Supporting Information for

Impact of Pahokee Peat Humic Acid and Buffer Identity on Goethite Aggregation and Reactivity

Environmental Science: Nano

Amanda M. Vindedahl[1], William A. Arnold[2], and R. Lee Penn[1*]

[1]Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455-0431

[2]Department of Civil, Environmental, and Geo-Engineering, University of Minnesota, 500 Pillsbury Dr. SE, Minneapolis, MN 55455-0116

Publication Date

Section S1: Synthetic Goethite Characterization by X-ray Diffraction

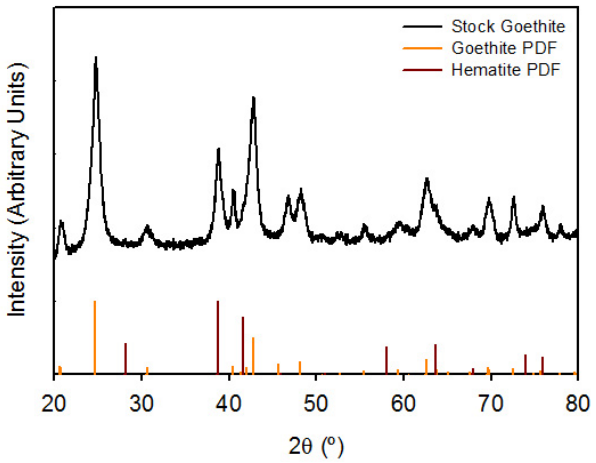

Figure S1: XRD pattern of the pre-reaction goethite suspension and PDF stick patterns of goethite (orange, #29-0713) and hematite (dark red, #33-0664).

Section S2: Reactor Preparation Conditions

Table S1: Average goethite nanoparticle aggregate size and rate of 4-ClNB degradation with varying equilibrium

Equilibration Time	**4-ClNB Degradation Rate (min^{-1})[a]**		**Average Goethite Aggregate Size (nm)[b]**	
	Fe(II)/PPHA	PPHA/Fe(II)	Fe(II)/PPHA	PPHA/Fe(II)
0 s	0.0344 ± 0.0018		2900 ± 1600	
20 s	0.0223 ± 0.0020	0.0299 ± 0.0023	2800 ± 2100	4500 ± 2300
21 h	0.0273 ± 0.0009	0.0358 ± 0.0040	3200 ± 3200	2800 ± 2200

[a]Errors represent 95% confidence intervals of triplicate trials
[b]Errors represent standard deviation of duplicate trials of 18 measurements

Statistical Analysis: t-test Results

4-ClNB Degradation Rates

Table S2: Statistical analysis of 4-ClNB degradation rates under each of the reactor preparation conditions. T-tests were calculated assuming equal variances. Abbreviations used: equilibration time (Equil. Time); observations (Obs); hypothesized mean difference (Hypoth. Mean Diff.).

Equil. Time	Order of Addition	Mean k (min^{-1})	Variance	Obs	Pooled Variance	Hypoth. Mean Diff.	df	t Stat	P(T<=t) one-tail	t Critical one-tail	P (T<=t) two-tail	t Critical two-tail
0s	NA	0.0344	0.000292	3	0.000186	0	4	1.09	0.169	2.13	0.338	2.78
20s	Fe(II), PPHA	0.0223	8.04E-5	3								
0s	NA	0.0344	0.000292	3	0.000391	0	4	0.279	0.397	2.13	0.794	2.78
20s	PPHA, Fe(II)	0.0299	0.000489	3								
0s	NA	0.0344	0.000292	3	0.000292	0	4	0.509	0.319	2.13	0.638	2.78
21h	Fe(II), PPHA	0.0273	0.000293	3								
0s	NA	0.0344	0.000292	3	0.000539	0	4	0.0774	0.471	2.13	0.942	2.78
21h	PPHA, Fe(II)	0.0358	0.000786	3								
20s	Fe(II), PPHA	0.0223	8.04E-5	3	0.000285	0	4	0.551	0.305	2.13	0.611	2.78
20s	PPHA, Fe(II)	0.0299	0.000489	3								
20s	Fe(II), PPHA	0.0223	8.04E-5	3	0.000186	0	4	0.448	0.339	2.13	0.677	2.78
21h	Fe(II), PPHA	0.0273	0.000293	3								
20s	Fe(II), PPHA	0.0223	8.04E-5	3	0.000433	0	4	0.798	0.235	2.13	0.469	2.78
21h	PPHA, Fe(II)	0.0358	0.000786	3								
20s	PPHA, Fe(II)	0.0299	0.000489	3	0.000391	0	4	0.161	0.440	2.13	0.880	2.78
21h	Fe(II), PPHA	0.0273	0.000293	3								
20s	PPHA, Fe(II)	0.0299	0.000489	3	0.000638	0	4	0.289	0.393	2.13	0.787	2.78
21h	PPHA, Fe(II)	0.0358	0.000786	3								
21h	Fe(II), PPHA	0.0273	0.000293	3	0.000539	0	4	0.452	0.337	2.13	0.675	2.78
21h	PPHA, Fe(II)	0.0358	0.000786	3								

Aggregate Size

Table S3: Statistical analysis average aggregate size under each of the reactor preparation conditions. T-tests were calculated assuming equal variances, unless where noted (*, unequal variances). Abbreviations used: equilibration time (Equil. Time); observations (Obs); hypothesized mean difference (Hypoth. Mean Diff.)

Equil. Time	Order of Addition	Mean Dia. (nm)	Variance	Obs	Pooled Variance	Hypoth. Mean Diff.	df	t Stat	P(T<=t) one-tail	t Critical one-tail	P (T<=t) two-tail	t Critical two-tail
0s	NA	2900	107989	2	65916	0	2	0.283	0.402	2.92	0.804	4.30
20s	Fe(II), PPHA	2800	23844	2								
0s	NA	2900	107989	2	599450	0	2	2.09	0.0859	2.92	0.172	4.30
20s	PPHA, Fe(II)	4500	1090912	2								
0s	NA	2900	107989	2	2143705	0	2	0.192	0.433	2.92	0.866	4.30
21h	Fe(II), PPHA	3200	4179422	2								
0s	NA	2900	107989	2	1219183	0	2	0.0741	0.474	2.92	0.948	4.30
21h	PPHA, Fe(II)	2800	2330377	2								
20s	Fe(II), PPHA	2800	23844	2	557378	0	2	2.26	0.0759	0.0759	0.152	4.30
20s	PPHA, Fe(II)	4500	1090912	2								
20s	Fe(II), PPHA	2800	23844	2	NA*	0*	1*	0.244*	0.424*	6.31*	0.848*	12.7*
21h	Fe(II), PPHA	3200	4179422	2								
20s	Fe(II), PPHA	2800	23844	2	1177111	0	2	0.00842	0.497	2.92	0.994	4.30
21h	PPHA, Fe(II)	2800	2330377	2								
20s	PPHA, Fe(II)	4500	1090912	2	2635167	0	2	0.824	0.248	2.92	0.497	4.30
21h	Fe(II), PPHA	3200	4179422	2								
20s	PPHA, Fe(II)	4500	1090912	2	1710644	0	2	1.30	0.162	2.92	0.323	4.30
21h	PPHA, Fe(II)	2800	2330377	2								
21h	Fe(II), PPHA	3200	4179422	2	3254899	0	2	0.201	0.430	2.92	0.859	4.30
21h	PPHA, Fe(II)	2800	2330377	2								

Section S3: Other Experimental Data

4-ClNB Degradation Control Experiments

Table S4: Average rate of 4-ClNB degradation in the presence of goethite only, Fe(II) only, and Fe(II) and various concentrations of PPHA in either 25 mM MOPS or 10 mM $NaHCO_3$.

Buffer	Species Present	$k_{4\text{-ClNB}}$ (min^{-1})
MOPS	goethite	-0.0022 ± 0.0015[a]
	Fe(II)	0.0014 ± 0.0013[b]
	goethite, Fe(II)	0.1507 ± 0.0009[a,c]
	Fe(II), 2 ppm PPHA	0.0004 ± 0.0012[b]
	Fe(II), 10 ppm PPHA	0.0002 ± 0.0009[b]
	Fe(II), 50 ppm PPHA	0.0002 ± 0.0010[b]
$NaHCO_3$	goethite	-0.0022 ± 0.0012[a]
	Fe(II)	0.0042 ± 0.0056[a]
	goethite, Fe(II)	0.0126 ± 0.0022[a,c]
	Fe(II), 2 ppm PPHA	-0.0009 ± 0.0076[a]
	Fe(II), 10 ppm PPHA	0.0058 ± 0.0055[a]
	Fe(II), 50 ppm PPHA	0.0009 ± 0.0016[a]

[a]Error represents 95% confidence intervals of duplicate trials
[b]Errors represent 95% confidence intervals of triplicate trials
[c]Reported in manuscript as 0 ppm OC_{PPHA}

Variation of DLS Measurements

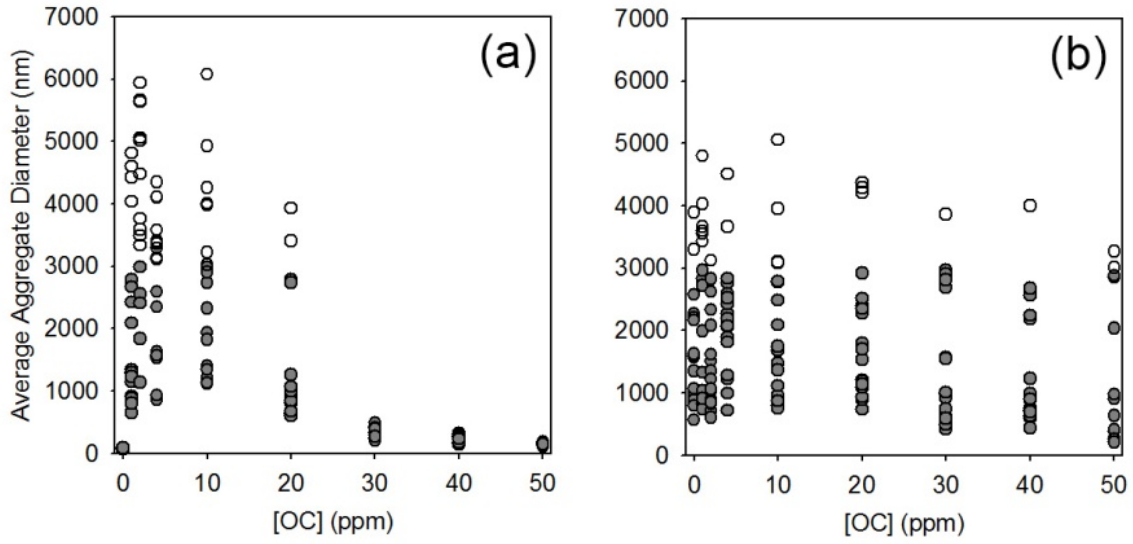

Figure S2: Average nanoparticle diameter of 0.325g/L goethite in (a) 25 mM MOPS and (b) 10 mM $NaHCO_3$ during reaction with 1.0 mM Fe(II) and 100 μM 4-ClNB. Open circles represent the average values that are above the quantitative limit of the instrumentation and grayed circles are within the quantitative range.

Dissolved Fe(II) Concentration vs. PPHA Concentration

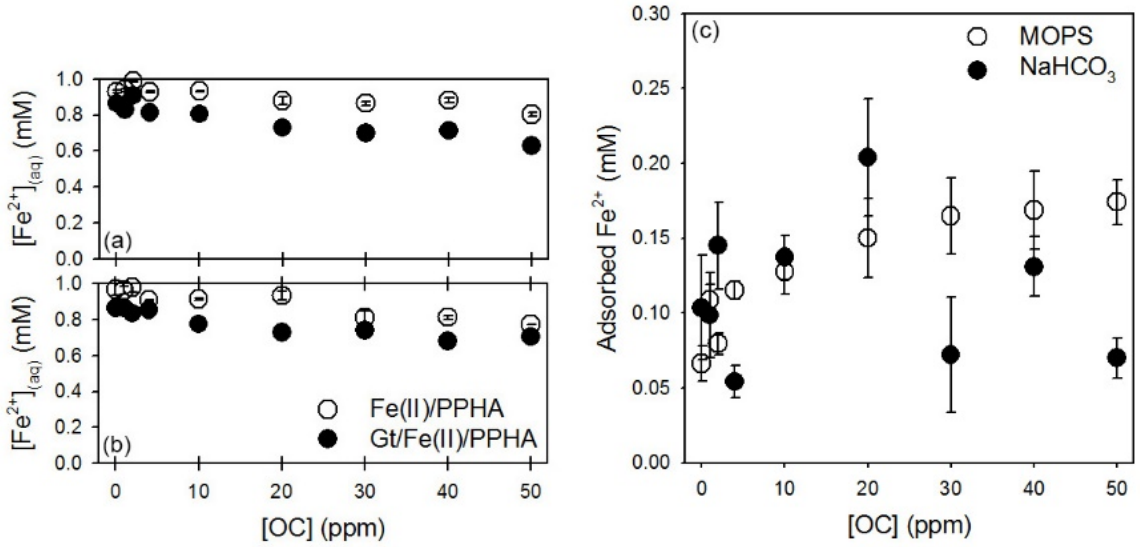

Figure S3: Aqueous Fe(II) concentration after 21 hours of equilibration in suspensions prepared with varying concentration of PPHA and with an initial Fe(II) concentration of 1.0 mM Fe(II) in the absence (open circles) and presence (closed circles) of 0.325 g/L goethite in (a) 25 mM MOPS and (b) 10 mM $NaHCO_3$. Adsorbed Fe(II), quantified as the difference in aqueous Fe(II) in the absence and presence of goethite, at each PPHA concentration is given in (c) for both buffers.

Zeta Potential, Electrophoretic Mobility, and Adsorbed PPHA

Table S5: Zeta potential, electrophoretic mobility, and adsorbed organic carbon measurements (before 4-ClNB degradation initiation) of 0.325 g/L goethite and 1.0 mM Fe(II) in in the presence of PPHA suspended in 25 mM MOPS and 10 mM $NaHCO_3$ pH 7 buffers.

Buffer	**[OC] (ppm)**	**Electrophoretic Mobility** $(\frac{micron}{second})/(\frac{Volt}{cm})$	**Zeta Potential (mV)**	**Adsorbed OC_{PPHA} (%)**
MOPS	0	3.1 ± 0.1	39.9 ± 1.6	N/A
	10	-2.0 ± 0.2	-25.0 ± 0.9	nd
	30	-2.4 ± 0.0_4	-31.0 ± 0.5	nd
$NaHCO_3$	0	0.6 ± 0.1	7.3 ± 2.0	N/A
	10	-2.2 ± 0.1	-28.5 ± 1.8	14
	30	-2.2 ± 0.1	-28.3 ± 1.7	59

nd – TOC signal from MOPS prevented quantification

Section S4: T-tests for Fe(II) Equilibration Times – Sequential Injections

Table S6: Statistical analysis of 4-ClNB degradation rates of Fe(II) equilibration times for each buffer: 21 hours used in all experiments except the sequential injection experiments where 19 hours (MOPS) and 15 hours ($NaHCO_3$) were used instead. T-tests were calculated assuming equal variances.

	MOPS		**$NaHCO_3$**	
	21h	**19h**	**21h**	**15h**
Mean	0.0162	0.0136	0.0109	0.0108
Variance	1.4E-05	2.45E-07	7.20E-07	4.21E-06
Observations	2	2	2	2
Pooled Variance	7.15E-06		2.46E-06	
Hypothesized Mean Difference	0		0	
df	2		2	
t Stat	0.973		0.0956	
P(T<=t) one-tail	0.217		0.466	
t Critical one-tail	2.92		2.92	
P(T<=t) two-tail	0.433		0.933	
t Critical two-tail	4.30		4.30	

Section S5: Pseudo-First Order Plots of Sequential 4-ClNB Degradation

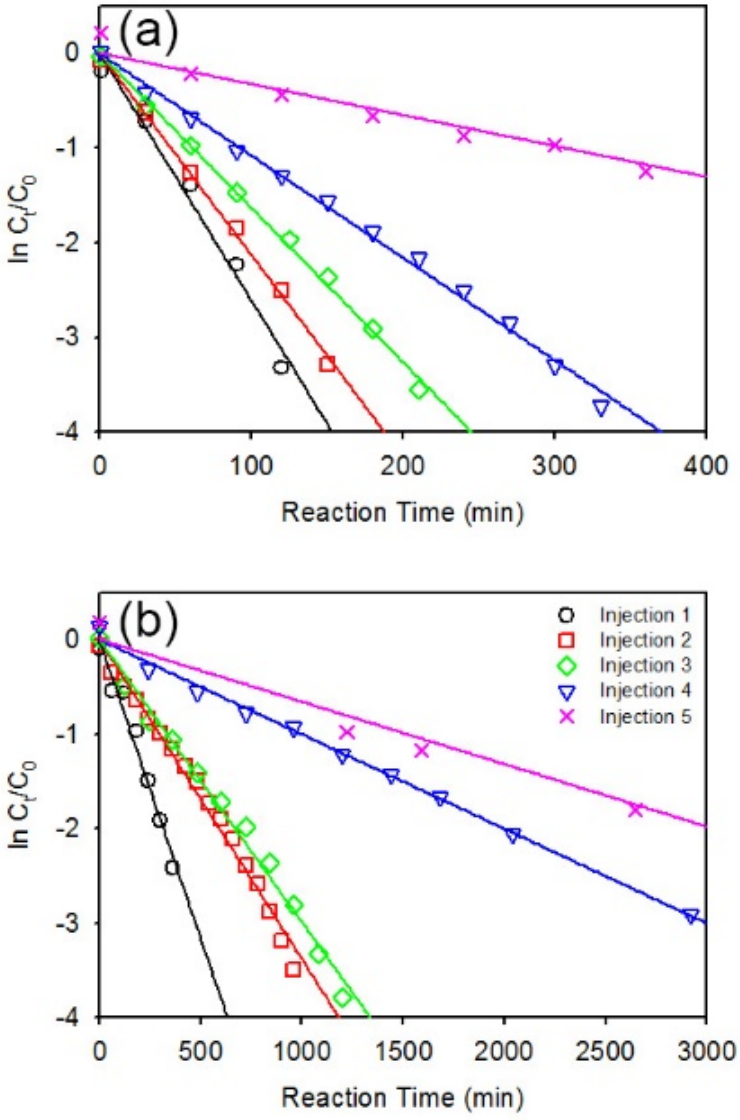

Figure S4: Pseudo-first order plots of 4-ClNB degradation by 0.325 g/L goethite and 1.0 mM Fe(II) in the presence of 10 ppm PPHA in pH 7 (a) 25 mM MOPS and (b) 10 mM $NaHCO_3$ buffer. 4-ClNB was allowed to completely degrade for each injection: 1 (black circles), 2 (red squares), 3 (green diamonds), 4 (blue triangles), and 5 (pink X).

Section S6: Goethite Particle Size Analysis of Sequential 4-ClNB Degradations

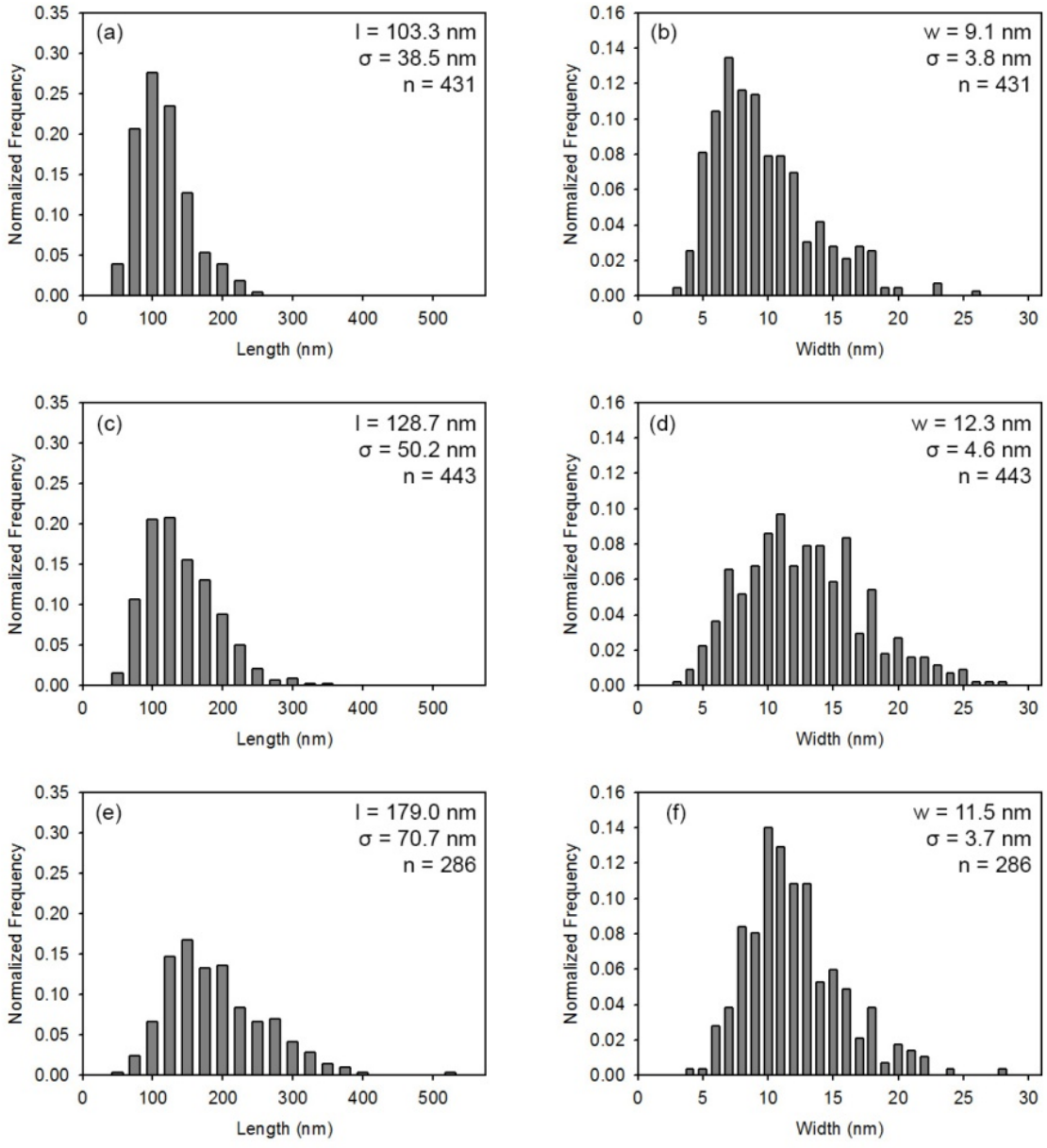

Figure S5: Histograms of the normalized frequency of length and width of goethite nanoparticles after (a, b) 1 injection of 4-ClNB, (c, d) 3 injections of 4-ClNB, and (e, f) 5 injections of 4-ClNB in 25 mM MOPS and 10 ppm OC PPHA. Figure insets list the average length or width, standard deviation, and number of measurements.

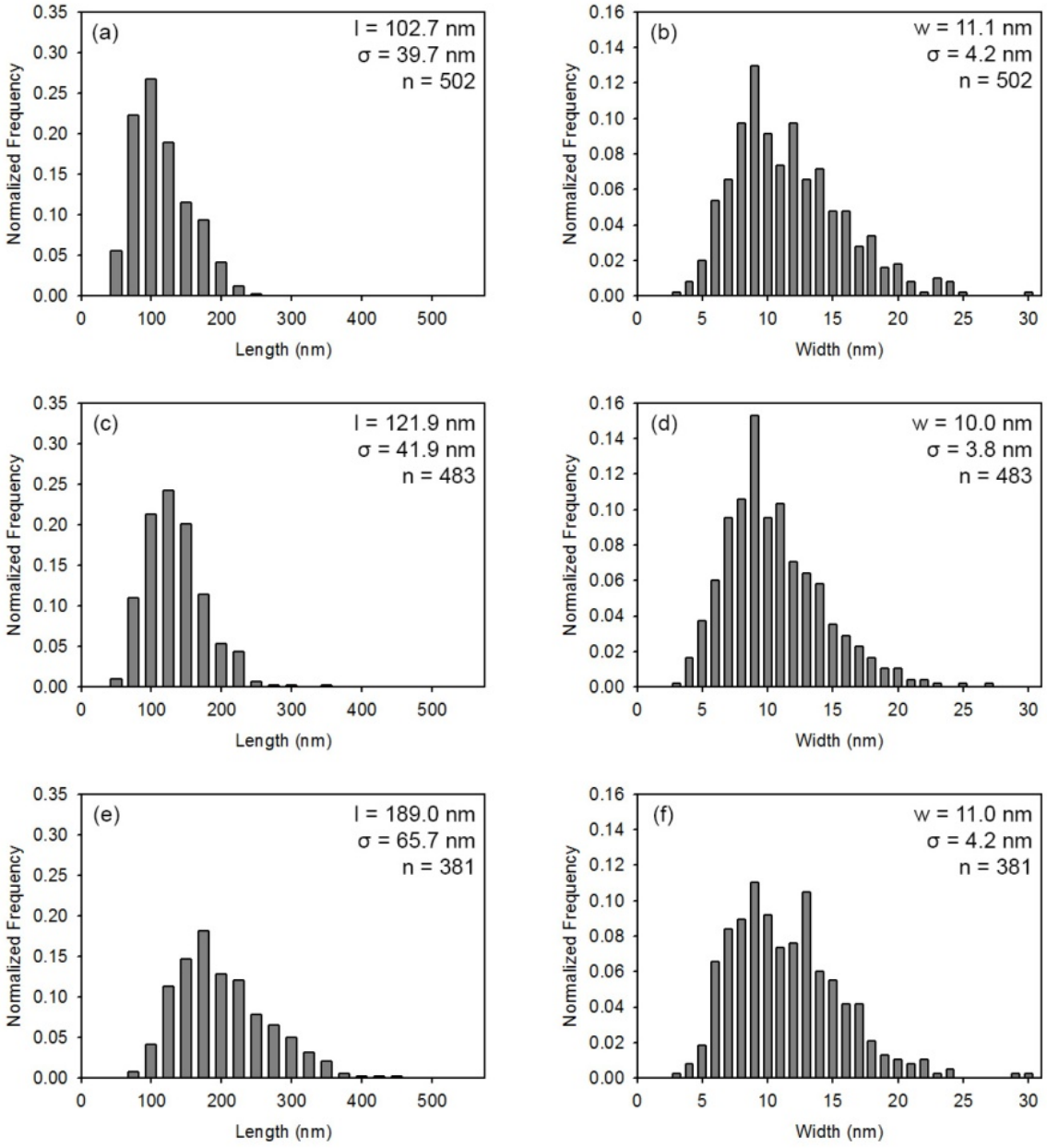

Figure S6: Histograms of the normalized frequency of length and width of goethite nanoparticles after (a, b) 1 injection of 4-ClNB, (c, d) 3 injections of 4-ClNB, and (e, f) 5 injections of 4-ClNB in 10 mM $NaHCO_3$ and 10 ppm OC PPHA. Figure insets list the average length or width, standard deviation, and number of measurements.

Section S7: Goethite Statistical Analysis of Sequential 4-ClNB Degradations

Table S7: Results of F tests for each nanoparticle dimension in each buffer comparing sequential 4-ClNB injections.

Buffer	Particle Dimension	Sample	Mean	Variance	Observations	df	F	P(F<=f) one-tail	F Critical one-tail
MOPS	Length	Stock	89.0	1221	460	459	1.22	0.0194	1.17
		Injection 1	103	1485	431	430			
		Injection 1	103	1485	431	430	170	2.10E-8	1.17
		Injection 3	129	2521	443	442			
		Injection 3	129	2521	443	442	1.98	4.73E-11	1.19
		Injection 5	179	5001	286	285			
	Width	Stock	10.0	17.8	460	459	1.20	0.0276	1.17
		Injection 1	9.1	14.8	431	430			
		Injection 1	9.1	14.8	431	430	1.46	4.01E-5	1.17
		Injection 3	12.3	21.6	443	442			
		Injection 3	12.3	21.6	443	442	1.56	2.55E-5	1.20
		Injection 5	11.5	13.8	286	285			
$NaHCO_3$	Length	Stock	89.0	1221	460	459	1.29	0.00282	1.16
		Injection 1	102	1574	502	501			
		Injection 1	102	1574	502	501	1.12	0.110	1.16
		Injection 3	122	1758	483	482			
		Injection 3	122	1758	483	482	2.45	9.93E-21	1.17
		Injection 5	189	4315	381	380			
	Width	Stock	10.0	17.8	460	459	1.01	0.470	1.16
		Injection 1	11.1	17.9	502	501			
		Injection 1	11.1	17.9	502	501	1.25	0.00717	1.16
		Injection 3	10.0	14.3	483	482			
		Injection 3	10.0	14.3	483	482	1.24	0.0135	1.17
		Injection 5	11.0	17.7	381	380			

Table S8: Results of t-tests for each nanoparticle dimension in each buffer comparing sequential 4-ClNB injections. Pooled variance is NA when the t-test is performed assuming unequal variances and has a value when the t-test is performed assuming equal variances.

Buffer	Particle Dimension	Sample	Mean	Variance	Obs	Pooled Variance	Hypoth. Mean Diff.	df	t Stat	P(T<=t) one-tail	t Critical one-tail	P (T<=t) two-tail	t Critical two-tail
MOPS	Length	Stock	89.0	1220	460	NA	0	866	-5.77	5.56E-9	1.65	1.11E-8	1.96
		Inject. 1	103	1485	431								
		Inject. 1	103	1485	431	NA	0	827	8.41	8.82E-17	1.65	1.76E-16	1.96
		Inject. 3	129	2521	443								
		Inject. 3	129	2521	443	NA	0	469	10.4	2.24E-23	1.65	4.48E-23	1.97
		Inject. 5	180	5001	286								
	Width	Stock	10.0	17.7	460	NA	0	888	3.42	0.00033	1.65	0.000659	1.96
		Inject. 1	9.1	14.8	431								
		Inject. 1	9.1	14.8	431	NA	0	850	11.0	7.44E-27	1.65	1.49E-26	1.96
		Inject. 3	12.3	21.6	443								
		Inject. 3	12.3	21.6	443	NA	0	694	-2.38	0.00883	1.65	0.0177	1.96
		Inject. 5	11.5	13.8	286								
$NaHCO_3$	Length	Stock	89.0	1220	460	NA	0	959	-5.56	1.74E-8	1.65	3.48E-8	1.96
		Inject. 1	102	1573	502								
		Inject. 1	102	1573	502	NA	0	974	7.48	8.10E-14	1.65	1.62E-13	1.96
		Inject. 3	122	1758	483								
		Inject. 3	122	1758	483	NA	0	614	17.3	2.02E-55	1.65	4.04E-55	1.96
		Inject. 5	189	4315	381								
	Width	Stock	10.0	17.7	460	17.8	0	960	3.92	4.80E-5	1.65	9.6E-5	1.96
		Inject. 1	11.1	17.9	502								
		Inject. 1	11.1	17.9	502	NA	0	978	4.29	9.77E-6	1.65	1.95E-5	1.96
		Inject. 3	10.0	14.3	483								
		Inject. 3	10.0	14.3	483	NA	0	772	-3.48	0.000269	1.65	0.000539	1.96
		Inject. 5	11.0	17.7	381								

Section S8: Other Experimental Data for Sequential 4-ClNB Degradations

Nanoparticle Composition After Each 4-ClNB Degradation

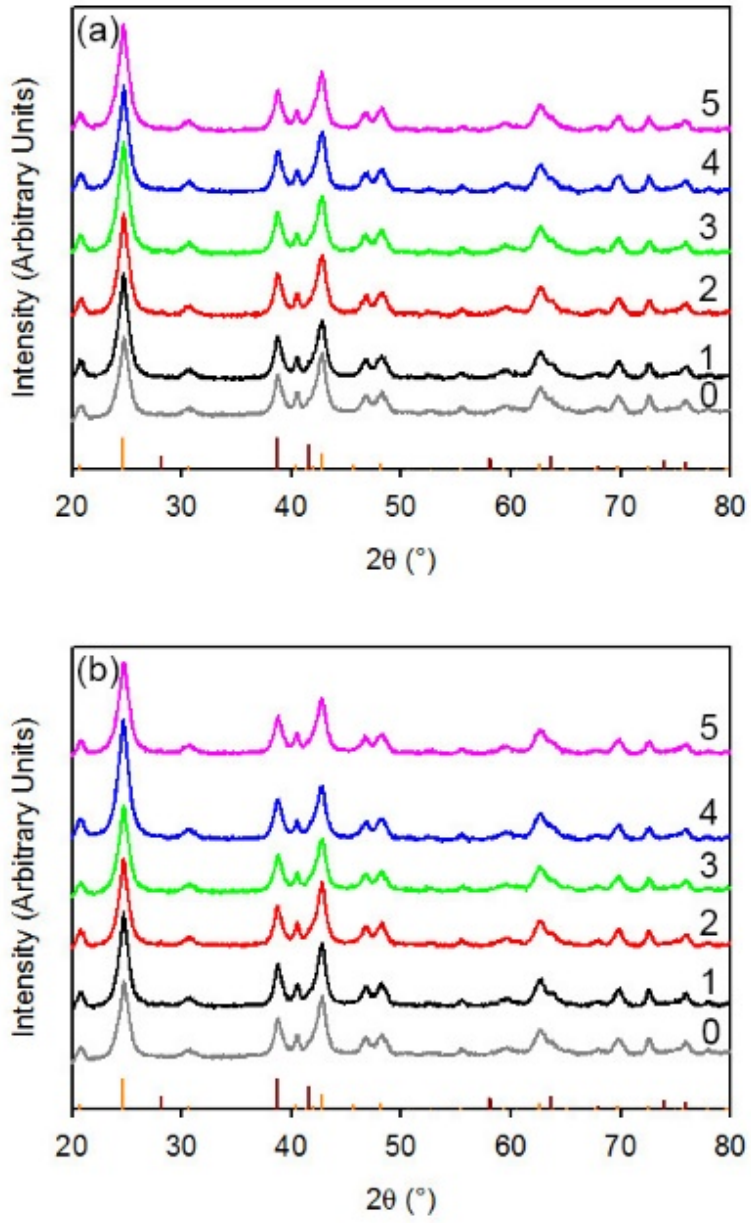

Figure S7: XRD patterns of the pre-reaction goethite suspension (grey) and the dried suspensions after each of the five 4-ClNB degradation reactions (1-black, 2-red, 3-green, 4-blue, and 5-pink) in pH 7 (a) 25 mM MOPS and (b) 10 mM $NaHCO_3$. PDF stick patterns of goethite (orange, #29-0713) and hematite (dark red, #33-0664) are also displayed.

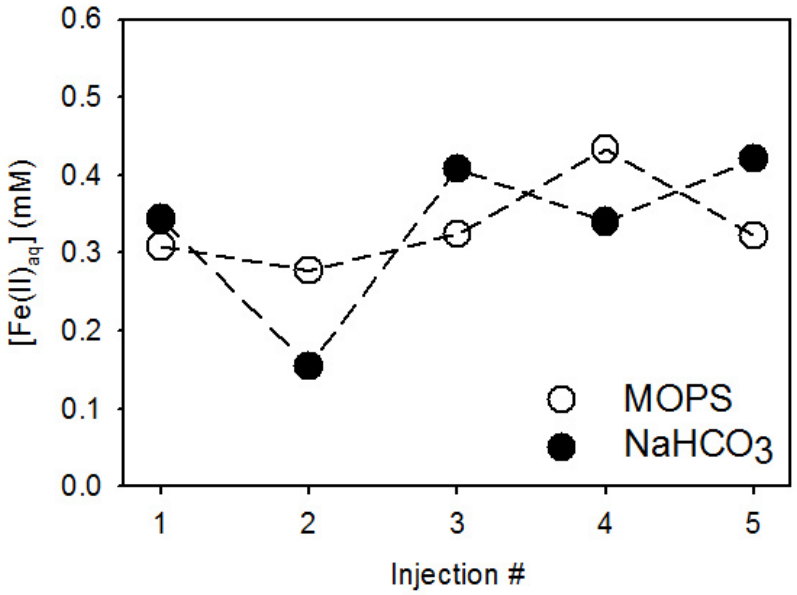

Figure S8: Final aqueous Fe(II) concentration after complete 4-ClNB degradation with 0.325 g/L goethite, 1.0 mM initial Fe(II), and 10 ppm PPHA in pH 7 25 mM MOPS (open circles) and 10 mM $NaHCO_3$ (closed circles) buffer.

Section S9: Calculation of Predicted Length of New Goethite by Mass Balance

Assumption: Goethite nanoparticles grew only in the length direction upon reaction with 4-ClNB

1. Moles of 4-ClNB reduced: A
2. Moles of electrons used for reduction: B = 6 x A
3. Mass of newly formed goethite: C = B x 88.86 g/mol
4. Total mass of goethite: M = X + C
5. Ratio of new goethite to total mass: R = (C+X)/X
6. Predicted length: L2 = R x L1

X: Mass of goethite in previous injection
L1: Average length of goethite in previous injection
L_{actual}: Mean value of goethite length from TEM analysis

Buffer	Injection	A (umol)	B (umol)	C (mg)	M (mg)	R	L1 (nm)	L2 (nm)	L_{actual}
MOPS	1	12.1	72.6	6.45	45.8	1.16	89	104	103
	3	24.2	145.2	12.9	58.7	1.28	103	132	129
	5	48.4	290.4	25.8	84.5	1.44	103	149	179
$NaHCO_3$	1	12.1	72.6	6.45	45.8	1.16	89	104	10
	3	24.2	145.2	12.9	58.7	1.28	102	131	122
	5	48.2	289.2	25.7	84.4	1.44	102	147	189