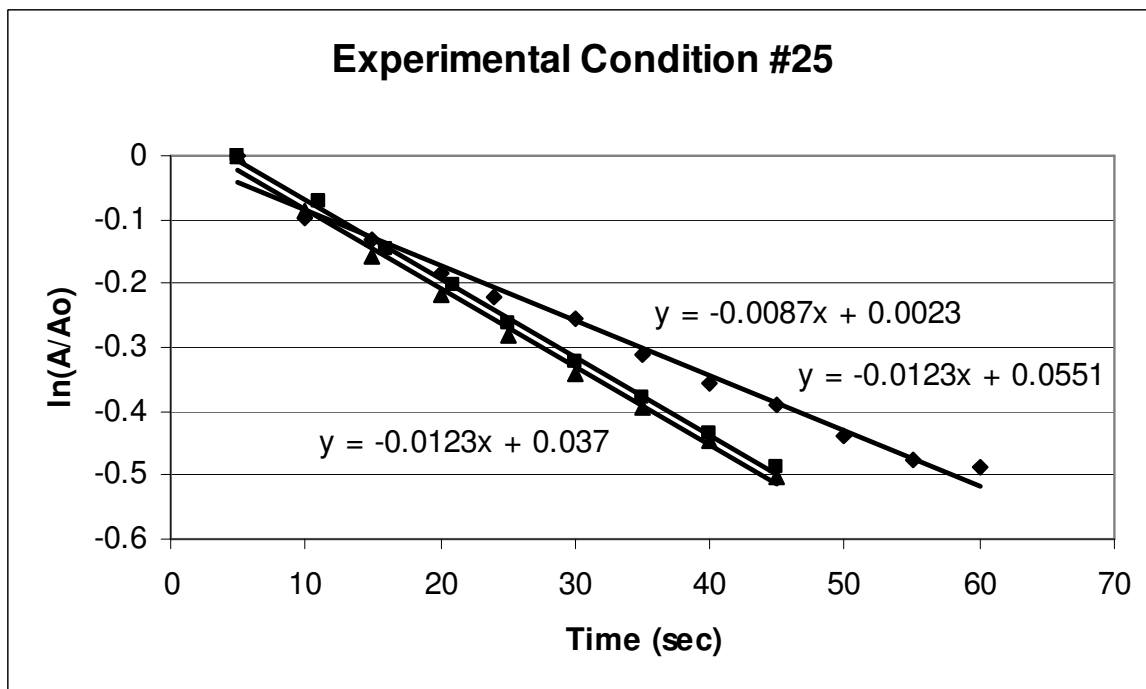
Supp. Figure 4.25 Experimental condition #25. $Cl^- = 316.4$ mM, $SO_4^{2-} = 16.4$ mM, $HCO_3^-/CO_3^{2-} = 1.41$, $F^- = 95.8$ µM, NOM = 21.3 mg/L, N = 3.
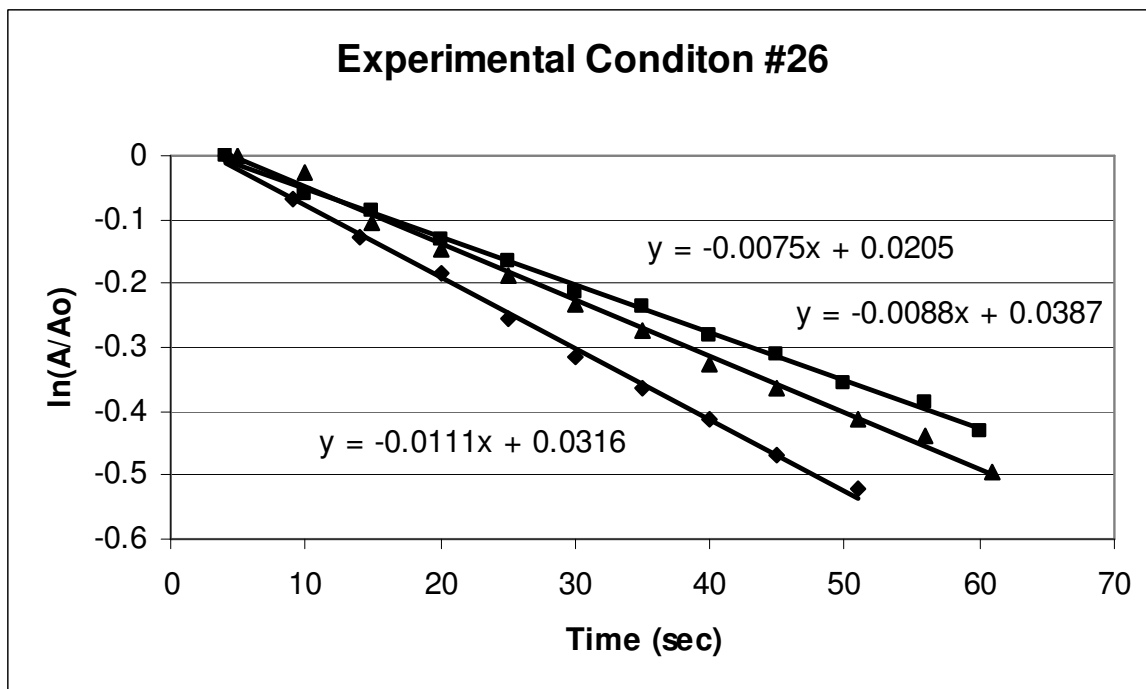
Supp. Figure 4.26 Experimental condition #26. $Cl^- = 777.5$ mM, $SO_4^{2-} = 16.4$ mM, $HCO_3^-/CO_3^{2-} = 1.41$, $F^- = 95.8$ μM, NOM = 21.3 mg/L, N = 3.

Experimental Condition #27

$y = -0.0068x + 0.0342$

$y = -0.0089x + 0.0456$

$y = -0.0099x + 0.0094$
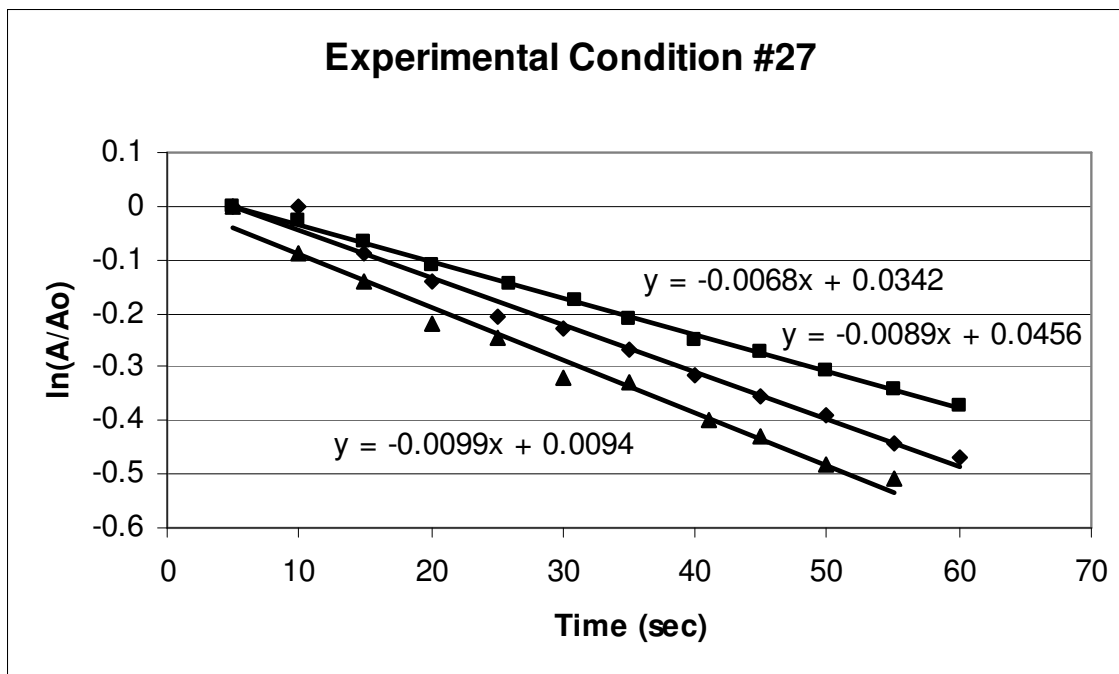
Supp. Figure 4.27 Experimental condition #27. $Cl^- = 316.4$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 1.41$, $F^- = 95.8$ µM, NOM = 21.3 mg/L, N = 3.

Experiment Condition #28

$y = -0.0073x + 0.0529$

$y = -0.0106x + 0.0432$

$y = -0.0124x + 0.0697$
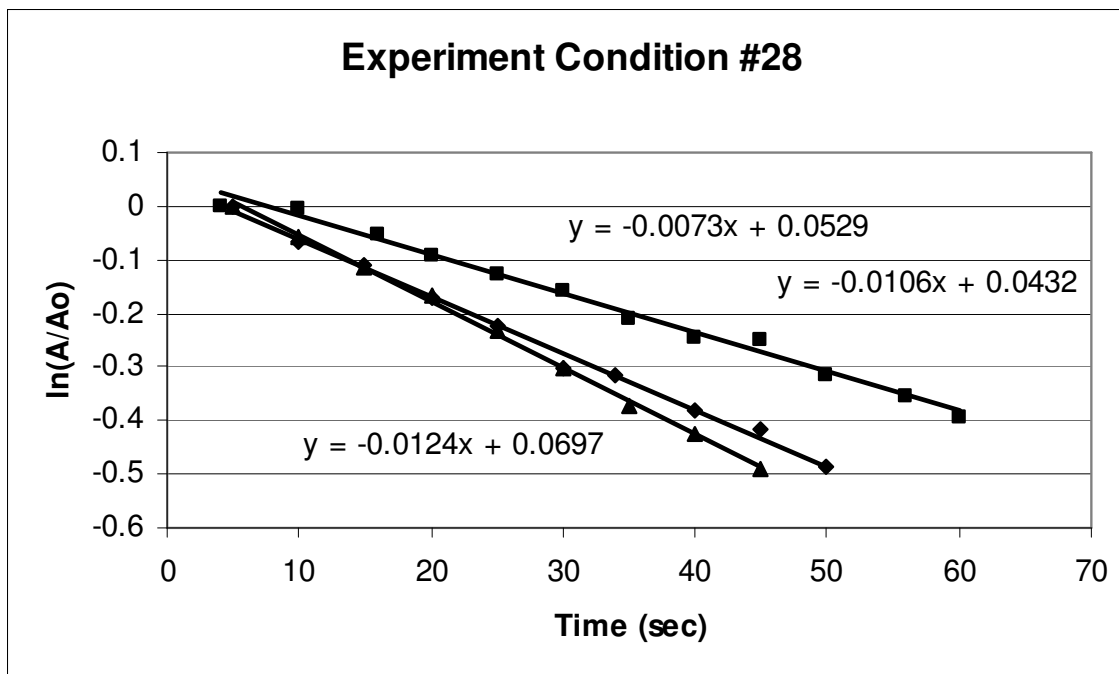
Supp. Figure 4.28 Experimental condition #28. $Cl^- = 777.5$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 1.41$, $F^- = 95.8$ μM, NOM = 21.3 mg/L, N = 3.

Experimental condition #29

$y = -0.0228x + 0.1144$

$y = -0.0288x + 0.1503$

$y = -0.0319x + 0.1831$
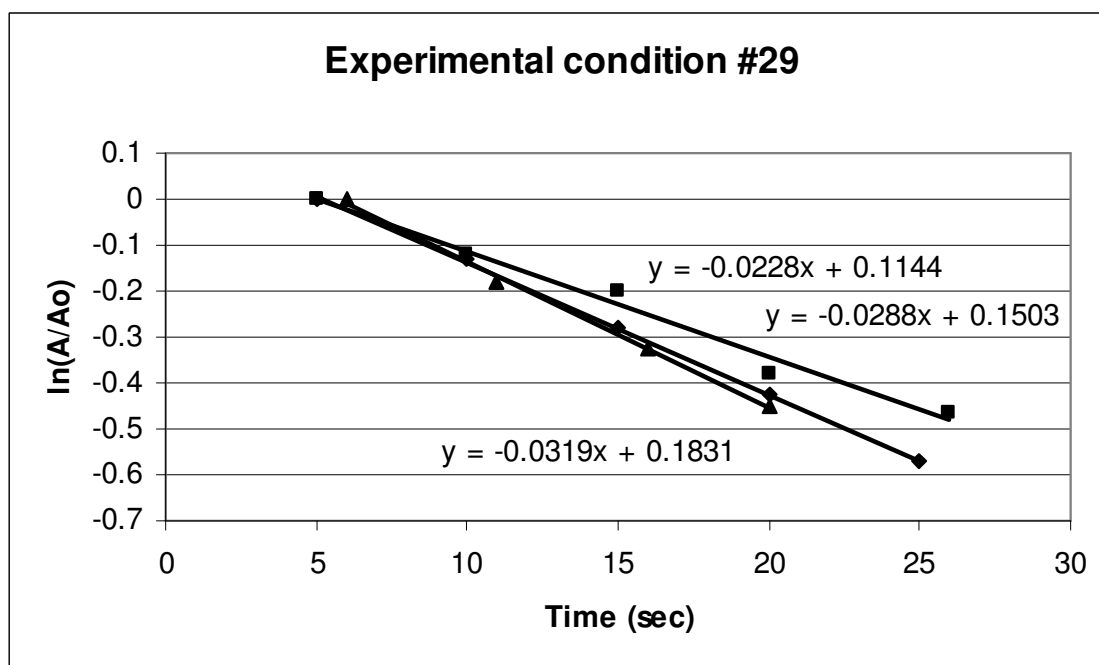
Supp. Figure 4.29 Experimental condition #29. $Cl^- = 316.4$ mM, $SO_4^{2-} = 16.4$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 95.8$ µM, NOM = 21.3 mg/L, N = 3.

Experimental Condition #30

$y = -0.0268x + 0.125$

$y = -0.0296x + 0.1577$

$y = -0.0345x + 0.1743$
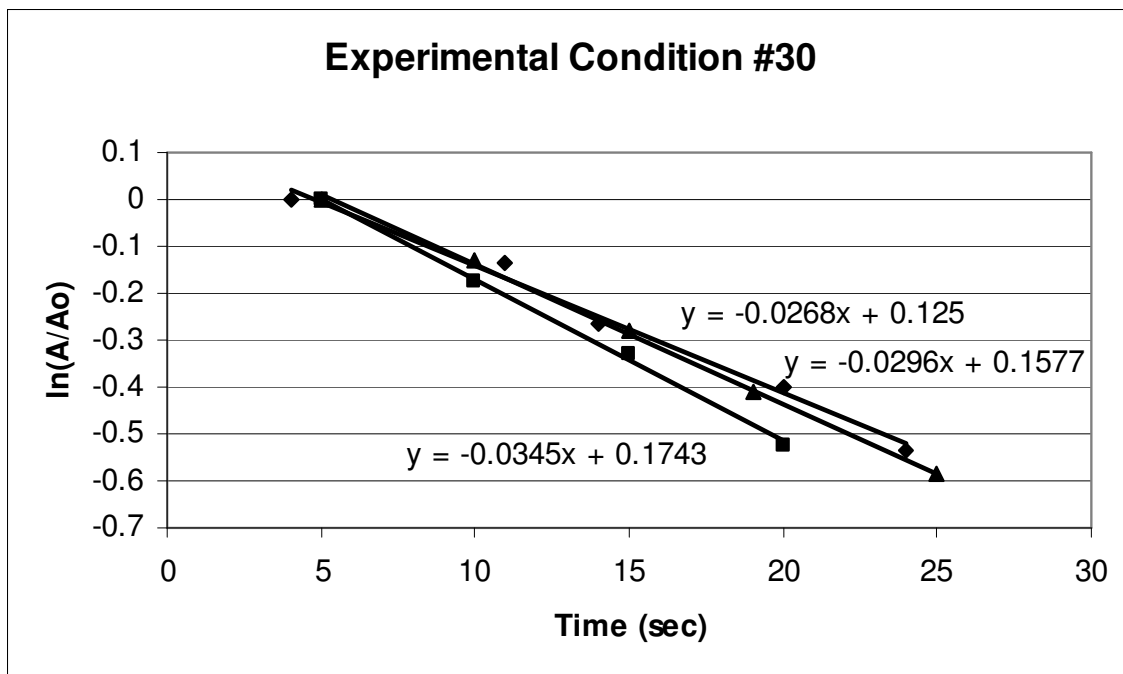
Supp. Figure 4.30 Experimental condition #30. $Cl^- = 777.5$ mM, $SO_4^{2-} = 16.4$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 95.8$ µM, NOM = 21.3 mg/L, N = 3.

Experimental Condition #31

Plot of $\ln(A/Ao)$ versus Time (sec):

$y = -0.0144x + 0.0893$

$y = -0.0219x + 0.1086$

$y = -0.0254x + 0.1071$
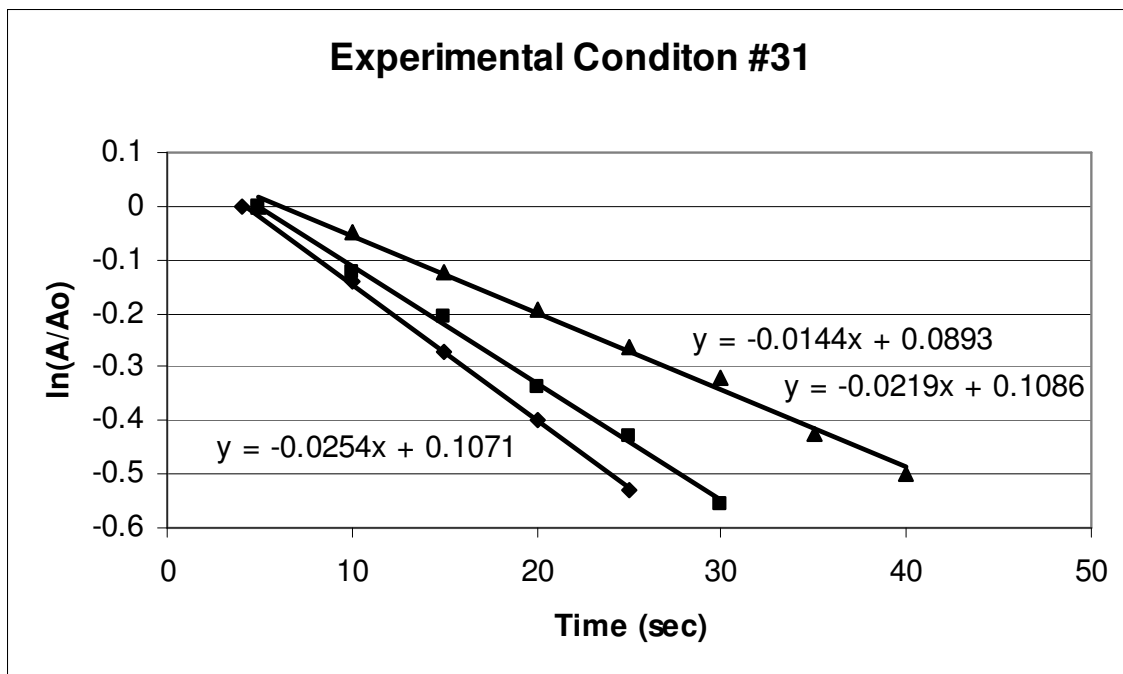
Supp. Figure 4.31 Experimental condition #31. $Cl^- = 316.4$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 95.8$ µM, NOM = 21.3 mg/L, N = 3.

Experimental Condition #32

$y = -0.0148x + 0.0743$
$R^2 = 0.9988$

$y = -0.0156x + 0.077$
$R^2 = 0.9864$

$y = -0.0184x + 0.0849$
$R^2 = 0.9991$
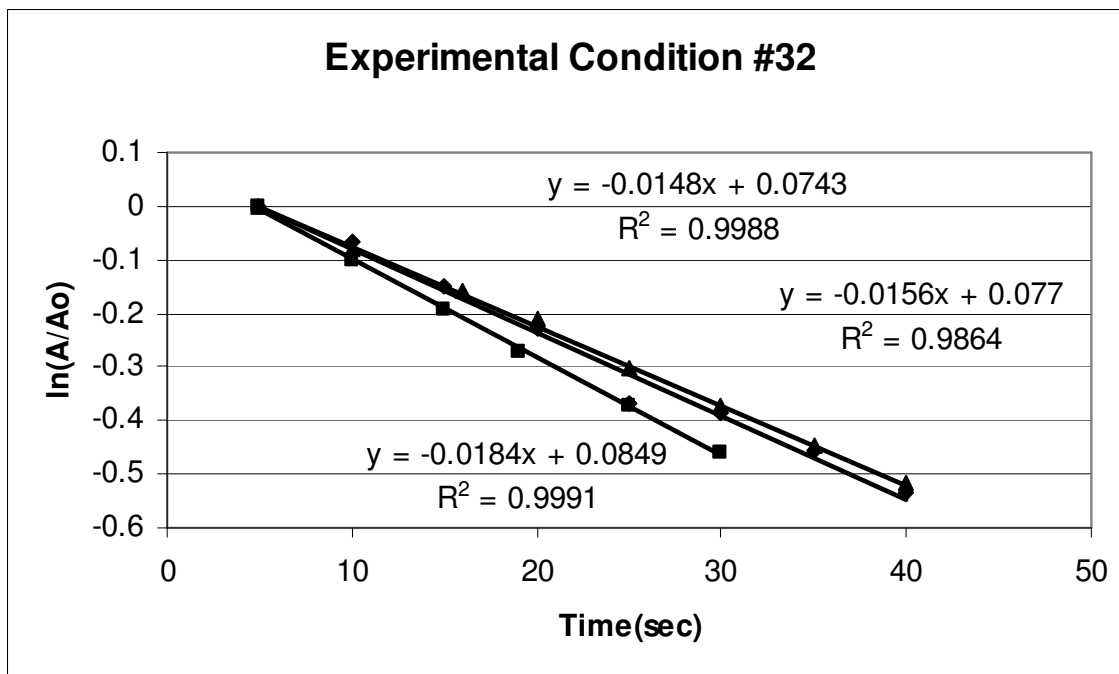
Supp. Figure 4.32 Experimental condition #32. $Cl^- = 777.5$ mM, $SO_4^{2-} = 40.1$ mM, $HCO_3^-/CO_3^{2-} = 3.14$, $F^- = 95.8$ µM, NOM = 21.3 mg/L, N = 3.

Experimental Conditon # 33

$y = -0.0105x + 0.0556$

$y = -0.0206x + 0.1038$

$y = -0.0204x + 0.1089$
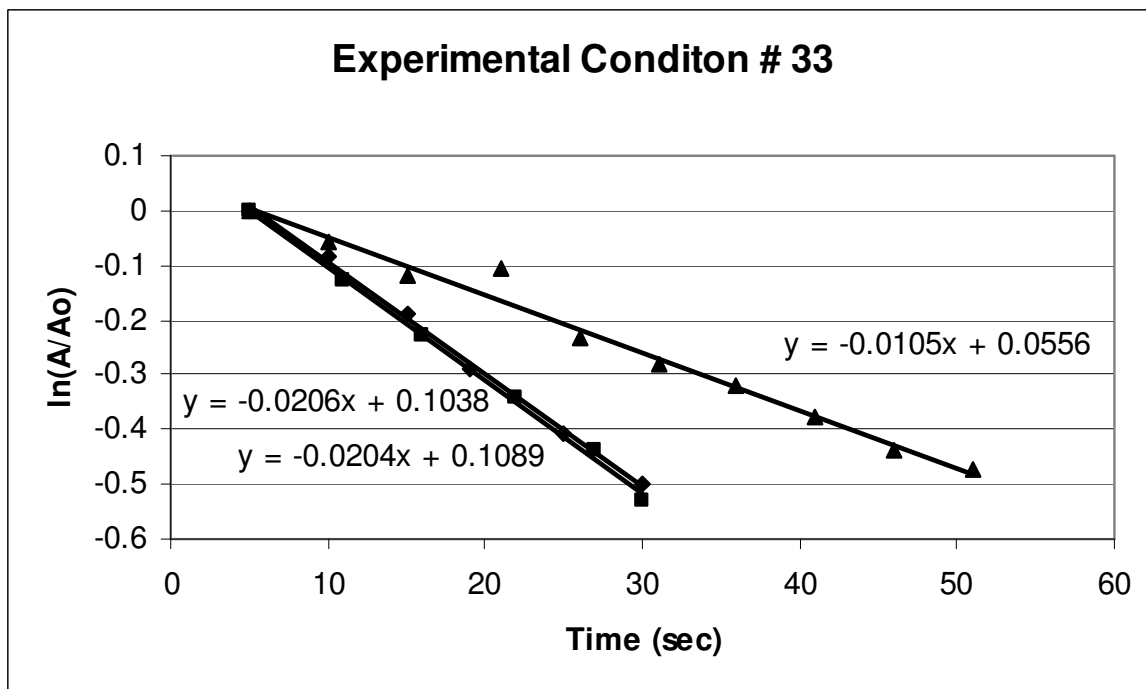
Supp. Figure 4.33 Experimental condition #33. $Cl^- = 0$ mM, $SO_4^{2-} = 28.2$ mM, HCO_3^- /$CO_3^{2-} = 2.28$, $F^- = 67.4$ µM, NOM = 15 mg/L, N = 3.
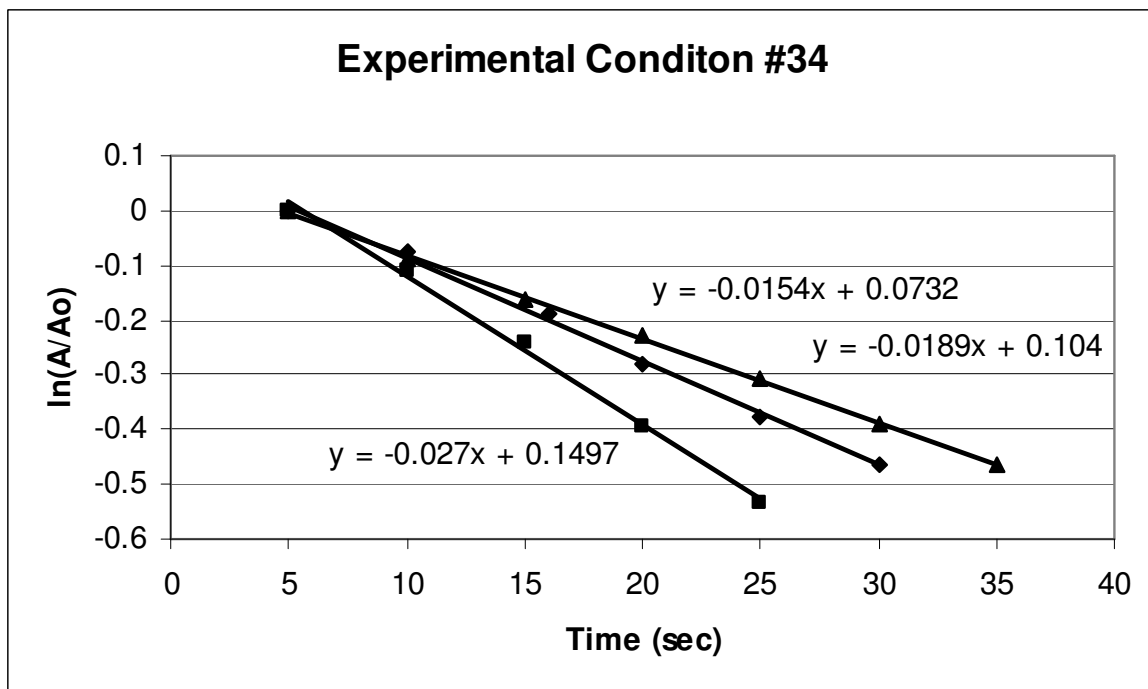
Supp. Figure 4.34 Experimental condition #34. $Cl^- = 1091.8$ mM, $SO_4^{2-} = 28.2$ mM, $HCO_3^-/CO_3^{2-} = 2.28$, $F^- = 67.4$ μM, NOM = 15 mg/L, N = 3.

Experimental Condition #35

$y = -0.0229x + 0.1168$

$y = -0.0266x + 0.1016$

$y = -0.0264x + 0.1274$
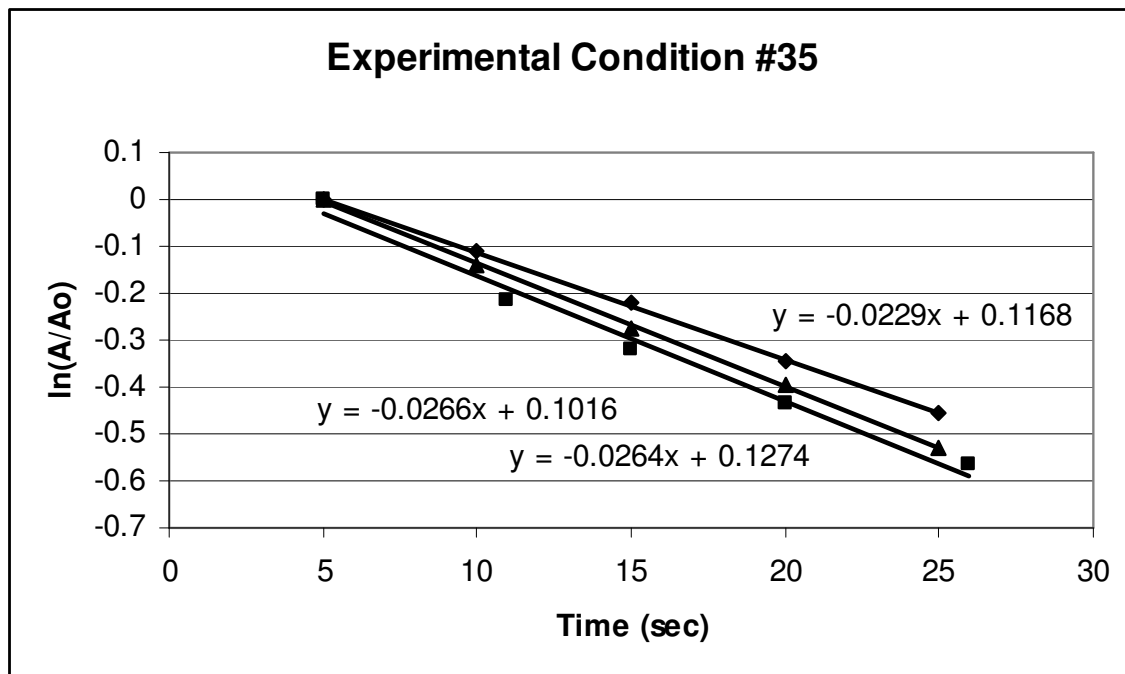
Supp. Figure 4.35 Experimental condition #35. $Cl^- = 545.9$ mM, $SO_4^{2-} = 0$ mM, $HCO_3^-/CO_3^{2-} = 2.28$, $F^- = 67.4$ μM, NOM = 15 mg/L, N = 3.

Experiemtal Conditon #36

$y = -0.0067x + 0.0203$
$R^2 = 0.9969$

$y = -0.0084x + 0.015$
$R^2 = 0.9876$

$y = -0.0117x + 0.0498$
$R^2 = 0.9958$
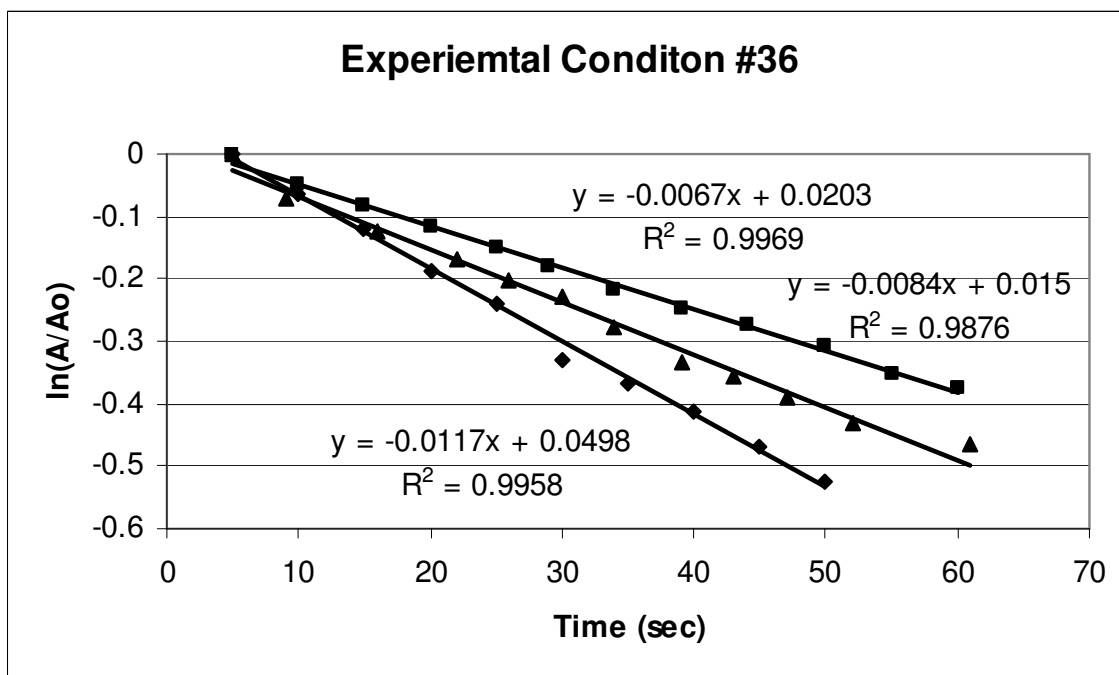
Supp. Figure 4.36 Experimental condition #36. $Cl^- = 545.9$ mM, $SO_4^{2-} = 56.4$ mM, $HCO_3^-/CO_3^{2-} = 2.28$, $F^- = 67.4$ µM, NOM = 15 mg/L, N = 3.

Experimental Condition #37

$y = -0.0008x + 0.0064$

$y = -0.0007x - 0.0102$

$y = -0.0013x - 0.0015$
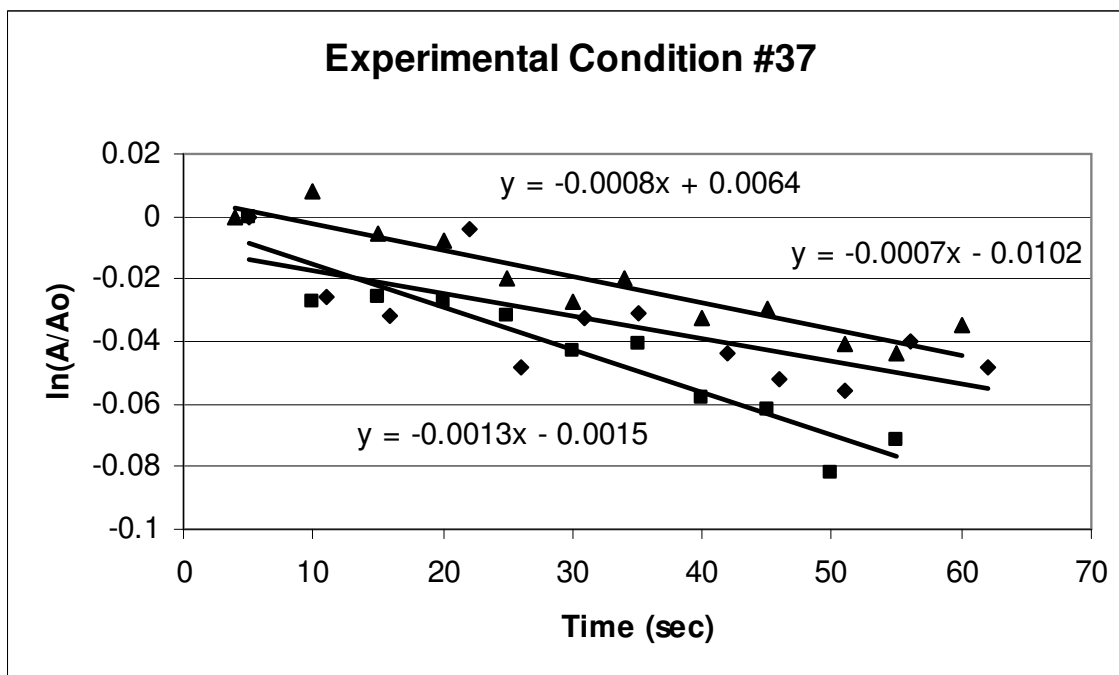
Supp. Figure 4.37 Experimental condition #37. $Cl^- = 545.9$ mM, $SO_4^{2-} = 28.2$ mM, $HCO_3^-/CO_3^{2-} = 0.21$, $F^- = 67.4$ µM, NOM = 15 mg/L, N = 3.

Experimental Condition #38

$y = -0.0286x + 0.1418$

$y = -0.0322x + 0.1547$

$y = -0.0326x + 0.1634$
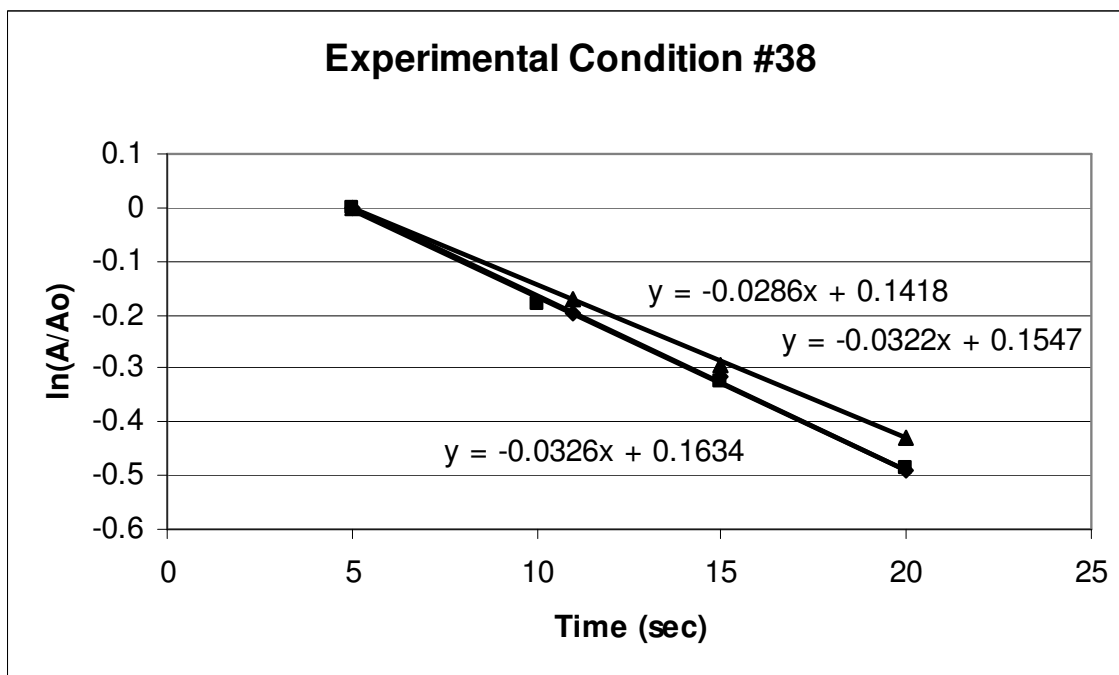
Supp. Figure 4.38 Experimental condition #38. $Cl^- = 545.9$ mM, $SO_4^{2-} = 28.2$ mM, $HCO_3^-/CO_3^{2-} = 4.34$, $F^- = 67.4$ µM, NOM = 15 mg/L, N = 3.
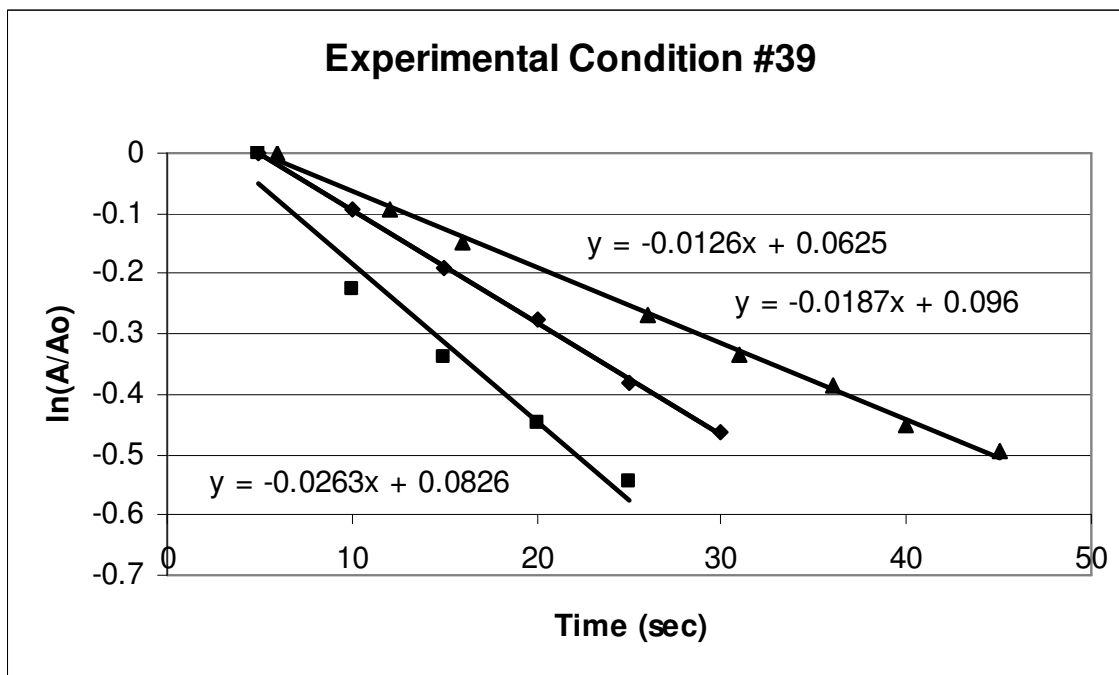
Supp. Figure 4.39 Experimental condition #39. $Cl^- = 545.9$ mM, $SO_4^{2-} = 28.2$ mM, $HCO_3^-/CO_3^{2-} = 2.28$, $F^- = 0$ µM, NOM = 15 mg/L, N = 3.

Experimental Conditon #40

y = -0.0113x + 0.0569

y = -0.012x + 0.0632

y = -0.0133x + 0.0671

ln(A/Ao) vs Time (sec)
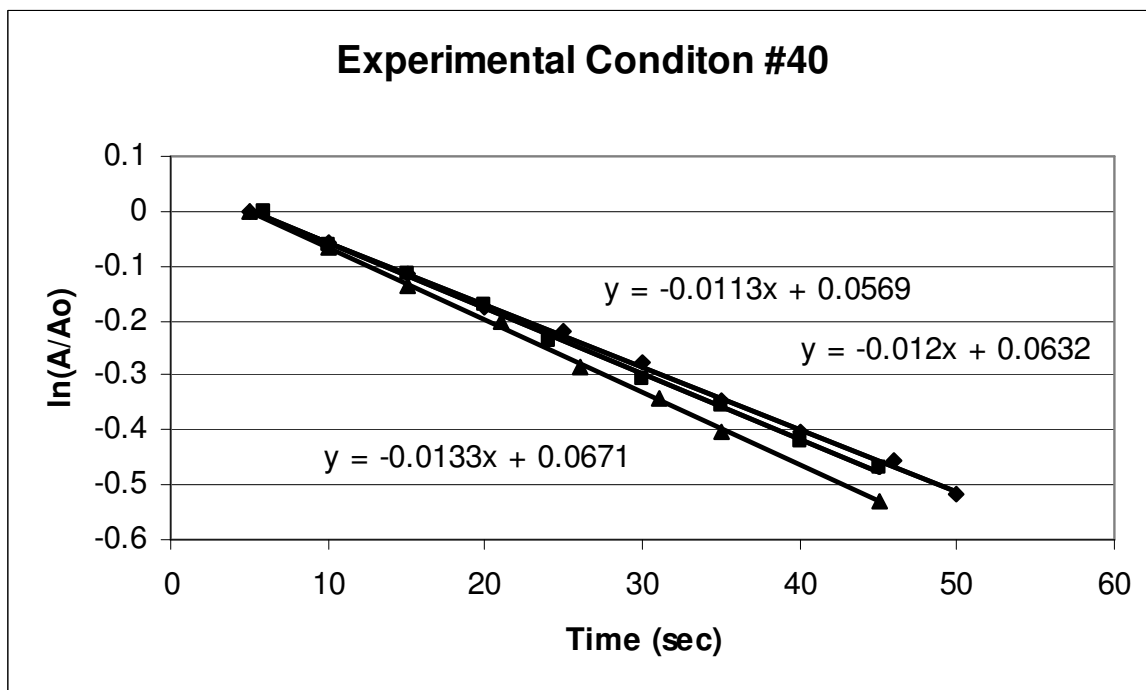
Supp. Figure 4.40 Experimental condition #40. $Cl^- = 545.9$ mM, $SO_4^{2-} = 28.2$ mM, $HCO_3^-/CO_3^{2-} = 2.28$, $F^- = 134.8$ µM, NOM = 15 mg/L, N = 3.
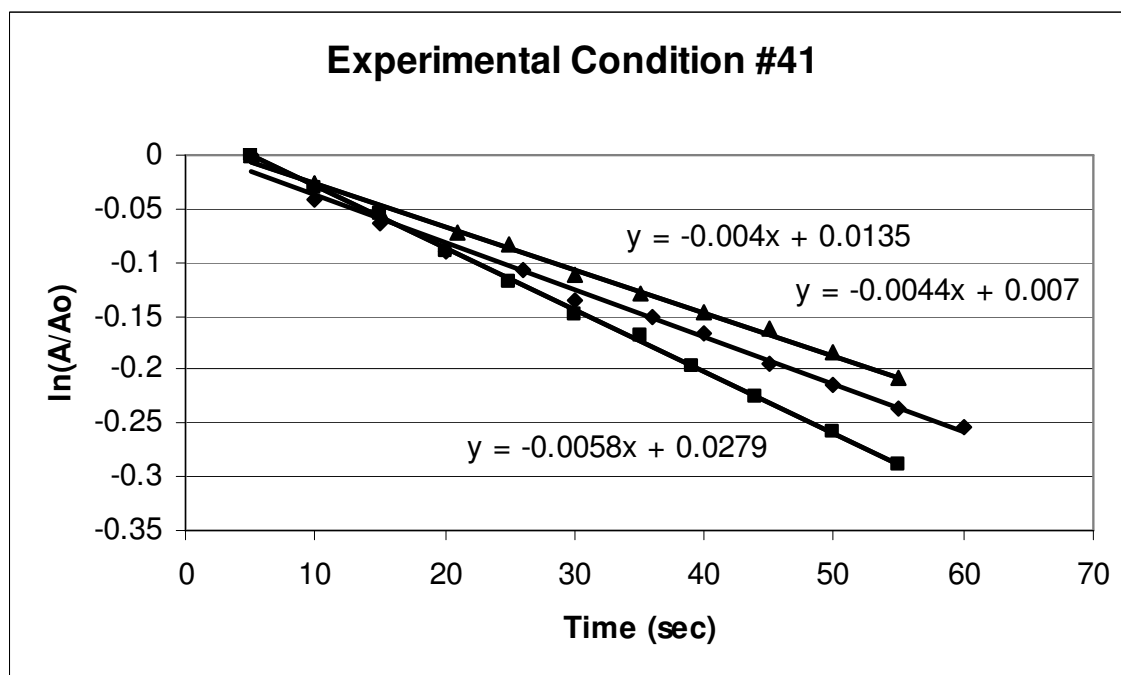
Supp. Figure 4.41 Experimental condition #41. $Cl^- = 545.9$ mM, $SO_4^{2-} = 28.2$ mM, $HCO_3^-/CO_3^{2-} = 2.28$, $F^- = 67.4$ μM, NOM = 0 mg/L, N = 3.

Experimental Condition #42

$y = -0.0164x + 0.0773$

$y = -0.0213x + 0.0976$

$y = -0.0217x + 0.1129$
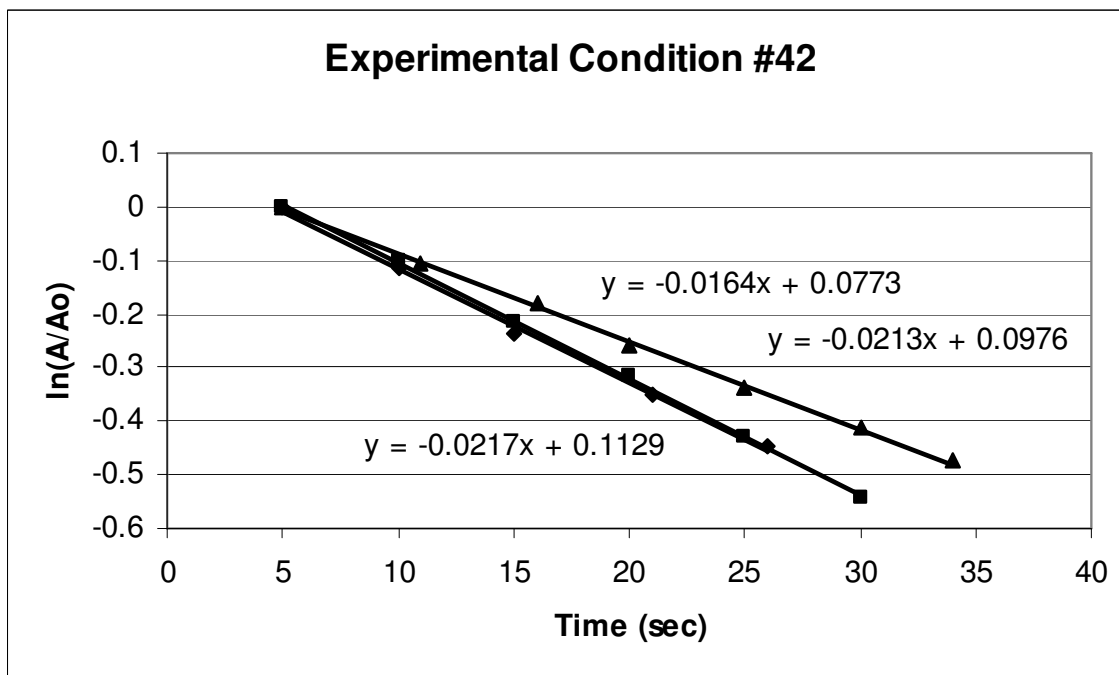
Supp. Figure 4.42 Experimental condition #42. $Cl^- = 545.9$ mM, $SO_4^{2-} = 28.2$ mM, $HCO_3^-/CO_3^{2-} = 2.28$, $F^- = 67.4$ µM, NOM = 30 mg/L, N = 3.

Experimental Condition #43

$y = -0.0115x + 0.0578$

$y = -0.0147x + 0.0665$

$y = -0.0189x + 0.0946$

$y = -0.0155x + 0.0307$

$y = -0.0181x + 0.0813$

$y = -0.0178x + 0.0691$
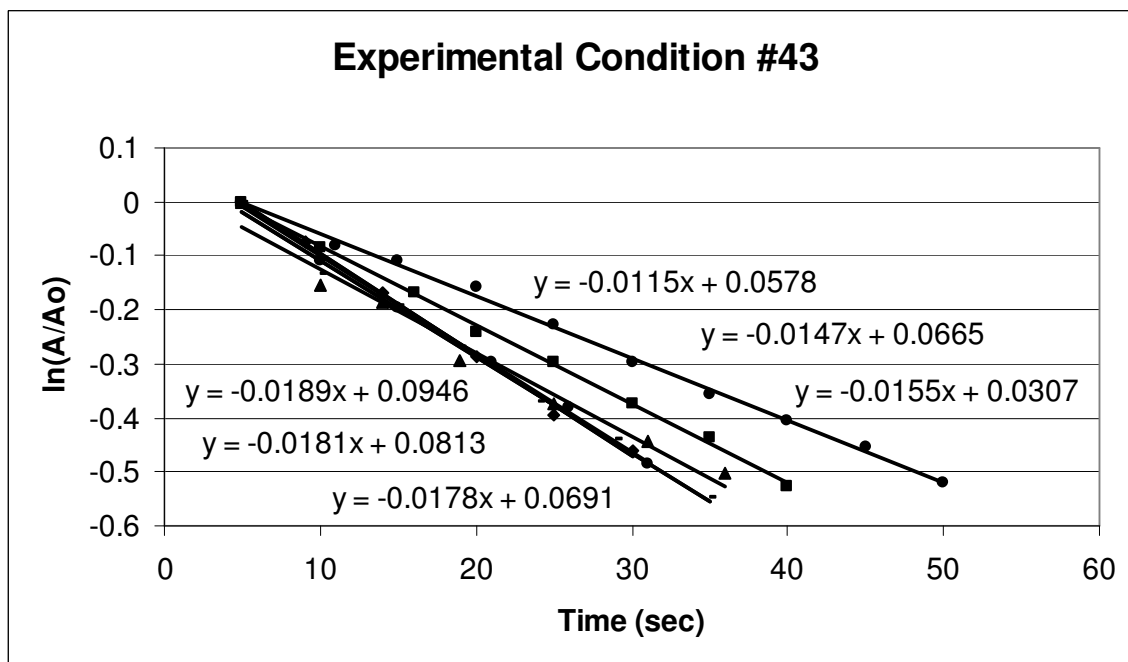
Supp. Figure 4.43 Experimental condition #43. $Cl^- = 545.9$ mM, $SO_4^{2-} = 28.2$ mM, $HCO_3^-/CO_3^{2-} = 2.28$, $F^- = 67.4$ μM, NOM = 15 mg/L, N = 6.

Description of Organic Matter Sources and Isolation

Isolation procedure of Humic and Fulvic acids supplied by the IHSS (Courtesy of the International Humic Substances Society)

Adapted from: Aiken, G.R. (1985) "Isolation and concentration techniques for aquatic humic substances", in G.R. Aiken, D.M. McKnight, R.L. Wershaw, and P. MacCarthy (Eds.), *Humic substances in soil, sediment and water: geochemistry and isolation*. Wiley-Interscience, New York

1. Filter water with a 0.45 µm silver or polymer membrane filter.
2. Lower pH to 2.0 with HCl.
3. Pass sample through column of XAD-8 resin to retain humic and fulvic acids. The preparative cleaning of the resin is described by Thurman and Malcolm (1981).
4. Elute HA and FA from the column with 0.1 M NaOH, in the reverse direction. Acidify immediately with HCl to avoid oxidation of humic substances.
5. Re-concentrate on a smaller XAD-8 column. Elute with NaOH and acidify. The eluted DOC should contain more that 500 mg C/L.
6. Adjust pH to 1.0 with HCl. Centrifuge to separate the humic acid (HA) from the fulvic acid (FA) fraction. Wash HA with water until wash is negative to the $AgNO_3$ test for chloride. Add sufficient 0.1 M NaOH to dissolve HA and then acidify by passing through a strong acid resin column.
7. Adjust FA fraction to pH 2.0 with NaOH and re-adsorb FA fraction on XAD-8. Wash with one void volume of distilled water to remove the salt.
8. Reverse flow and elute column with 0.1 M NaOH.
9. Immediately pass FA eluate through cation-exchange resin and hydrogen saturate. Pass HA in 0.1 M NaOH through cation-exchange resin and hydrogen saturate. Repeat until Na^+ is less than 1 mg/L.
10. Freeze dry HA and FA samples.

REFERENCE

Thurman, E.M., and R.L. Malcolm. 1981. Preparative isolation of aquatic humic substances. *Environ. Sci. Technol.* **15**:463-466.

Location and isolation method information for Suwannee river NOM (Courtesy of the International Humic Substances Society)

IHSS has recently used reverse osmosis to isolate more than 1000g of natural organic matter (NOM) from the Suwannee River. The sample was collected from the same site that was used originally to collect the standard Suwannee River humic and fulvic acids. The new NOM sample is now available from the IHSS for $20 per 100mg. The elemental composition of dry Suwannee River NOM is: 48.8 %C; 3.9 %H; 39.7 %O; 1.02 %N; 0.60 %S; 0.02 %P; 7.0 %Ash (Total 101.0%). A brief description of the sampling trip and isolation procedure follows.

From May 1 through May 9, 1999, a group representing the International Humic Substances Society (IHSS) visited the Suwannee River in south Georgia, U.S.A. to collect a new reference sample of natural organic matter (NOM). This reference NOM sample will complement the standard and reference humic and fulvic acids that were previously collected from the Suwannee River. The members of this group included Dr. James Alberts and Dr. Monika Takács of the University of Georgia Marine Institute at Sapelo Island and Dr. Michael Perdue and Ms. Lili Ding of the School of Earth and Atmospheric Sciences at the Georgia Institute of Technology.

The sample was collected at the first dam on the Suwannee River sill, on the southwestern edge of the Okefenokee Swamp near Fargo, GA. The project was authorized by the Board of Directors of IHSS, and access to the sill was granted by the Okefenokee National Wildlife Refuge in Folkston, GA. During the nine-day project, 33 concentrated samples were collected. For each sample, a 120-gallon aliquot of Suwannee River water was prefiltered successively through 1 µm and 0.4 µm polypropylene filters and concentrated to about six gallons using a RealSoft PROS/2S portable reverse osmosis system. After a concenrated sample was obtained, its temperature was maintained at or below the temperature of the river. Overall, 3960 gallons of water (about 14,990 liters) were concentrated to a final volume of 199 gallons (about 753 liters).

Because the chemical composition of the Suwannee River was expected to vary during the time required to collect the entire sample, a volume-weighted composite sample of the prefiltered Suwannee River water was prepared by collecting and combining 10-mL aliquots at periodic intervals (every 40 gallons). The composite sample, which was stored on ice at all times, had a pH of 3.93 and a TOC concentration of 39.2 mg/L (3.27 mmol/L).

While a sample was being concentrated, it was circulated continuously through a cation exchange resin (H^+-form) to remove most major cations. The "field-desalted" concentrated samples had pH values of 2.8 ± 0.1, well below the average pH of 3.93 for the prefiltered water. During the operation of the reverse osmosis system, the permeate flow rate gradually decreased due to adsorption of organic matter on the reverse osmosis membranes. At the low pH values of the concentrated samples, the adsorbed organic matter was probably enriched in humic acids. To recover this organic matter and to increase the permeate flow rate, a single 12-liter solution of 0.01 M NaOH was used on three occasions (about once every three days) to rinse the reverse osmosis membranes. Its final pH was about 6.5.

The samples were transported to Dr. Perdue's laboratory at Georgia Tech on May 10, 1999. In the laboratory, the reverse osmosis membranes were rinsed a final time with 10 liters of 0.01 M NaOH to recover some additional adsorbed organic matter. The two

NaOH rinse solutions were desalted using a cation exchange resin (H+-form) and then mixed into the other 33 concentrated samples. The concentrated samples were then desalted for a final time, using 250-ml columns of cation exchange resin (H+-form) at a flow rate of about 100 ml/min. A volume-weighted composite sample was prepared from the desalted, concentrated samples. Its pH was 2.54 and its TOC concentration was 725 mg/L (60.4 mmol/L). From the volumes and TOC concentrations of the prefiltered water and the final concentrated samples, the percent recovery of organic carbon was calculated to be 92.9%.

During the three weeks that the samples were being processed in Dr. Perdue's laboratory at Georgia Tech, they were stored in a cold room at 4-6 °C. For two days, while the cold room was not operational, the samples were cooled with ice.

On May 31, the 31 carboys of desalted, concentrated samples were shipped by truck to Van Drunen Farms in Momence, IL, where they were stored in a cold room until an IHSS representative could arrive to supervise the freeze-drying process. Finally, on June 7-9, the samples were freeze-dried under the supervision of Dr. Perdue. Approximately 1060 g of freeze-dried natural organic matter was obtained. The freeze-dried product was transferred back to Georgia Tech for pulverization, homogenization, and final drying.

Location and isolation method information for Nordic reservoir NOM (Courtesy of the International Humic Substances Society)

This sample was obtained from a drinking water reservoir at Vallsjøen, Skarnes, Norway on October 29 to November 3, 1997 under the direction of Egil Gjessing. The reservoir is at 225 m above sea level and has a maximum depth of depth of about 14 m. The sample was obtained from the Sør-Odal County Waterworks intake pipe that draws water from at depth of 10m (pH = 5.6, EC = 2.1 mS/m and DOC = 10.7 mg/L). The water temperature was 4o C.
The initial concentration was done using a RealSoft PROS/2S portable reverse osmosis system (Serkiz & Perdue). The water was first pumped through a sodium saturated Dowex -50 cation exchanger. No filtration was used. The permeate was discarded and the retentate was recirculated back to the sample reservoir. For every 1 m3 of water isolated, the RO membrane and the cation exchanger were back washed with 0.006 M NaOH.
The resulting 130 L of RO-isolate was concentrated further by roto evaporation. The temperature of the concentrate did not at any time exceed 25o C during this low-pressure evaporation. The remaining 10 L of concentrate containing about 250 mg of C was filtered under 7 atmospheres of pressure through 142 mm Sartorius membrane filters with nominal pore size of 0.45 µm. The filtered concentrate was freeze dried.
The Nordic Chapter of the IHSS distributed the Nordic NOM sample until 2001 when it became part of the IHSS collection.
Reference:
Serkiz, S.M. and Perdue, E.M. (1990) Isolation of dissolved organic matter from Suwannee River using reverse osmosis. *Water Res.* **24**, 911 - 916.