“User-Friendly” Geochemical Modeling to Evaluate Treatment Options for Coal-Mine Discharges

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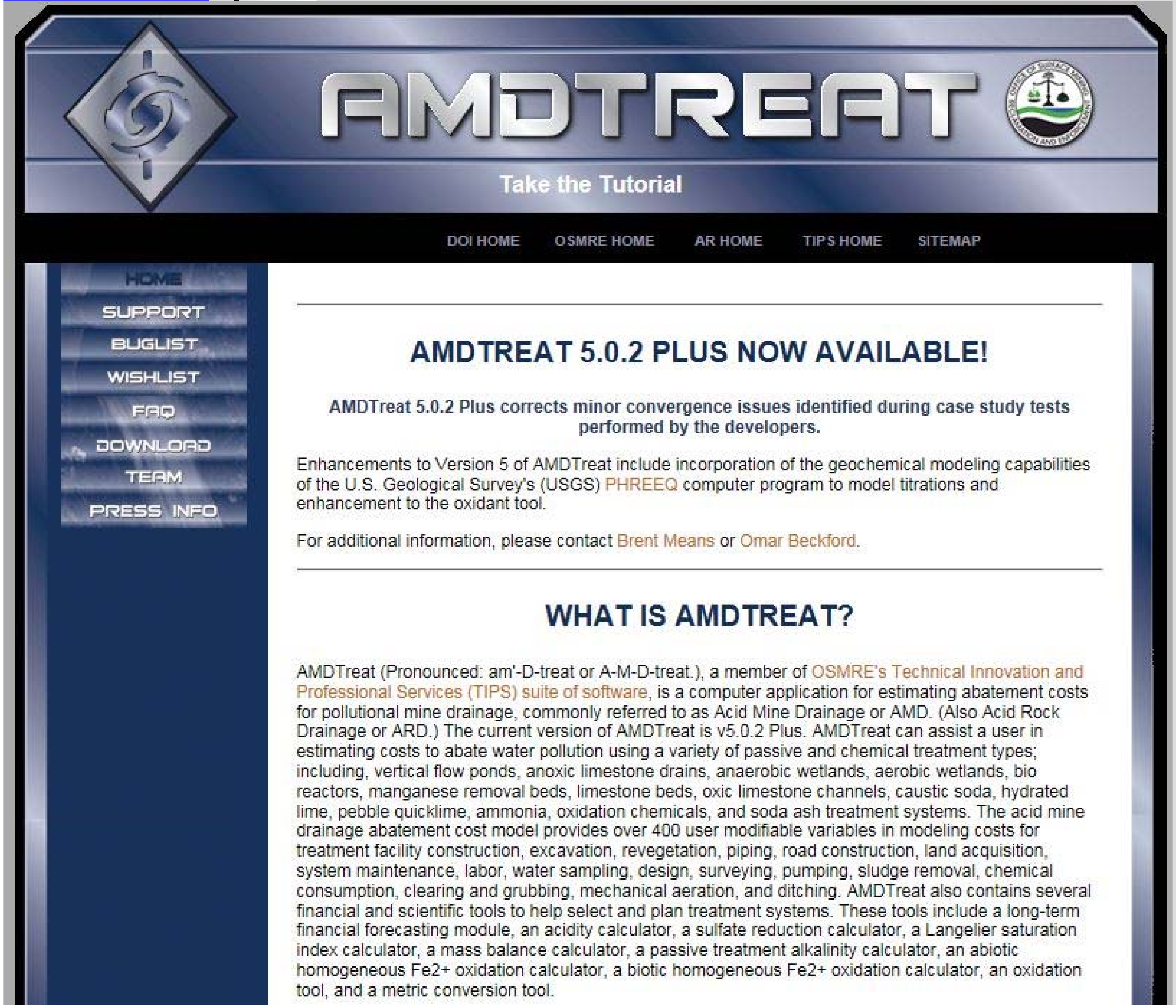
“PHREEQ-N-AMDTREAT”

http://amd.osmre.gov/



AMDTREAT 5.0.2 PLUS NOW AVAILABLE!

AMDTreat 5.0.2 Plus corrects minor convergence issues identified during case study tests performed by the developers.

Enhancements to Version 5 of AMDTreat include incorporation of the geochemical modeling capabilities of the U.S. Geological Survey's (USGS) PHREEQ computer program to model titrations and enhancement to the oxidant tool.

For additional information, please contact Brent Means or Omar Beckford.

WHAT IS AMDTREAT?

AMDTreat (Pronounced: am'-D-treat or A-M-D-treat.), a member of OSMRE's Technical Innovation and Professional Services (TIPS) suite of software, is a computer application for estimating abatement costs for pollutional mine drainage, commonly referred to as Acid Mine Drainage or AMD. (Also Acid Rock Drainage or ARD.) The current version of AMDTreat is v5.0.2 Plus. AMDTreat can assist a user in estimating costs to abate water pollution using a variety of passive and chemical treatment types; including, vertical flow ponds, anoxic limestone drains, anaerobic wetlands, aerobic wetlands, bio reactors, manganese removal beds, limestone beds, oxic limestone channels, caustic soda, hydrated lime, pebble quicklime, ammonia, oxidation chemicals, and soda ash treatment systems. The acid mine drainage abatement cost model provides over 400 user modifiable variables in modeling costs for treatment facility construction, excavation, revegetation, piping, road construction, land acquisition, system maintenance, labor, water sampling, design, surveying, pumping, sludge removal, chemical consumption, clearing and grubbing, mechanical aeration, and ditching. AMDTreat also contains several financial and scientific tools to help select and plan treatment systems. These tools include a long-term financial forecasting module, an acidity calculator, a sulfate reduction calculator, a Langelier saturation index calculator, a mass balance calculator, a passive treatment alkalinity calculator, an abiotic homogeneous Fe2+ oxidation calculator, a biotic homogeneous Fe2+ oxidation calculator, an oxidation tool, and a metric conversion tool.

AMDTreat is a computer application for estimating abatement costs for AMD (acidic or alkaline mine drainage).

AMDTreat is maintained by OSMRE.

The current version of AMDTreat 5.0+ is being recoded from FoxPro to C++ to facilitate its use on computer systems running Windows 10. The PHREEQC geochemical models described below will be incorporated to run with the recoded program.

“User Friendly” PHREEQC Kinetics Models for AMDTreat

- ✓ Atmospheric exchange: O_2 ingassing, CO_2 outgassing, and pH.
- ✓ Iron and manganese oxidation: pH-dependent homogeneous and heterogeneous rate laws (pH, pO_2, sorption) plus contributions by acidophilic and neutrophilic iron-oxidizing bacteria.
- ✓ Limestone dissolution: considers solution chemistry (pH, pCO_2) plus surface area of limestone fragments (particle size).
- ✓ Organic-carbon oxidation: reduction of sulfate and nitrate by carbon, plus Fe^{III} by adsorbed sulfide (from sulfate reduction).
- ✓ Potential water quality from various treatments can be considered to estimate system size (feasibility) and for benefits/costs analysis.

TREATMENT OF COAL MINE DRAINAGE

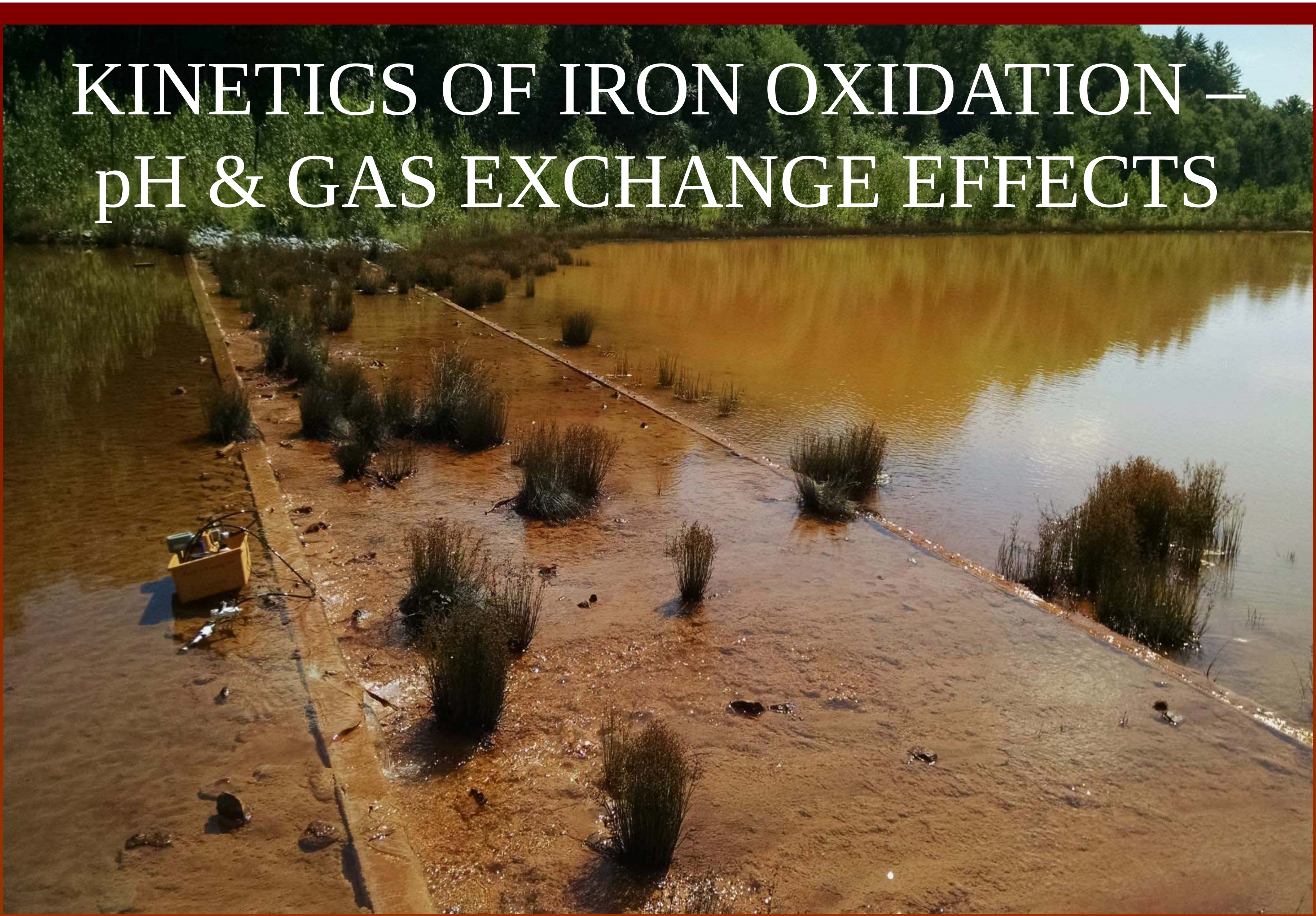
Al^{3+}

Fe^{2+} / Fe^{3+}

Mn^{2+}

Passive	Active
Increase pH/oxidation with aeration, natural substrates & microbes	Increase pH/oxidation with aeration &/or industrial chemicals
Reactions slow	Reactions fast, efficient
Large area footprint	Moderate area footprint
Low maintenance	High maintenance

KINETICS OF IRON OXIDATION – pH & GAS EXCHANGE EFFECTS



Iron Oxidation Kinetics are pH Dependent (abiotic and microbial processes can be involved)

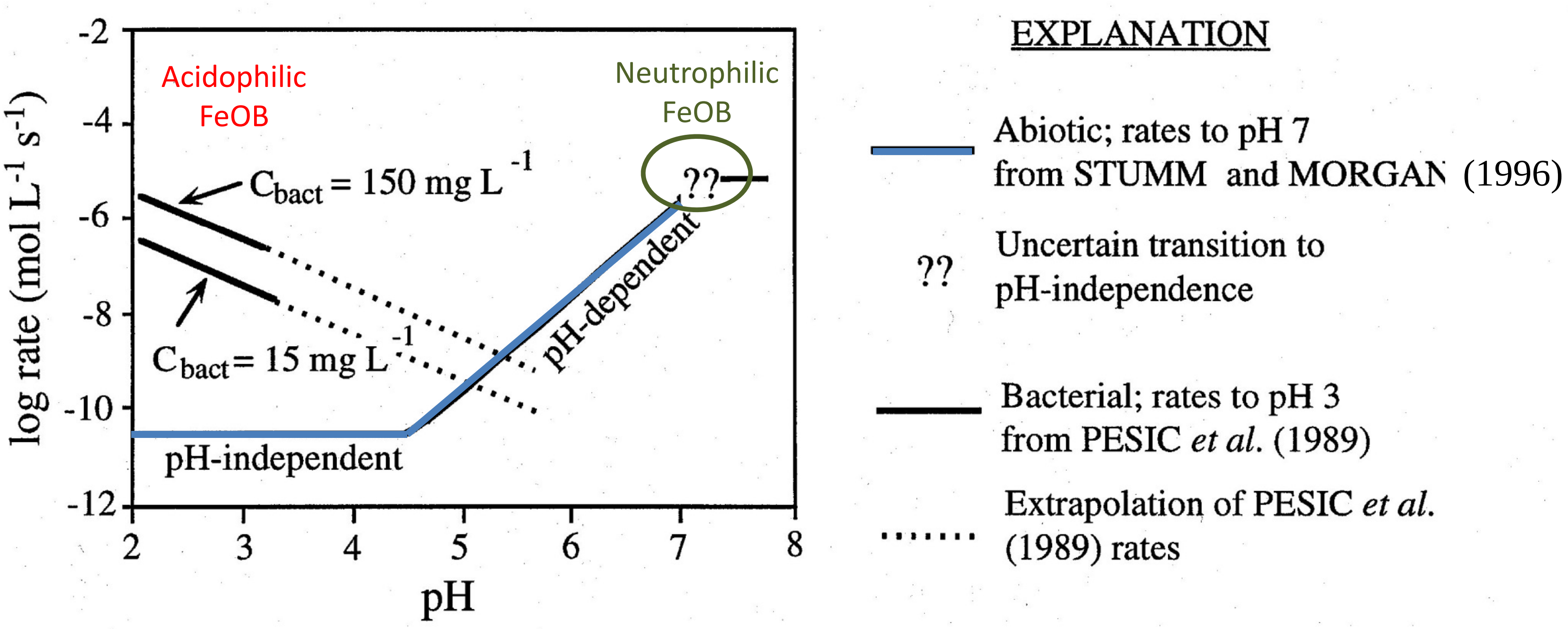


Fig. 3. Rate of Fe(II) oxidation versus pH based on abiotic and biological rate laws (Kirby et al., 1999)

** C_{bact} is concentration of iron-oxidizing bacteria (FeOB), in mg/L, as dry weight of bacteria (2.8E-13 g/cell or 2.8E-10 mg/cell).

The AMDTreat FeII oxidation kinetic model uses most probable number of iron-oxidizing bacteria per liter (MPNbact).

C_{bact} = 150 mg/L is equivalent to MPNbact = 5.3E11, where Cbact = MPNbact ·(2.8E-10).

Neutrophilic rate is adjusted for optimum conditions of pH (6.5-7.5) and low DO (1.9-2.2 mg/L) (Eggerichs et al., 2014).

Iron Oxidation Rate Model combines homogeneous and heterogeneous abiotic and microbial processes

The homogeneous oxidation rate law (Stumm and Lee, 1961; Stumm and Morgan, 1996), expressed in terms of $[O_2]$ and $\{H^+\}$ ($=10^{-pH}$), describes abiotic oxidation of dissolved Fe^{II}:

$$-d[Fe^{II}]/dt = k_1 \cdot [Fe^{II}] \cdot [O_2] \cdot \{H^+\}^{-2}$$

The heterogeneous oxidation rate law describes the catalytic abiotic oxidation of sorbed Fe^{II} on surfaces of hydrous ferric oxide (HFO) (Tamura et al., 2001):

$$-d[Fe(II)]/dt = k'_2\,(Fe(III)) \cdot [Fe(II)] \cdot [O_2] \cdot \{H^+\}^{-1} \quad \textit{or} \quad -d[Fe^{II}]/dt = k_2 \cdot [HFO\_Fe^{II}] \cdot [O_2]$$

The microbial oxidation rate laws describe the catalytic oxidation of Fe^{II} by:
(1) *acidophilic iron-oxidizing bacteria*, which become relevant at pH < 5 (Kirby et al., 1999):

$$-d[Fe^{II}]/dt = k_{bio1} \cdot C_{bact} \cdot [Fe^{II}] \cdot [O_2] \cdot \{H^+\}$$

and (2) *neutrophilic iron-oxidizing bacteria*, which have optimum rate at pH 6.5-7.5 and DO 1.9-2.2 mg/L (Eggerichs et al., 2014):

$$-d[Fe^{II}]/dt = k_{bio2} \cdot C_{bact} \cdot [HFO\_Fe^{II}] \cdot [O_2]$$

similar functions are used for manganese oxidation

Effects of O_2 Ingassing and CO_2 Outgassing on pH and Fe^{II} Oxidation Rates

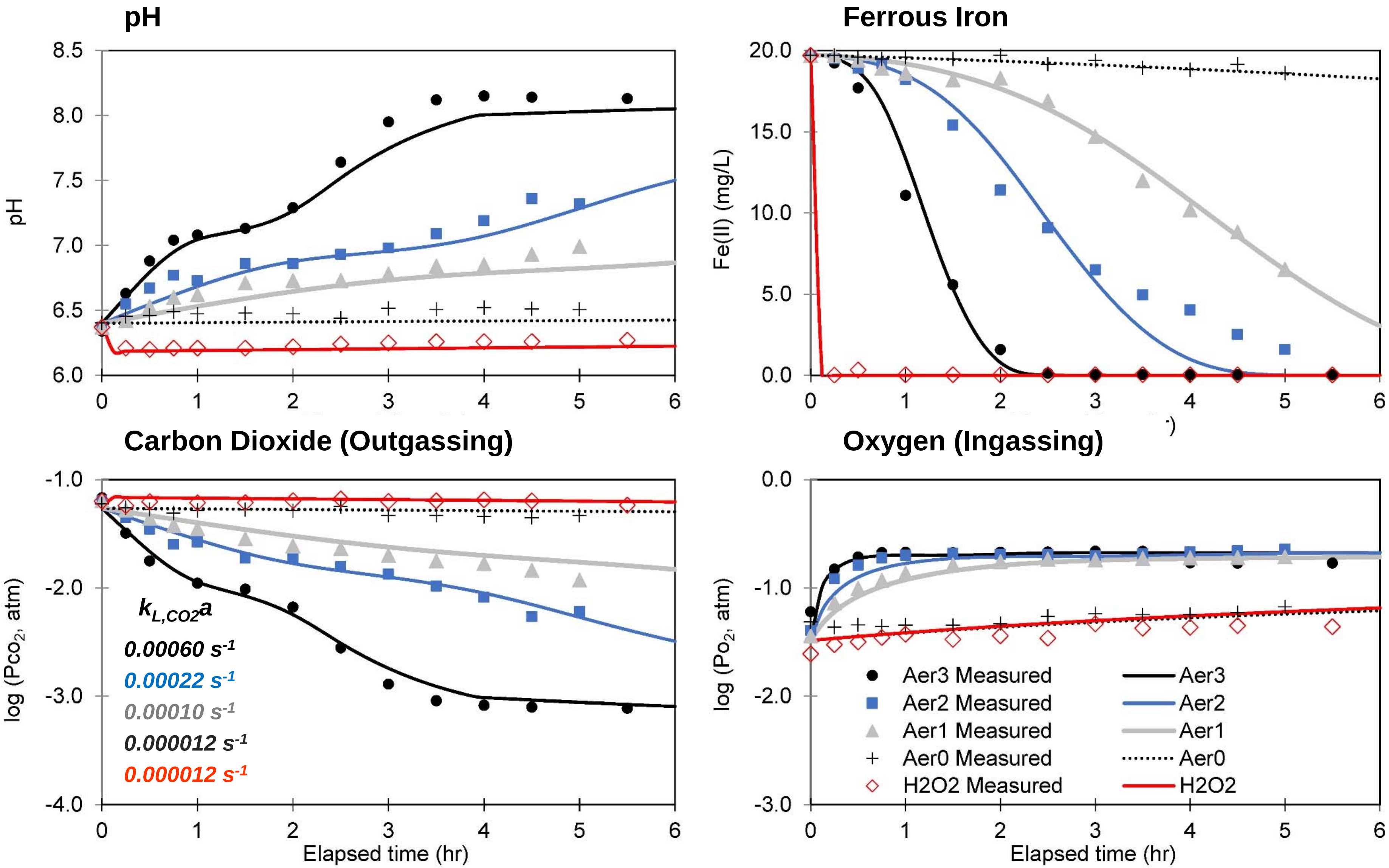
Batch Aeration Tests at Oak Hill Boreholes (summer 2013)

Control Not Aerated

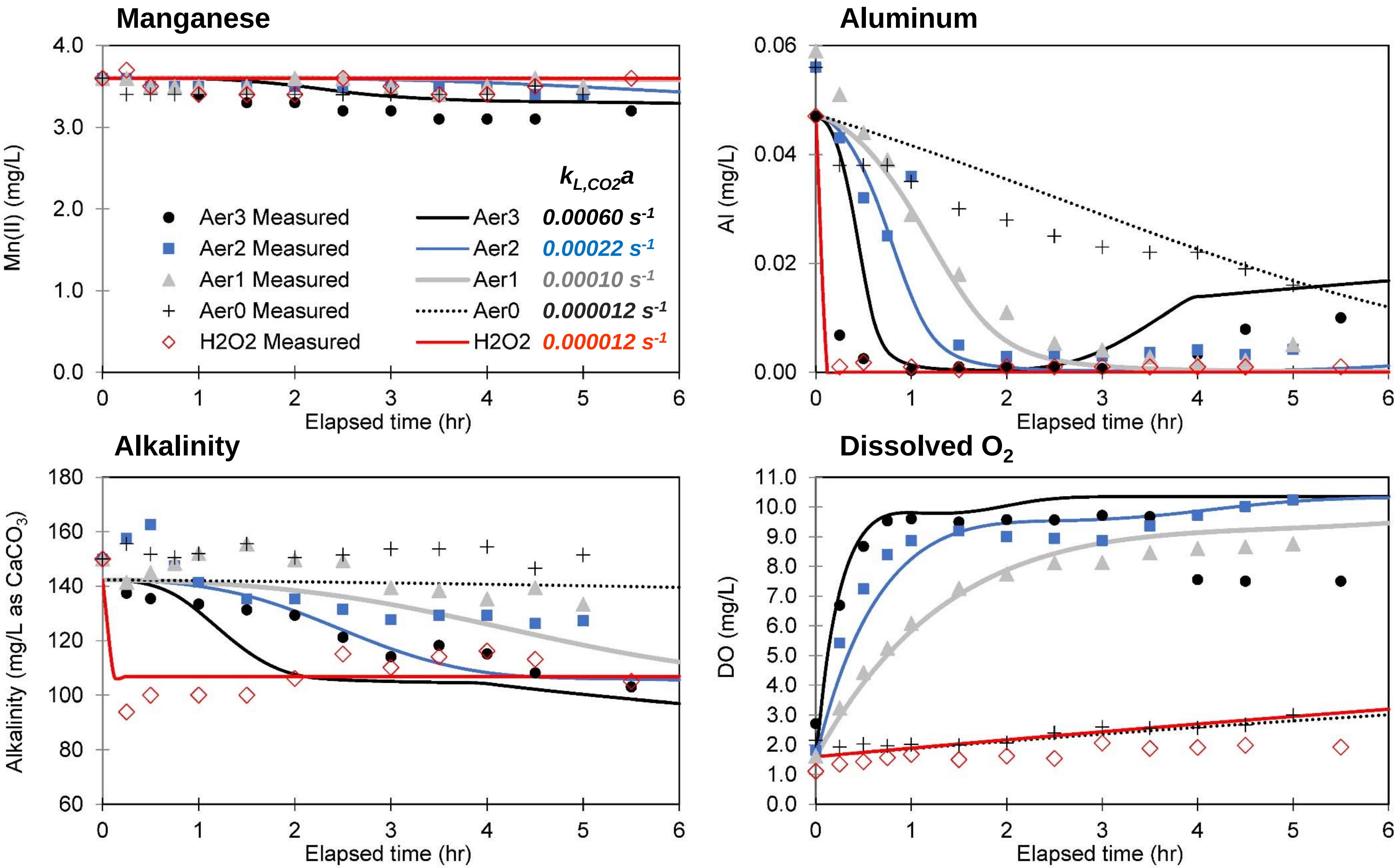
Aerated

H_2O_2 Addition

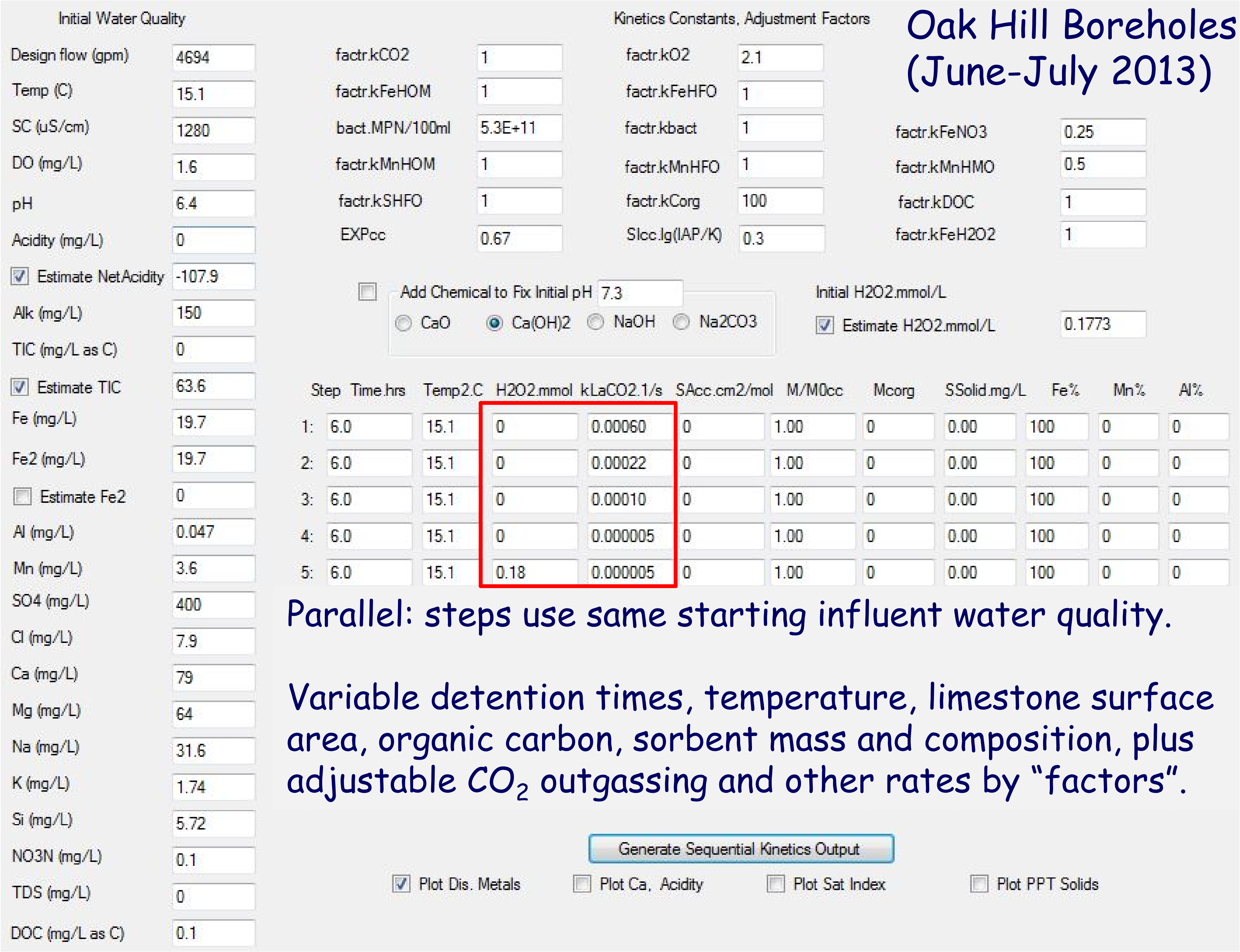
PHREEQC Coupled Kinetic Model of CO_2 Outgassing & Oxidation of Fe^{II} and Mn^{II} — Oak Hill Boreholes



PHREEQC Coupled Kinetic Model of CO_2 Outgassing & Oxidation of Fe^{II} and Mn^{II} — Oak Hill Boreholes



PHREEQC Coupled Kinetic Models--Parallel



Oak Hill Boreholes (June-July 2013)

Initial Water Quality

Design flow (gpm)	4694
Temp (C)	15.1
SC (uS/cm)	1280
DO (mg/L)	1.6
pH	6.4
Acidity (mg/L)	0
☑ Estimate NetAcidity	-107.9
Alk (mg/L)	150
TIC (mg/L as C)	0
☑ Estimate TIC	63.6
Fe (mg/L)	19.7
Fe2 (mg/L)	19.7
☐ Estimate Fe2	0
Al (mg/L)	0.047
Mn (mg/L)	3.6
SO4 (mg/L)	400
Cl (mg/L)	7.9
Ca (mg/L)	79
Mg (mg/L)	64
Na (mg/L)	31.6
K (mg/L)	1.74
Si (mg/L)	5.72
NO3N (mg/L)	0.1
TDS (mg/L)	0
DOC (mg/L as C)	0.1

Kinetics Constants, Adjustment Factors

factr.kCO2	1	factr.kO2	2.1		
factr.kFeHOM	1	factr.kFeHFO	1		
bact.MPN/100ml	5.3E+11	factr.kbact	1	factr.kFeNO3	0.25
factr.kMnHOM	1	factr.kMnHFO	1	factr.kMnHMO	0.5
factr.kSHFO	1	factr.kCorg	100	factr.kDOC	1
EXPcc	0.67	SIcc.lg(IAP/K)	0.3	factr.kFeH2O2	1

☐ Add Chemical to Fix Initial pH 7.3

○ CaO ● Ca(OH)2 ○ NaOH ○ Na2CO3

Initial H2O2.mmol/L

☑ Estimate H2O2.mmol/L 0.1773

Step	Time.hrs	Temp2.C	H2O2.mmol	kLaCO2.1/s	SAcc.cm2/mol	M/M0cc	Mcorg	SSolid.mg/L	Fe%	Mn%	Al%	Treatment
1:	6.0	15.1	0	0.00060	0	1.00	0	0.00	100	0	0	Aer3
2:	6.0	15.1	0	0.00022	0	1.00	0	0.00	100	0	0	Aer2
3:	6.0	15.1	0	0.00010	0	1.00	0	0.00	100	0	0	Aer1
4:	6.0	15.1	0	0.000005	0	1.00	0	0.00	100	0	0	Aer0
5:	6.0	15.1	0.18	0.000005	0	1.00	0	0.00	100	0	0	H2O2

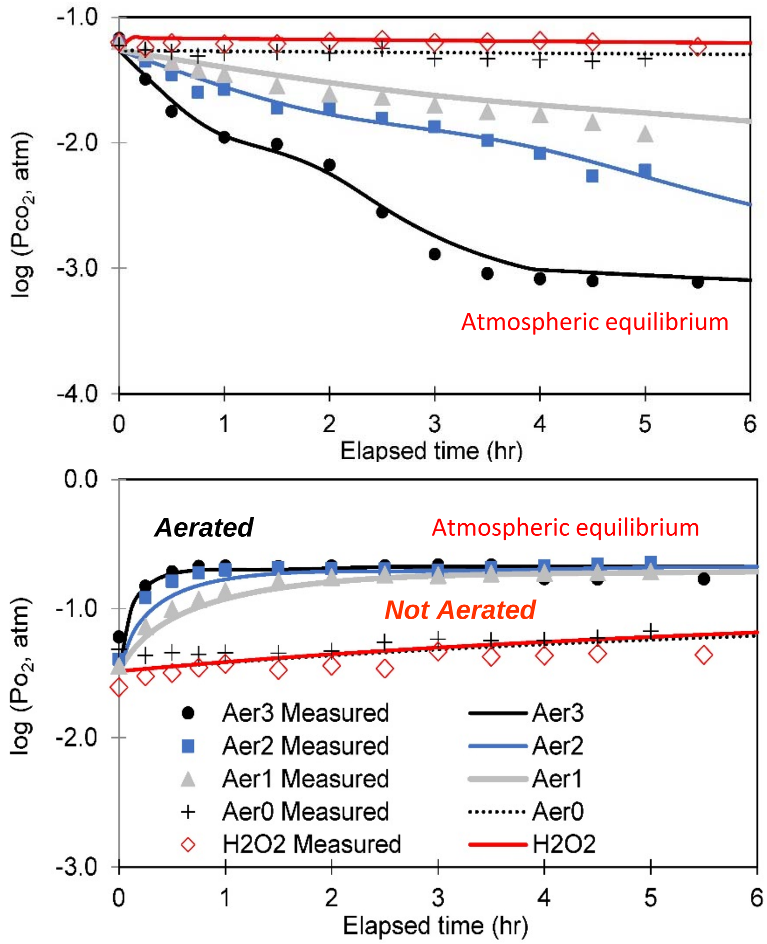
Parallel: steps use same starting influent water quality.

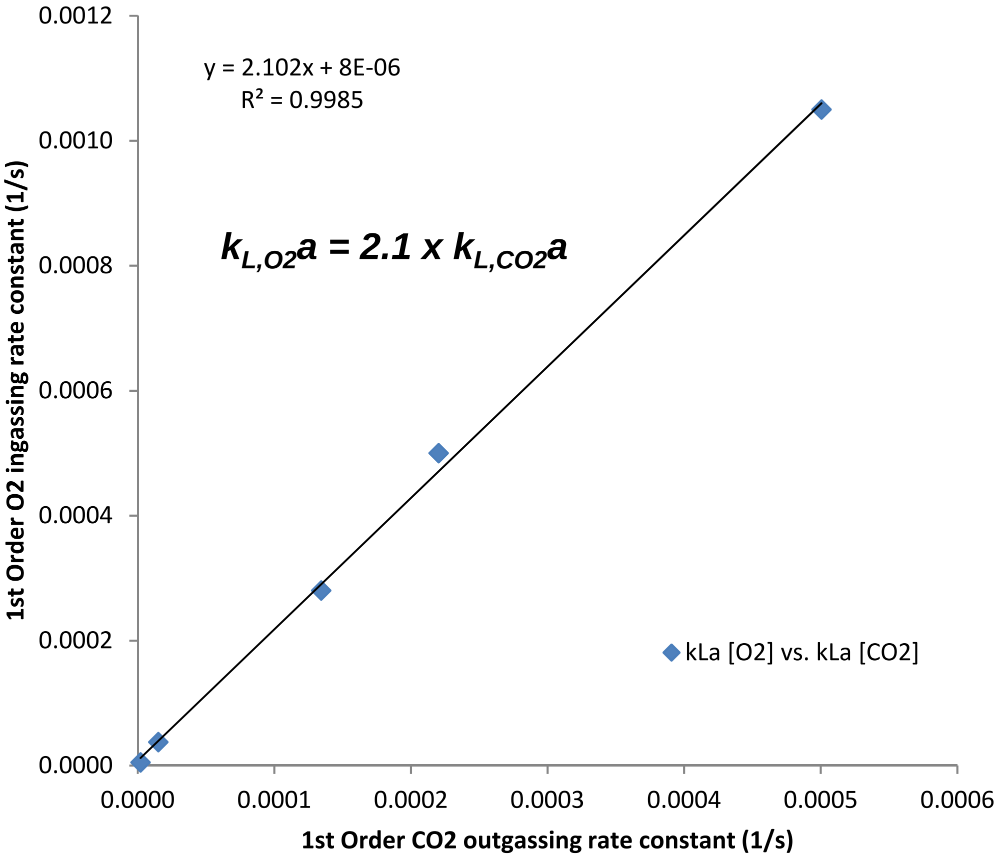
Variable detention times, temperature, limestone surface area, organic carbon, sorbent mass and composition, plus adjustable CO_2 outgassing and other rates by “factors”.

☑ Plot Dis. Metals ☐ Plot Ca, Acidity ☐ Plot Sat Index ☐ Plot PPT Solids

CO_2 Outgassing is Proportional to O_2 Ingassing (model specifies first-order rates for out/in gassing)

$-d[C]/dt = k_{L,C}a \cdot ([C] - [C]_S)$ exponential, asymptotic approach to steady state





$k_{L,O2}a = 2.1 \times k_{L,CO2}a$

Estimated CO_2 Outgassing & O_2 Ingassing Rate Constants for Various Treatment Technologies

***Table S.4** Values of rate constants for CO_2 outgassing and O_2 ingassing used for kinetic models*

Site	Temper-ature (°C)	CO_2 Outgas $k_{L,CO2}a$ (s^{-1})		$\log(s^{-1})$
Treatment Systems				
Maelstrom (Sykesville, Trent, St.Michaels)	20	0.03	Fast	-1.52
Surface Aerator (Renton, other)	20	0.001		-3.00
Mechanical Aerator (Lancashire)	20	0.0006		-3.22
Aeration Cascade/Level Spreader (Silver Cr)	20	0.01		-2.00
Rip-rap Spillway/Ditch (Silver Cr, Pine Forest,	20	0.005		-2.30
Pond (Silver Cr, Pine Forest, Lion Mining, Flight93)	20	0.00001	Slow	-5.00
Wetland (Silver Cr, Pine Forest, Lion Mining)	20	0.00001		-5.00
Oak Hill Aeration Expts.				
Aer3	20	0.00060	Fast	-3.22
Aer2	20	0.00022		-3.66
Aer1	20	0.00010		-4.00
Aer0	20	0.000012	Slow	-4.92

*Gas mass-transfer rate corrected to 20°C per Rathbun (1998, Eq. 56) using the expression:

kL,a_20 = kL,a_TC /(1.0241^(TC-20)).

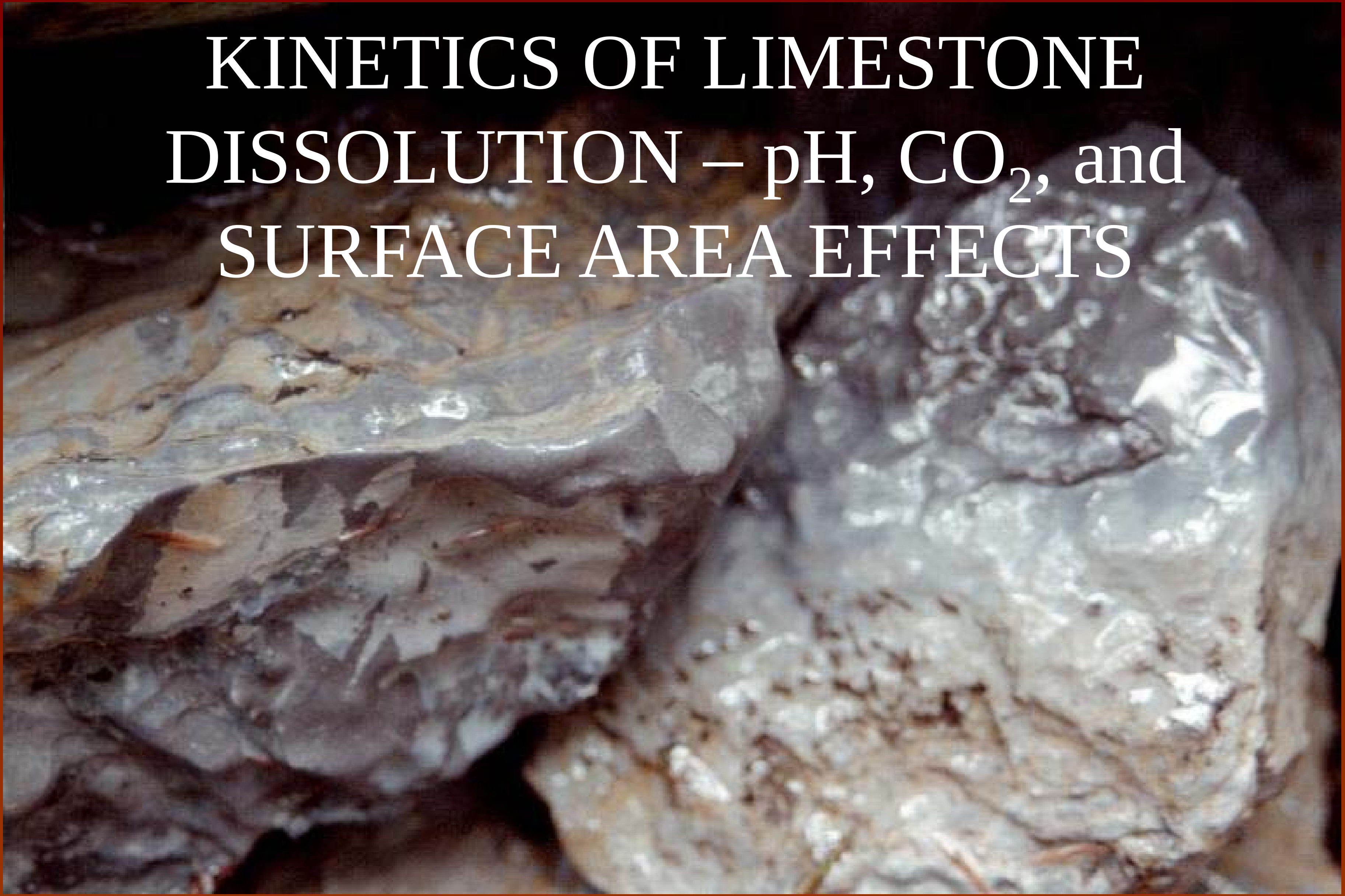
kL,a_TC = kL,a_20 * (1.0241^(TC-20)).

$$kL,a\_20 = (LN((C_1-C_S)/(C_2-C_S))/t) / (1.0241^{(TEMPC - 20)})$$, where C is CO_2 or O_2.

Dissolved O_2, temperature, and pH were measured using submersible electrodes.

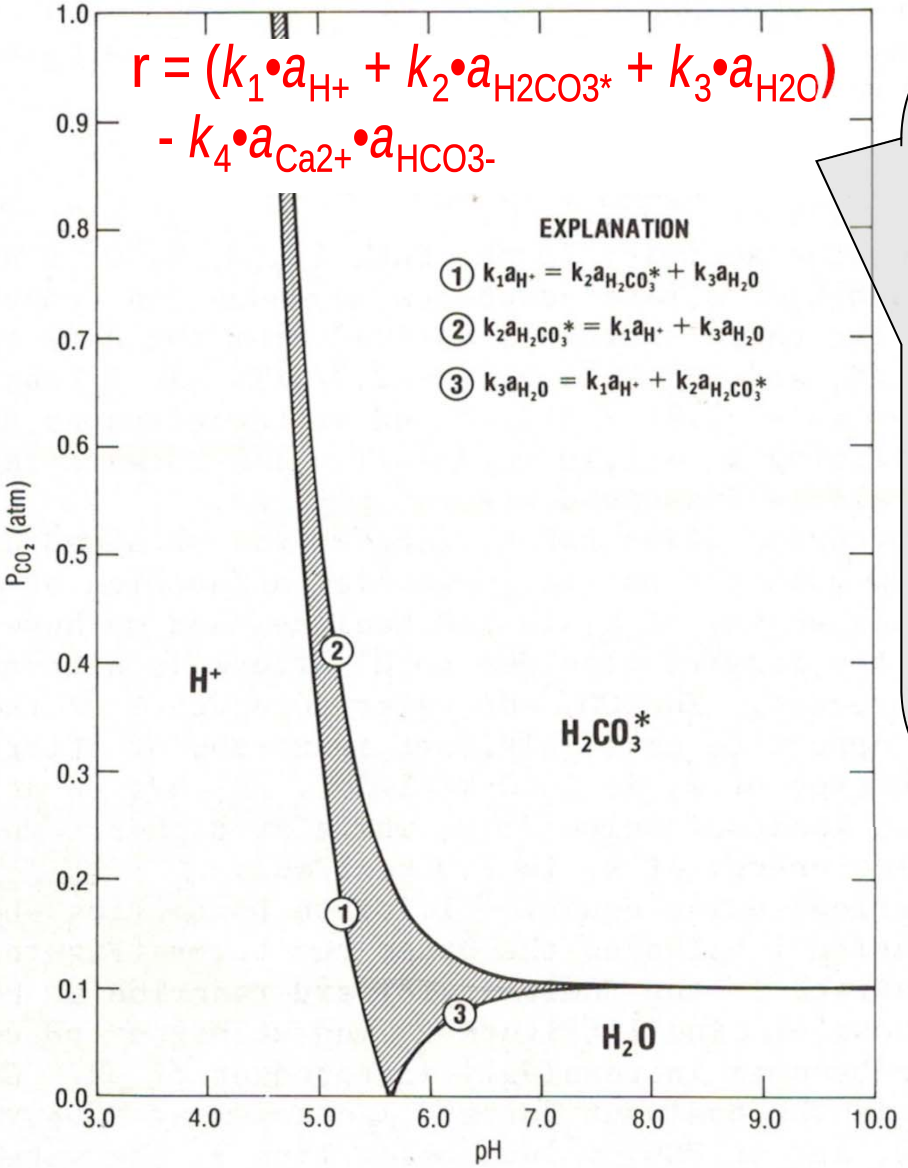
Dissolved CO_2 was computed from alkalinity, pH, and temperature data.

KINETICS OF LIMESTONE DISSOLUTION – pH, CO_2, and SURFACE AREA EFFECTS



Limestone Dissolution Rate Model for AMDTreat ("PWP" model emphasizes pH and CO_2)

$$r = (k_1 \bullet a_{H+} + k_2 \bullet a_{H2CO3*} + k_3 \bullet a_{H2O}) - k_4 \bullet a_{Ca2+} \bullet a_{HCO3-}$$



According to Plummer, Wigley, and Parkhurst (1978), the rate of $CaCO_3$ dissolution is a function of three forward (dissolution) reactions:

$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$ k_1

$CaCO_3 + H_2CO_3^* \rightarrow Ca^{2+} + 2\,HCO_3^-$ k_2

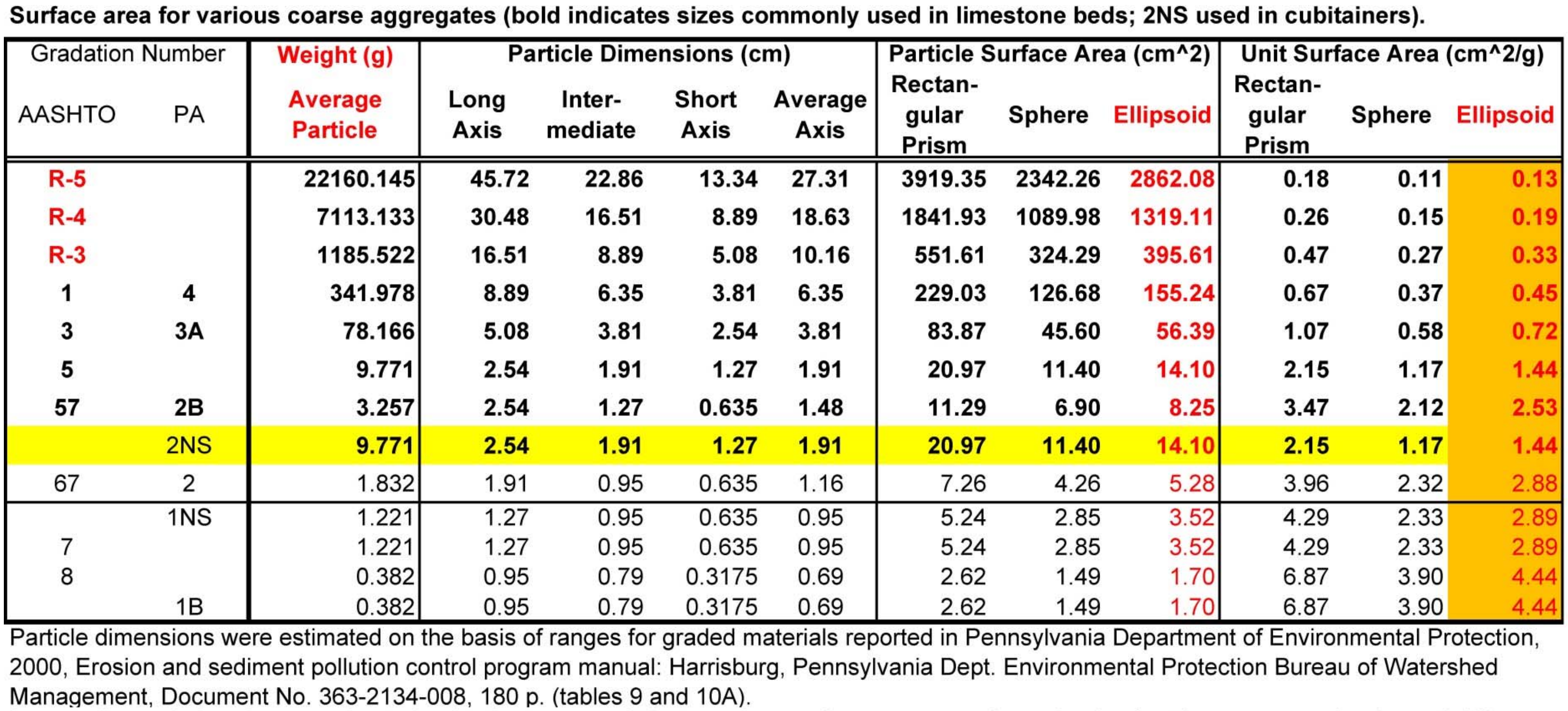
$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^-$ k_3

and the backward (precipitation) reaction:

$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+$ k_4

Although H^+, $H_2CO_3^*$, and H_2O reaction with calcite occur simultaneously, the forward rate is dominated by a single species in the fields shown. More than one species contributes significantly to the forward rate in the gray stippled area. Along the lines labeled 1, 2, and 3, the forward rate attributable to one species balances that of the other two.

Limestone Dissolution Rate Model for AMDTreat (surface area correction for coarse aggregate)



Surface area for various coarse aggregates (bold indicates sizes commonly used in limestone beds; 2NS used in cubitainers).

Gradation Number		Weight (g)	Particle Dimensions (cm)				Particle Surface Area (cm^2)			Unit Surface Area (cm^2/g)		
AASHTO	PA	Average Particle	Long Axis	Inter-mediate	Short Axis	Average Axis	Rectan-gular Prism	Sphere	Ellipsoid	Rectan-gular Prism	Sphere	Ellipsoid
R-5		**22160.145**	**45.72**	**22.86**	**13.34**	**27.31**	**3919.35**	**2342.26**	**2862.08**	**0.18**	**0.11**	**0.13**
R-4		**7113.133**	**30.48**	**16.51**	**8.89**	**18.63**	**1841.93**	**1089.98**	**1319.11**	**0.26**	**0.15**	**0.19**
R-3		**1185.522**	**16.51**	**8.89**	**5.08**	**10.16**	**551.61**	**324.29**	**395.61**	**0.47**	**0.27**	**0.33**
1	**4**	**341.978**	**8.89**	**6.35**	**3.81**	**6.35**	**229.03**	**126.68**	**155.24**	**0.67**	**0.37**	**0.45**
3	**3A**	**78.166**	**5.08**	**3.81**	**2.54**	**3.81**	**83.87**	**45.60**	**56.39**	**1.07**	**0.58**	**0.72**
5		**9.771**	**2.54**	**1.91**	**1.27**	**1.91**	**20.97**	**11.40**	**14.10**	**2.15**	**1.17**	**1.44**
57	**2B**	**3.257**	**2.54**	**1.27**	**0.635**	**1.48**	**11.29**	**6.90**	**8.25**	**3.47**	**2.12**	**2.53**
	2NS	**9.771**	**2.54**	**1.91**	**1.27**	**1.91**	**20.97**	**11.40**	**14.10**	**2.15**	**1.17**	**1.44**
67	2	1.832	1.91	0.95	0.635	1.16	7.26	4.26	5.28	3.96	2.32	2.88
	1NS	1.221	1.27	0.95	0.635	0.95	5.24	2.85	3.52	4.29	2.33	2.89
7		1.221	1.27	0.95	0.635	0.95	5.24	2.85	3.52	4.29	2.33	2.89
8		0.382	0.95	0.79	0.3175	0.69	2.62	1.49	1.70	6.87	3.90	4.44
	1B	0.382	0.95	0.79	0.3175	0.69	2.62	1.49	1.70	6.87	3.90	4.44

Particle dimensions were estimated on the basis of ranges for graded materials reported in Pennsylvania Department of Environmental Protection, 2000, Erosion and sediment pollution control program manual: Harrisburg, Pennsylvania Dept. Environmental Protection Bureau of Watershed Management, Document No. 363-2134-008, 180 p. (tables 9 and 10A).

Plummer, Wigley, and Parkhurst (1978) reported unit surface area (SA) of 44.5 and 96.5 cm^2/g for “coarse” and “fine” particles, respectively, used for empirical testing and development of PWP rate model. These SA values are 100 times larger than those for typical limestone aggregate. *Multiply cm^2/g by 100 g/mol to get surface area (A) units of cm^2/mol used in AMDTreat rate model.*

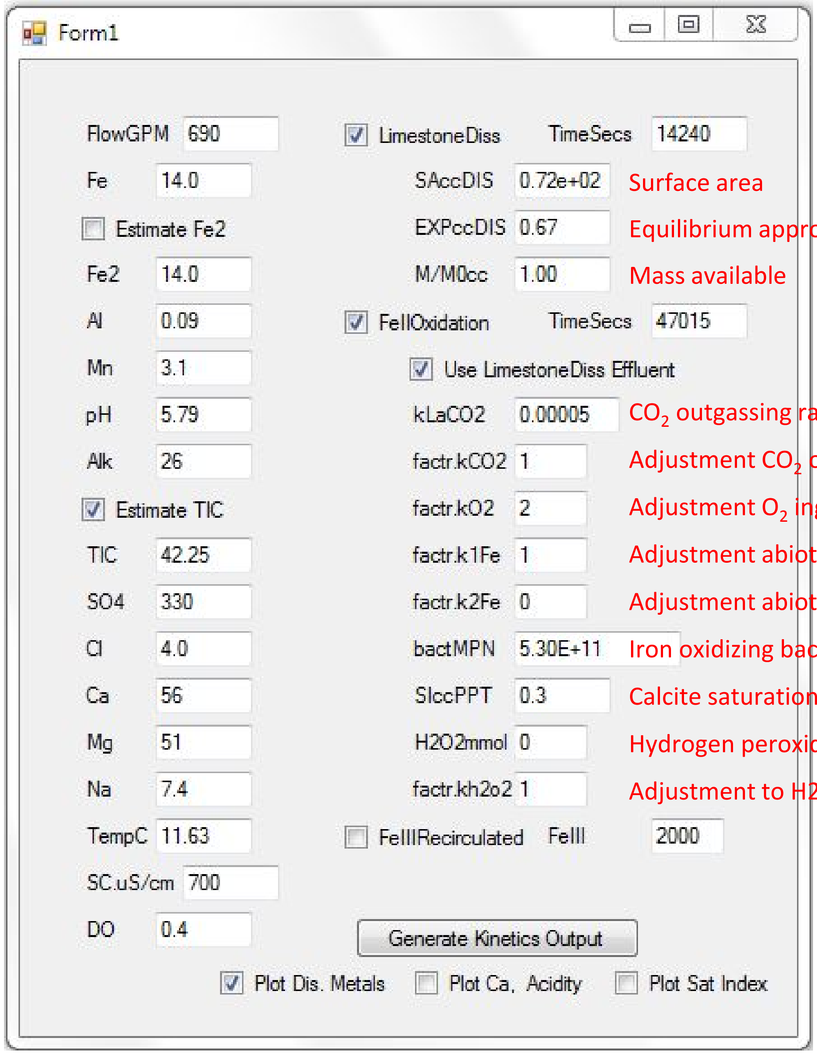
Surface area computed for various geometric forms:

Sphere: 4pi*(Average of Axes/2)^2
Rectangular Prism: 2*(Long Axis*Short Axis)+2*(Long Axis*Intermediate Axis)+2*(Short Axis*Intermediate Axis)
Ellipsoid: (pi*D^2)/S, where D=2*(vol/(4/3pi))^(1/3) S=1.15-0.25E E=Long Axis/D

Volume computed for same geometric forms:

Sphere: 4/3*pi*(Average Axis/2)^3
Rectangular Prism: (Long Axis*Short Axis*Intermediate Axis)
Ellipsoid: 4/3*pi* (Long Axis/2*Short Axis/2*Intermediate Axis/2)
For ellipsoid sphere, this reduces to 0.5236*Long Axis*Short Axis*Intermediate Axis
Santomartino and Webb (2007, AG, 22:2344–2361) estimated volume of ellipsoid as 0.6*volume of rectangular prism of same dimensions.

"2017 Model" For AMDTreat — PHREEQC Coupled Kinetic Models of Limestone Dissolution & Fe^{II} Oxidation



FlowGPM 690
Fe 14.0
☐ Estimate Fe2
Fe2 14.0
Al 0.09
Mn 3.1
pH 5.79
Alk 26
☑ Estimate TIC
TIC 42.25
SO4 330
Cl 4.0
Ca 56
Mg 51
Na 7.4
TempC 11.63
SC.uS/cm 700
DO 0.4

☑ LimestoneDiss TimeSecs 14240
SAccDIS 0.72e+02 Surface area
EXPccDIS 0.67 Equilibrium approach
M/M0cc 1.00 Mass available
☑ FeIIOxidation TimeSecs 47015
☑ Use LimestoneDiss Effluent
kLaCO2 0.00005 CO_2 outgassing rate
factr.kCO2 1 Adjustment CO_2 outgassing rate
factr.kO2 2 Adjustment O_2 ingassing rate (x kLaCO2)
factr.k1Fe 1 Adjustment abiotic homogeneous rate
factr.k2Fe 0 Adjustment abiotic heterogeneous rate
bactMPN 5.30E+11 Iron oxidizing bacteria
SIccPPT 0.3 Calcite saturation limit
H2O2mmol 0 Hydrogen peroxide added
factr.kh2o2 1 Adjustment to H2O2 rate
☐ FeIIIRecirculated FeIII 2000

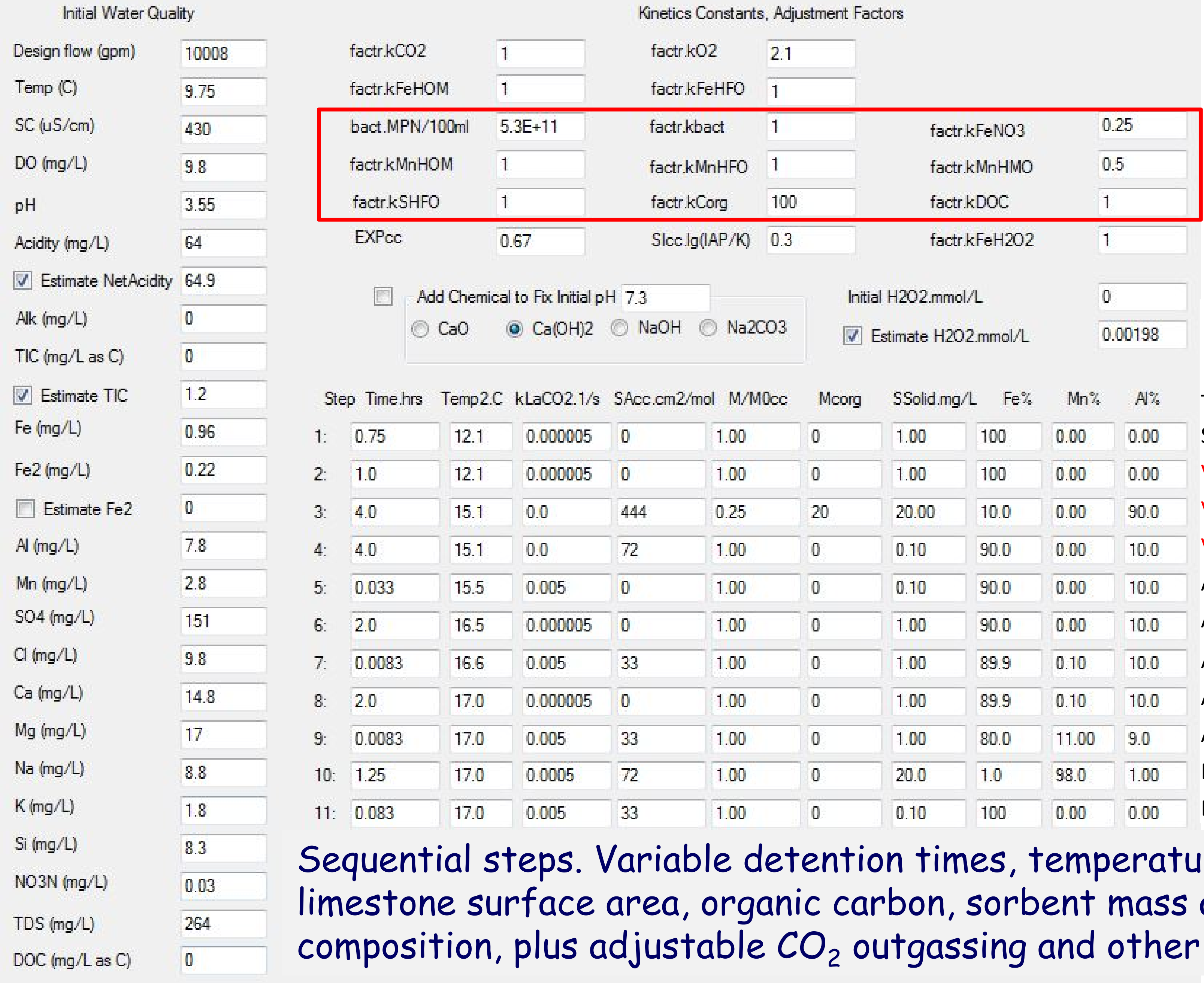
☑ Plot Dis. Metals ☐ Plot Ca, Acidity ☐ Plot Sat Index

Rate models for calcite dissolution, CO_2 outgassing and O_2 ingassing, and Fe^{II} oxidation are combined to evaluate possible reactions in passive treatment systems.

Limestone+FeII.exe

Can simulate limestone treatment followed by gas exchange and Fe^{II} oxidation in an aerobic pond or aerobic wetland, or the independent treatment steps (not in sequence).

New "User-Friendly" Model:



Initial Water Quality

Design flow (gpm)	10008
Temp (C)	9.75
SC (uS/cm)	430
DO (mg/L)	9.8
pH	3.55
Acidity (mg/L)	64
☑ Estimate NetAcidity	64.9
Alk (mg/L)	0
TIC (mg/L as C)	0
☑ Estimate TIC	1.2
Fe (mg/L)	0.96
Fe2 (mg/L)	0.22
☐ Estimate Fe2	0
Al (mg/L)	7.8
Mn (mg/L)	2.8
SO4 (mg/L)	151
Cl (mg/L)	9.8
Ca (mg/L)	14.8
Mg (mg/L)	17
Na (mg/L)	8.8
K (mg/L)	1.8
Si (mg/L)	8.3
NO3N (mg/L)	0.03
TDS (mg/L)	264
DOC (mg/L as C)	0

Kinetics Constants, Adjustment Factors

factr.kCO2	1	factr.kO2	2.1		
factr.kFeHOM	1	factr.kFeHFO	1		
bact.MPN/100ml	5.3E+11	factr.kbact	1	factr.kFeNO3	0.25
factr.kMnHOM	1	factr.kMnHFO	1	factr.kMnHMO	0.5
factr.kSHFO	1	factr.kCorg	100	factr.kDOC	1
EXPcc	0.67	SIcc.lg(IAP/K)	0.3	factr.kFeH2O2	1

☐ Add Chemical to Fix Initial pH 7.3

○ CaO ● Ca(OH)2 ○ NaOH ○ Na2CO3

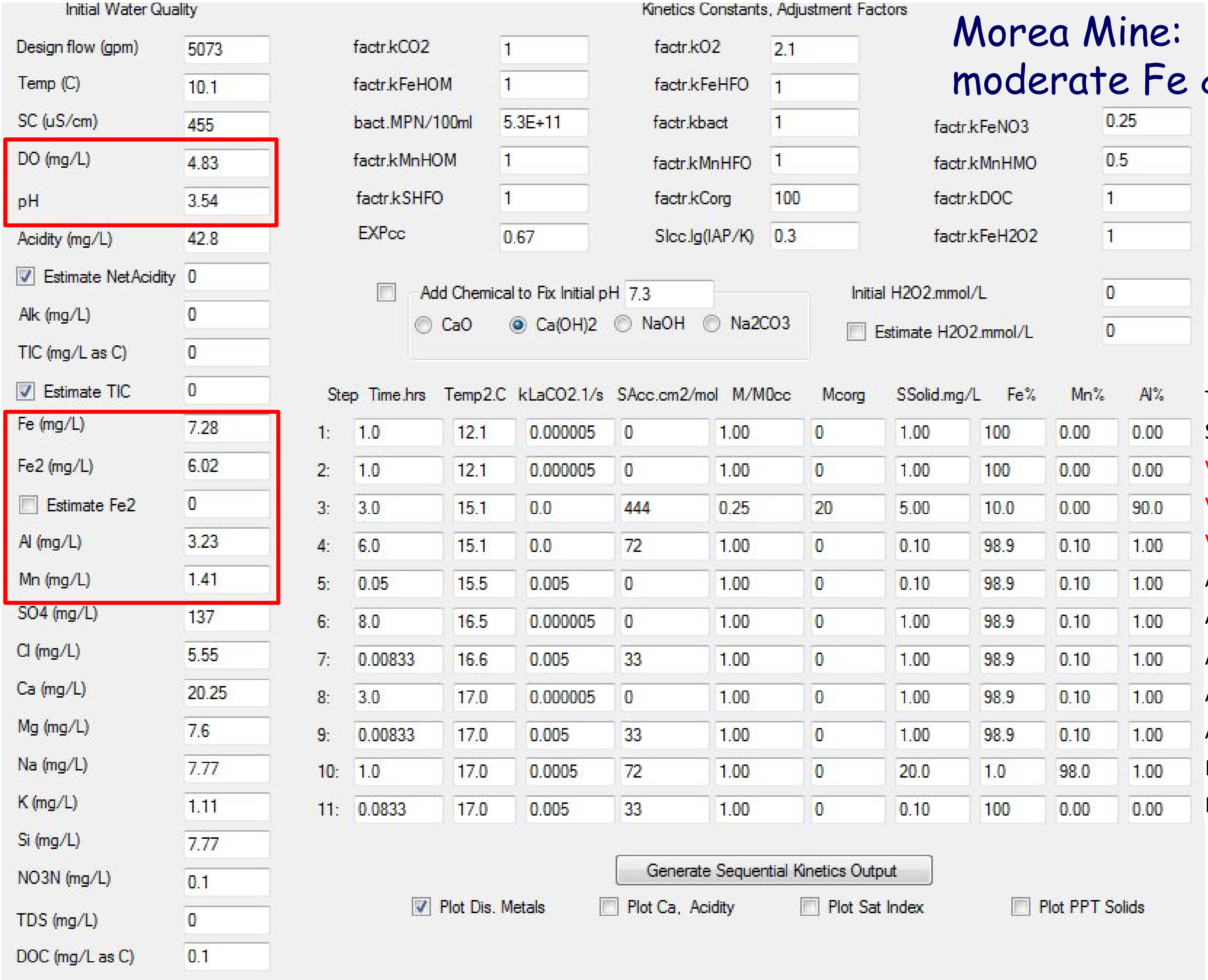
Initial H2O2.mmol/L 0

☑ Estimate H2O2.mmol/L 0.00198

Step	Time.hrs	Temp2.C	kLaCO2.1/s	SAcc.cm2/mol	M/M0cc	Mcorg	SSolid.mg/L	Fe%	Mn%	Al%	Treatment
1:	0.75	12.1	0.000005	0	1.00	0	1.00	100	0.00	0.00	Sedimentation pond
2:	1.0	12.1	0.000005	0	1.00	0	1.00	100	0.00	0.00	VFP water
3:	4.0	15.1	0.0	444	0.25	20	20.00	10.0	0.00	90.0	VFP compost
4:	4.0	15.1	0.0	72	1.00	0	0.10	90.0	0.00	10.0	VFP limestone
5:	0.033	15.5	0.005	0	1.00	0	0.10	90.0	0.00	10.0	Aeration cascades
6:	2.0	16.5	0.000005	0	1.00	0	1.00	90.0	0.00	10.0	Aerobic Wetland
7:	0.0083	16.6	0.005	33	1.00	0	1.00	89.9	0.10	10.0	Aeration, LS riprap
8:	2.0	17.0	0.000005	0	1.00	0	1.00	89.9	0.10	10.0	Aerobic Wetland
9:	0.0083	17.0	0.005	33	1.00	0	1.00	80.0	11.00	9.0	Aeration, LS riprap
10:	1.25	17.0	0.0005	72	1.00	0	20.0	1.0	98.0	1.00	Mn removal bed
11:	0.083	17.0	0.005	33	1.00	0	0.10	100	0.00	0.00	Ditch, LS riprap

Sequential steps. Variable detention times, temperature, limestone surface area, organic carbon, sorbent mass and composition, plus adjustable CO_2 outgassing and other rates.

"VFP" + Aerobic Pond + Wetlands + Mn-Removal Bed



Morea Mine:
moderate Fe & Al

Initial Water Quality

Design flow (gpm)	5073
Temp (C)	10.1
SC (uS/cm)	455
DO (mg/L)	4.83
pH	3.54
Acidity (mg/L)	42.8
☑ Estimate NetAcidity	0
Alk (mg/L)	0
TIC (mg/L as C)	0
☑ Estimate TIC	0
Fe (mg/L)	7.28
Fe2 (mg/L)	6.02
☐ Estimate Fe2	0
Al (mg/L)	3.23
Mn (mg/L)	1.41
SO4 (mg/L)	137
Cl (mg/L)	5.55
Ca (mg/L)	20.25
Mg (mg/L)	7.6
Na (mg/L)	7.77
K (mg/L)	1.11
Si (mg/L)	7.77
NO3N (mg/L)	0.1
TDS (mg/L)	0
DOC (mg/L as C)	0.1

Kinetics Constants, Adjustment Factors

factr.kCO2	1	factr.kO2	2.1		
factr.kFeHOM	1	factr.kFeHFO	1		
bact.MPN/100ml	5.3E+11	factr.kbact	1	factr.kFeNO3	0.25
factr.kMnHOM	1	factr.kMnHFO	1	factr.kMnHMO	0.5
factr.kSHFO	1	factr.kCorg	100	factr.kDOC	1
EXPcc	0.67	SIcc.lg(IAP/K)	0.3	factr.kFeH2O2	1

☐ Add Chemical to Fix Initial pH 7.3
○ CaO ● Ca(OH)2 ○ NaOH ○ Na2CO3

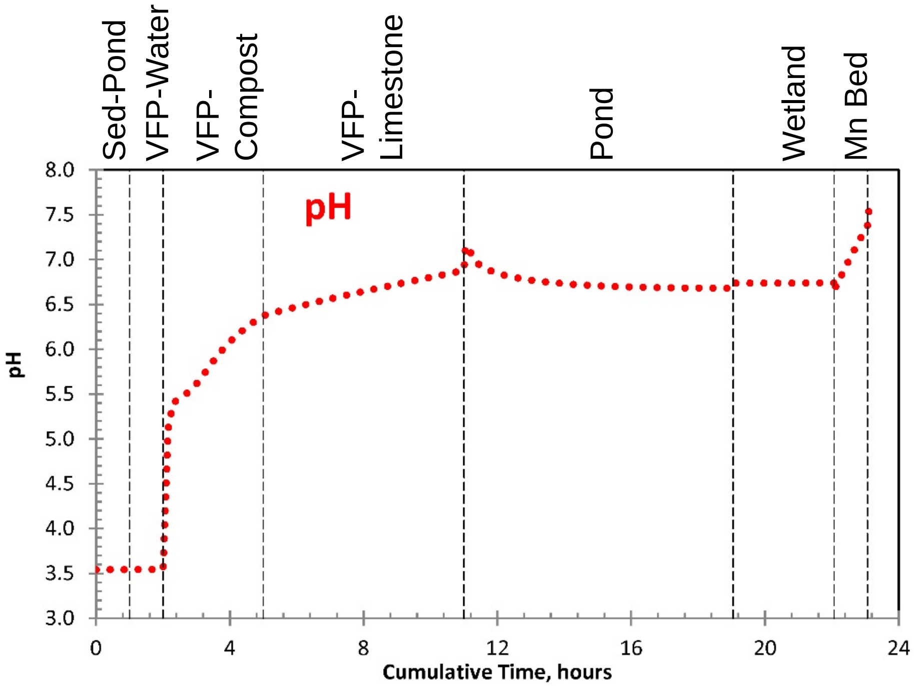
Initial H2O2.mmol/L 0
☐ Estimate H2O2.mmol/L 0

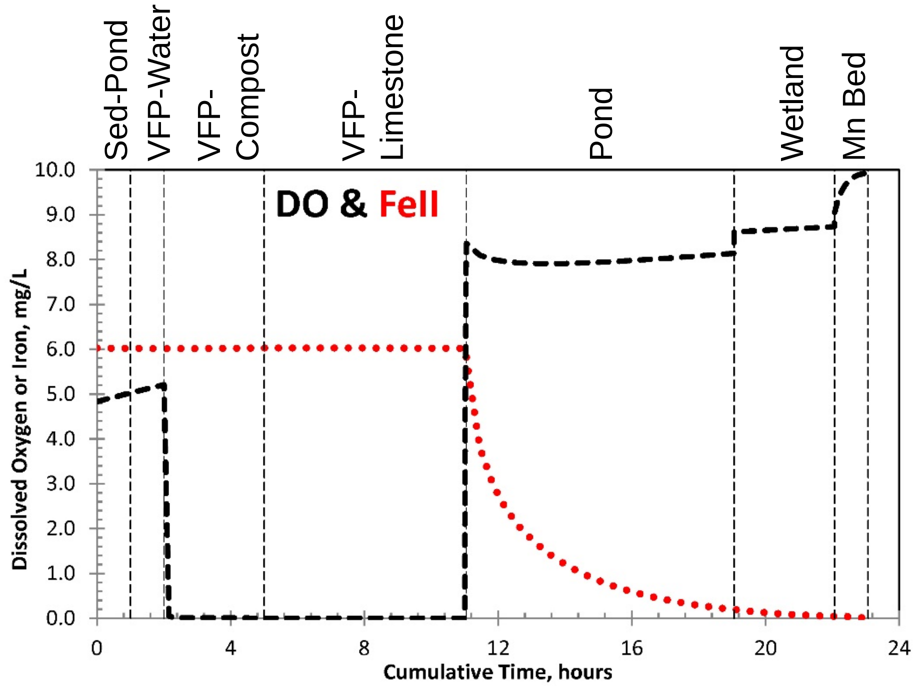
Step	Time.hrs	Temp2.C	kLaCO2.1/s	SAcc.cm2/mol	M/M0cc	Mcorg	SSolid.mg/L	Fe%	Mn%	Al%	Treatment
1:	1.0	12.1	0.000005	0	1.00	0	1.00	100	0.00	0.00	Sedimentation pond
2:	1.0	12.1	0.000005	0	1.00	0	1.00	100	0.00	0.00	VFP water
3:	3.0	15.1	0.0	444	0.25	20	5.00	10.0	0.00	90.0	VFP compost
4:	6.0	15.1	0.0	72	1.00	0	0.10	98.9	0.10	1.00	VFP limestone
5:	0.05	15.5	0.005	0	1.00	0	0.10	98.9	0.10	1.00	Aeration cascades
6:	8.0	16.5	0.000005	0	1.00	0	1.00	98.9	0.10	1.00	Aerobic Wetland
7:	0.00833	16.6	0.005	33	1.00	0	1.00	98.9	0.10	1.00	Aeration, LS riprap
8:	3.0	17.0	0.000005	0	1.00	0	1.00	98.9	0.10	1.00	Aerobic Wetland
9:	0.00833	17.0	0.005	33	1.00	0	1.00	98.9	0.10	1.00	Aeration, LS riprap
10:	1.0	17.0	0.0005	72	1.00	0	20.0	1.0	98.0	1.00	Mn removal bed
11:	0.0833	17.0	0.005	33	1.00	0	0.10	100	0.00	0.00	Ditch, LS riprap

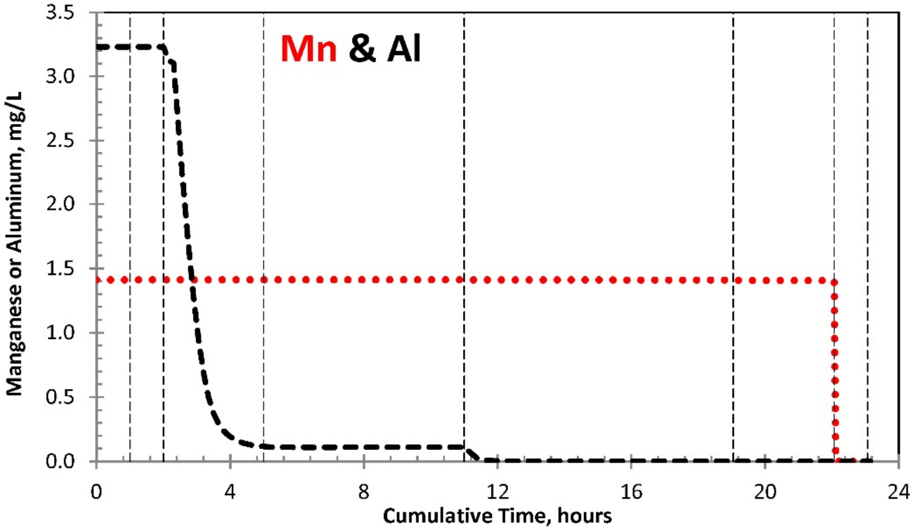
☑ Plot Dis. Metals ☐ Plot Ca, Acidity ☐ Plot Sat Index ☐ Plot PPT Solids

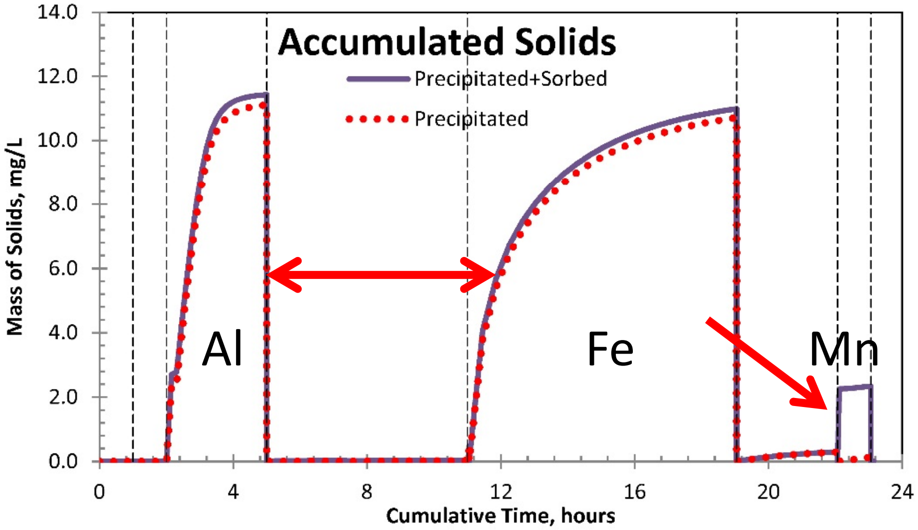
"VFP" + Pond + Wetlands + Mn-Removal Bed

Morea Mine Discharge, Mill Creek Watershed









"VFP" + Pond + Wetlands + Mn-Removal Bed

Morea Discharge, Mill Creek Watershed

Step	Treatment	flow rate, ft3/s	deten-tion time, secs	deten-tion time, hr	depth, ft	porosity	volume, ft3	area of water surface, ft2	area of water surface, acres	AASHTO lime-stone particle size	CaCO3 fraction in bulk, M/M0cc	lime-stone mass, tons	compost organics mass, tons
1	Sedimentation pond	11.30	3600	1.00	4.00	1.00	40697	10174	0.23		1.00	0	0
2	VFP water	11.30	3600	1.00	2.00	1.00	40697				1.00	0	0
3	VFP compost	11.30	10800	3.00	2.00	0.45	271310			8	0.25	3086	6244
4	VFP limestone	11.30	21600	6.00	4.00	0.45	542620	106828	2.45	3	1.00	24686	0
5	Aeration	11.30	180	0.05	0.10	1.00	2035	20348	0.47		1.00	0	0
6	Oxidation Pond	11.30	28800	8.00	4.00	1.00	325572	81393	1.87		1.00	0	0
7	Aeration	11.30	30	0.01	0.10	0.45	754	7536	0.17	R-3	1.00	34	0
8	Aerobic Wetland	11.30	10800	3.00	1.00	1.00	122090	122090	2.80		1.00	0	0
9	Aeration	11.30	30	0.01	0.10	0.45	754	7536	0.17	R-3	1.00	34	0
10	Mn removal bed	11.30	3600	1.00	0.50	0.45	90437	180873	4.15	3	1.00	4114	0
11	Ditch	11.30	300	0.08	0.50	0.45	7536	15073	0.35	R-3	1.00	343	0
1 to 11	**Total:**			**23.15**	**18.30**			**551852**	**12.66**			**32298**	**6244**

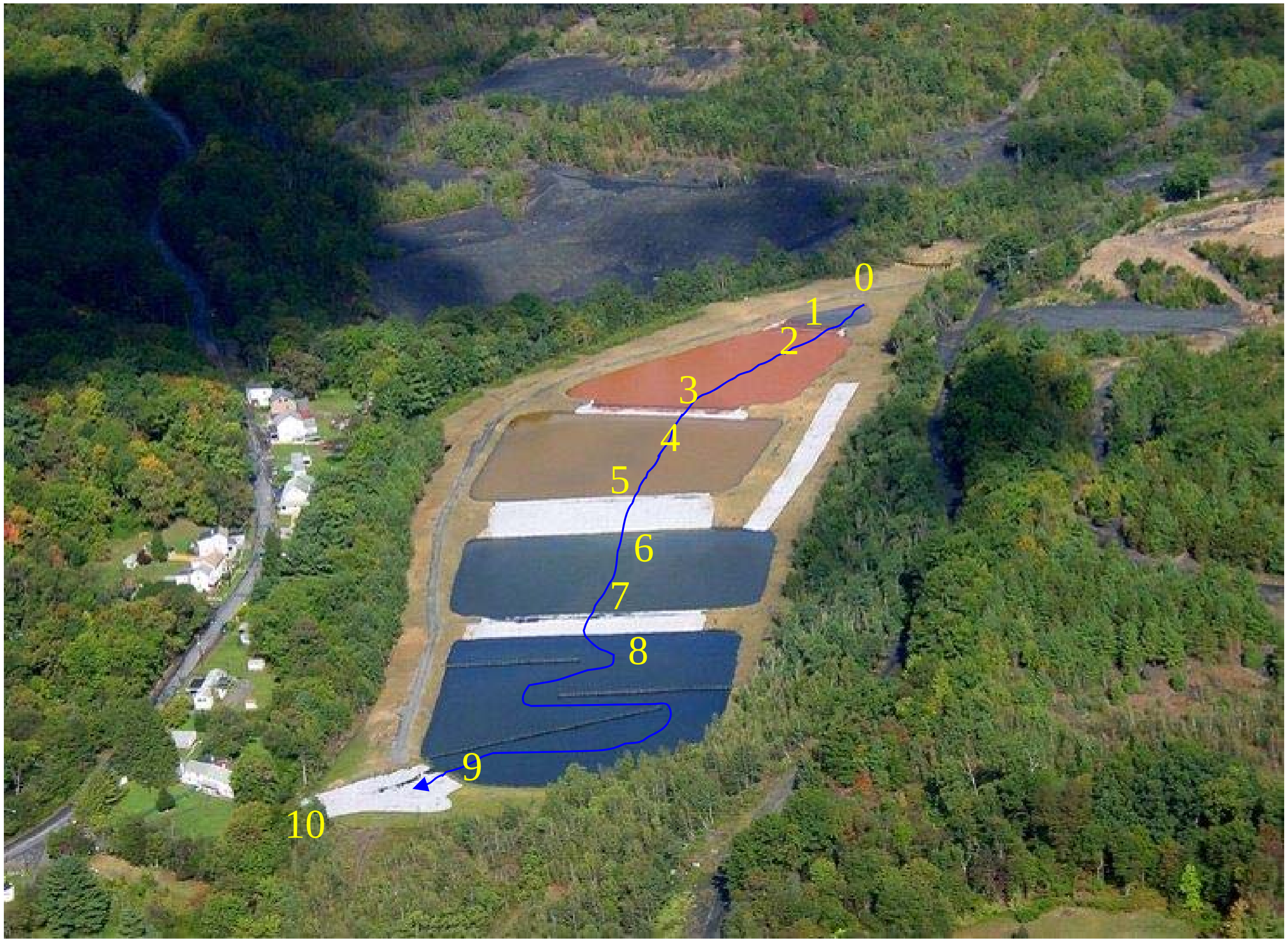
AASHTO average particle diameter: R-3, 4 inch (10.16 cm); 3, 1.5 inch (3.81 cm); 8, 0.25 inch (0.69 cm).

Volume is computed as the product of flow rate and detention time. Design flow rate of 5073 gal/min = 11.30 ft^3/s.

Area is computed as the volume divided by depth; for the VFP, volumes and depths for each of the three steps are summed before computing area.

Masses of limestone and compost are computed as the product of their respective volume and bulk density.

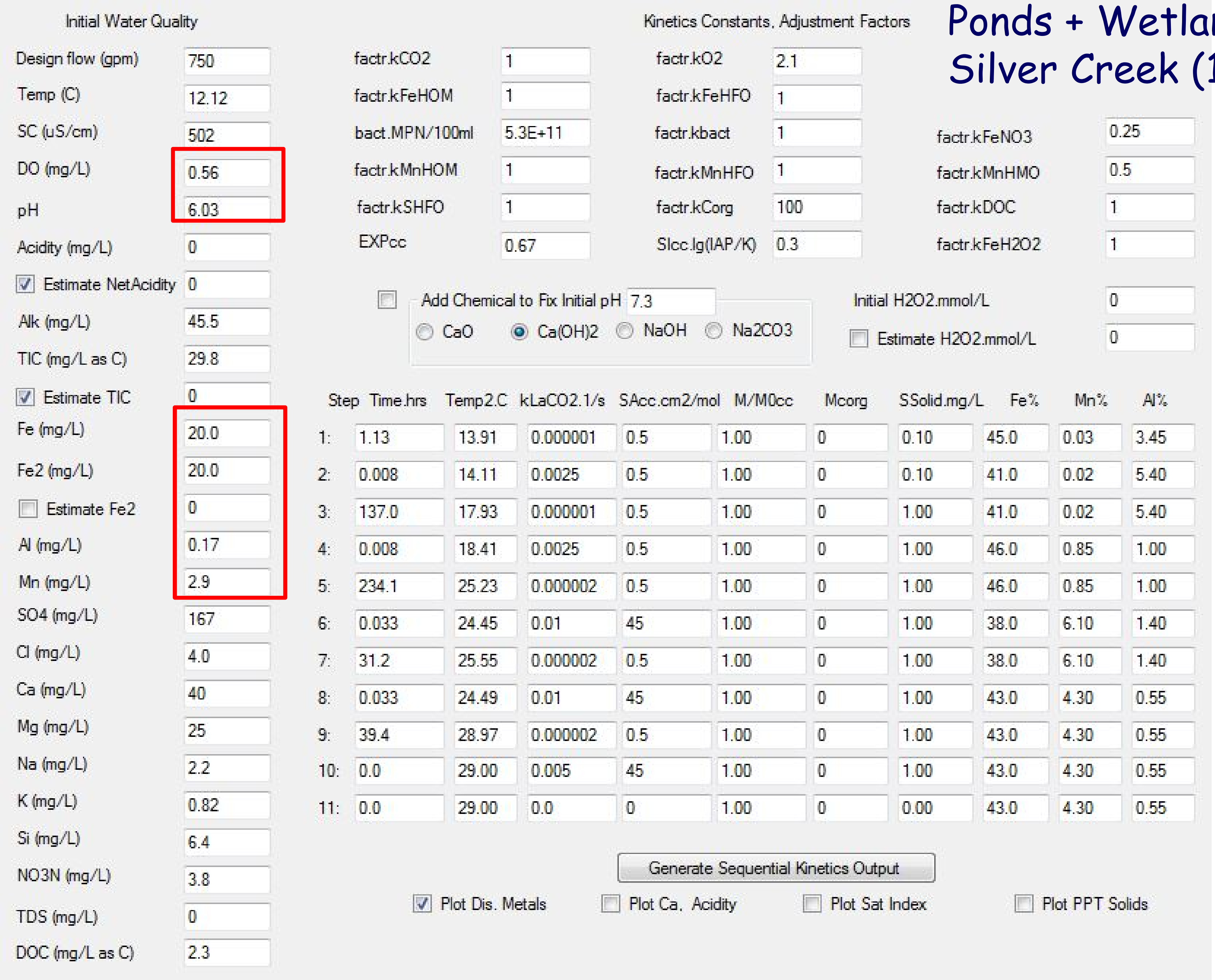
PHREEQC Coupled Kinetic Models Sequential Steps—Silver Creek Aerobic Wetlands



Step	Treatment
0	Untreated
1	Pond
2	Cascade
3	Pond
4	Cascade
5	Pond
6	Riprap
7	Wetland
8	Riprap
9	Wetland
10	Riprap
11	NULL

PHREEQC Coupled Kinetic Models--Sequential Steps

Ponds + Wetlands
Silver Creek (160808)



Initial Water Quality

Design flow (gpm)	750
Temp (C)	12.12
SC (uS/cm)	502
DO (mg/L)	0.56
pH	6.03
Acidity (mg/L)	0
☑ Estimate NetAcidity	0
Alk (mg/L)	45.5
TIC (mg/L as C)	29.8
☑ Estimate TIC	0
Fe (mg/L)	20.0
Fe2 (mg/L)	20.0
☐ Estimate Fe2	0
Al (mg/L)	0.17
Mn (mg/L)	2.9
SO4 (mg/L)	167
Cl (mg/L)	4.0
Ca (mg/L)	40
Mg (mg/L)	25
Na (mg/L)	2.2
K (mg/L)	0.82
Si (mg/L)	6.4
NO3N (mg/L)	3.8
TDS (mg/L)	0
DOC (mg/L as C)	2.3

Kinetics Constants, Adjustment Factors

factr.kCO2	1	factr.kO2	2.1		
factr.kFeHOM	1	factr.kFeHFO	1		
bact.MPN/100ml	5.3E+11	factr.kbact	1	factr.kFeNO3	0.25
factr.kMnHOM	1	factr.kMnHFO	1	factr.kMnHMO	0.5
factr.kSHFO	1	factr.kCorg	100	factr.kDOC	1
EXPcc	0.67	SIcc.lg(IAP/K)	0.3	factr.kFeH2O2	1

☐ Add Chemical to Fix Initial pH 7.3

○ CaO ● Ca(OH)2 ○ NaOH ○ Na2CO3

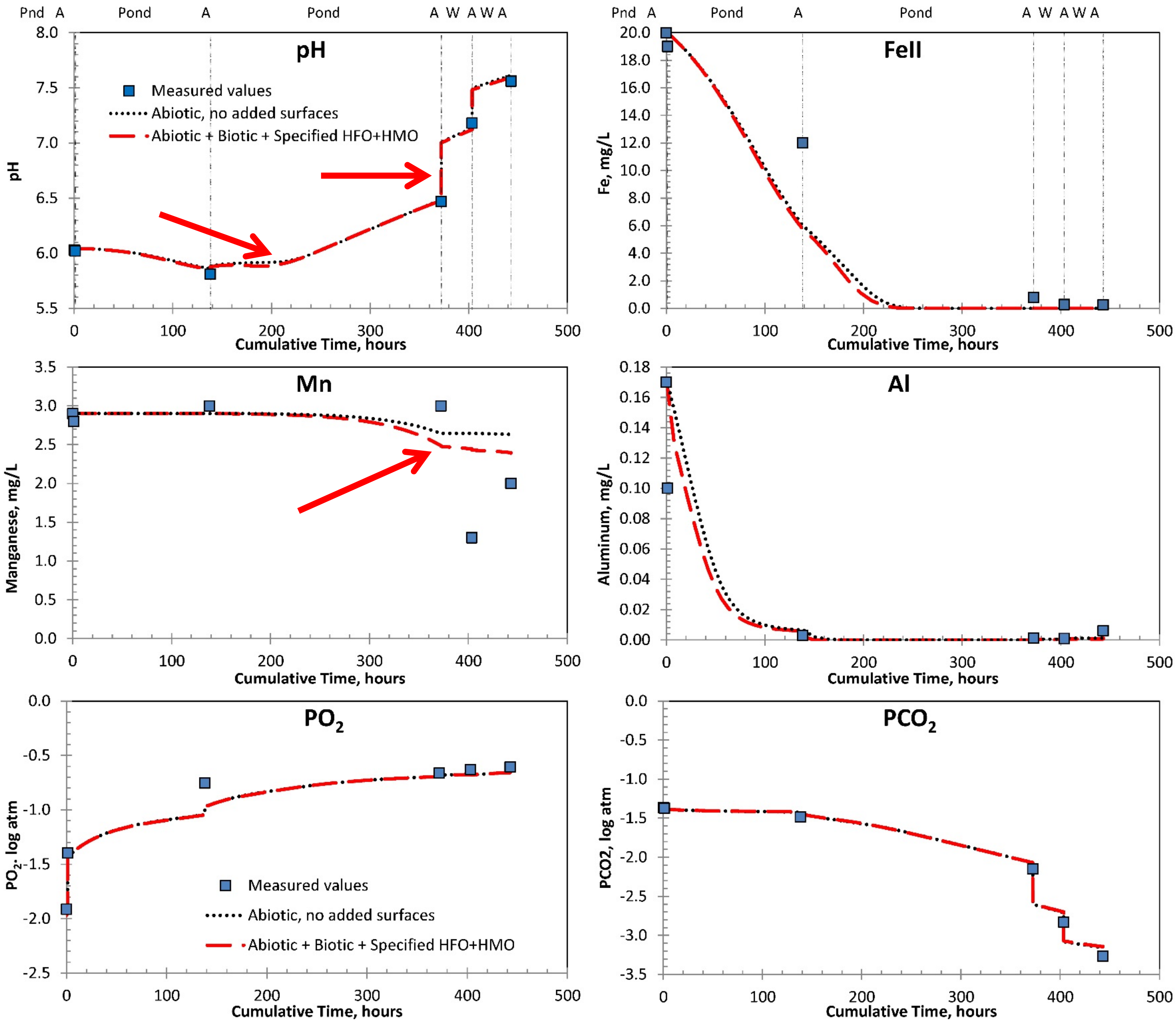
Initial H2O2.mmol/L 0

☐ Estimate H2O2.mmol/L 0

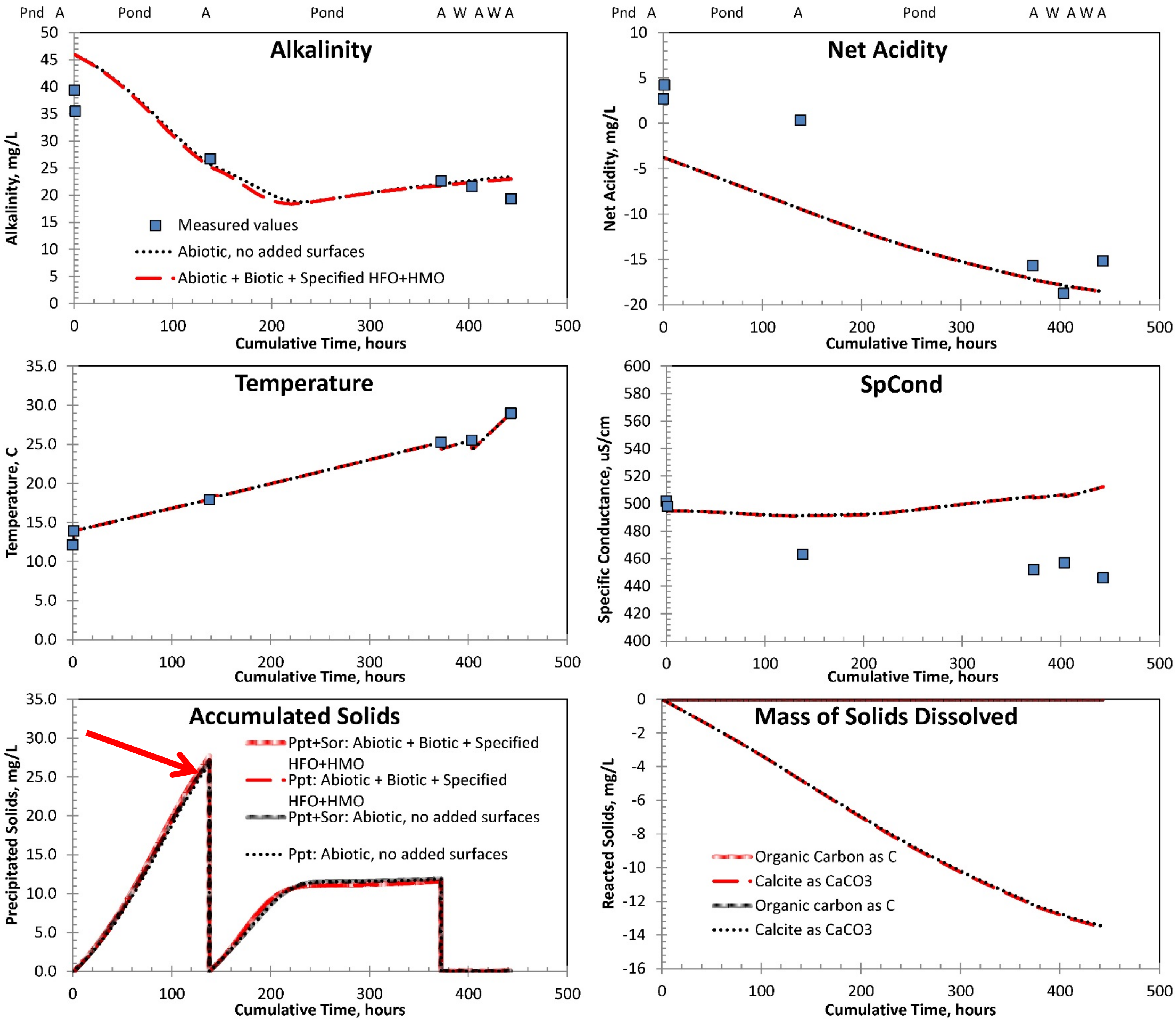
Step	Time.hrs	Temp2.C	kLaCO2.1/s	SAcc.cm2/mol	M/M0cc	Mcorg	SSolid.mg/L	Fe%	Mn%	Al%	Treatment
1:	1.13	13.91	0.000001	0.5	1.00	0	0.10	45.0	0.03	3.45	Pond
2:	0.008	14.11	0.0025	0.5	1.00	0	0.10	41.0	0.02	5.40	Aeration cascades
3:	137.0	17.93	0.000001	0.5	1.00	0	1.00	41.0	0.02	5.40	Pond
4:	0.008	18.41	0.0025	0.5	1.00	0	1.00	46.0	0.85	1.00	Aeration cascades
5:	234.1	25.23	0.000002	0.5	1.00	0	1.00	46.0	0.85	1.00	Pond
6:	0.033	24.45	0.01	45	1.00	0	1.00	38.0	6.10	1.40	Riprap cascades
7:	31.2	25.55	0.000002	0.5	1.00	0	1.00	38.0	6.10	1.40	Aerobic Wetland
8:	0.033	24.49	0.01	45	1.00	0	1.00	43.0	4.30	0.55	Riprap cascades
9:	39.4	28.97	0.000002	0.5	1.00	0	1.00	43.0	4.30	0.55	Aerobic Wetland
10:	0.0	29.00	0.005	45	1.00	0	1.00	43.0	4.30	0.55	Ditch, riprap
11:	0.0	29.00	0.0	0	1.00	0	0.00	43.0	4.30	0.55	NULL

☑ Plot Dis. Metals ☐ Plot Ca, Acidity ☐ Plot Sat Index ☐ Plot PPT Solids

Silver Creek Aerobic Wetlands



Silver Creek Aerobic Wetlands

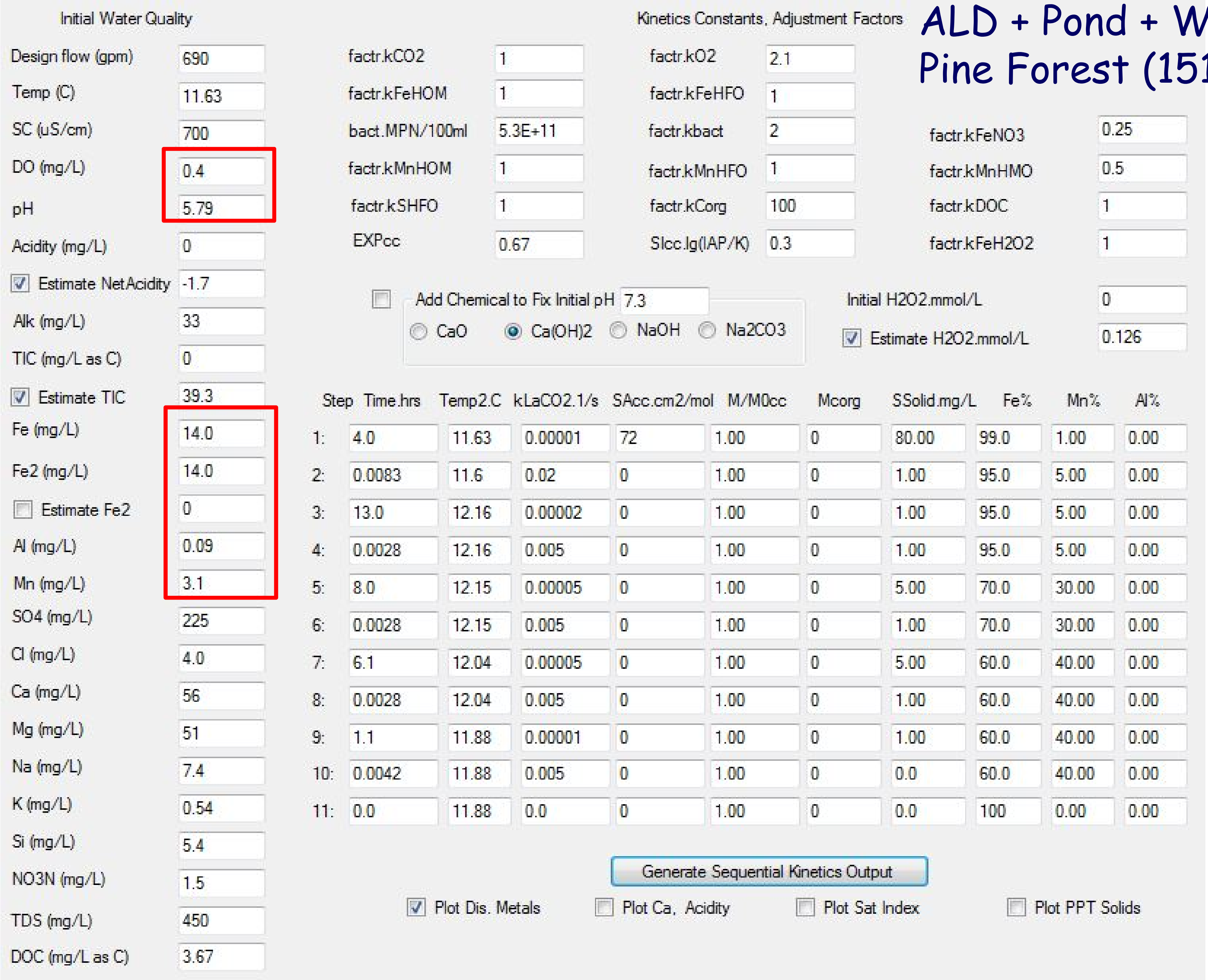


PHREEQC Coupled Kinetic Models Sequential Steps—Pine Forest ALD + Pond + Aerobic Wetlands

Step	Treatment
0	Untreated
1	ALD
2	Riprap
3	Pond
4	Riprap
5	Wetland
6	Cascade
7	Wetland
8	Cascade
9	Wetland
10	Riprap
11	NULL

PHREEQC Coupled Kinetic Models--Sequential Steps

ALD + Pond + Wetlands
Pine Forest (151212)



Initial Water Quality

Design flow (gpm)	690
Temp (C)	11.63
SC (uS/cm)	700
DO (mg/L)	0.4
pH	5.79
Acidity (mg/L)	0
☑ Estimate NetAcidity	-1.7
Alk (mg/L)	33
TIC (mg/L as C)	0
☑ Estimate TIC	39.3
Fe (mg/L)	14.0
Fe2 (mg/L)	14.0
☐ Estimate Fe2	0
Al (mg/L)	0.09
Mn (mg/L)	3.1
SO4 (mg/L)	225
Cl (mg/L)	4.0
Ca (mg/L)	56
Mg (mg/L)	51
Na (mg/L)	7.4
K (mg/L)	0.54
Si (mg/L)	5.4
NO3N (mg/L)	1.5
TDS (mg/L)	450
DOC (mg/L as C)	3.67

Kinetics Constants, Adjustment Factors

factr.kCO2	1	factr.kO2	2.1		
factr.kFeHOM	1	factr.kFeHFO	1		
bact.MPN/100ml	5.3E+11	factr.kbact	2	factr.kFeNO3	0.25
factr.kMnHOM	1	factr.kMnHFO	1	factr.kMnHMO	0.5
factr.kSHFO	1	factr.kCorg	100	factr.kDOC	1
EXPcc	0.67	SIcc.lg(IAP/K)	0.3	factr.kFeH2O2	1

☐ Add Chemical to Fix Initial pH 7.3

○ CaO ● Ca(OH)2 ○ NaOH ○ Na2CO3

Initial H2O2.mmol/L 0

☑ Estimate H2O2.mmol/L 0.126

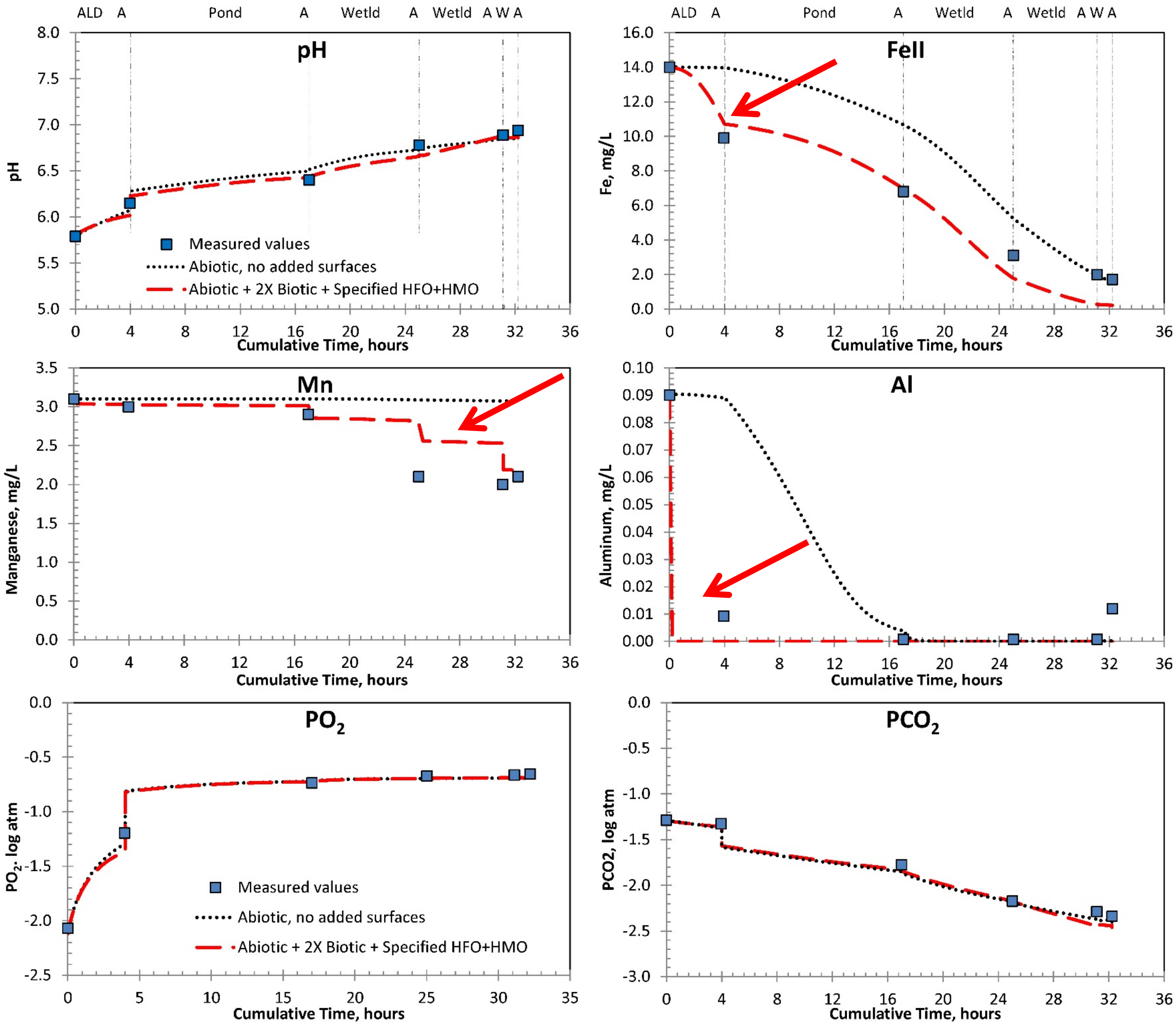
Step	Time.hrs	Temp2.C	kLaCO2.1/s	SAcc.cm2/mol	M/M0cc	Mcorg	SSolid.mg/L	Fe%	Mn%	Al%
1:	4.0	11.63	0.00001	72	1.00	0	80.00	99.0	1.00	0.00
2:	0.0083	11.6	0.02	0	1.00	0	1.00	95.0	5.00	0.00
3:	13.0	12.16	0.00002	0	1.00	0	1.00	95.0	5.00	0.00
4:	0.0028	12.16	0.005	0	1.00	0	1.00	95.0	5.00	0.00
5:	8.0	12.15	0.00005	0	1.00	0	5.00	70.0	30.00	0.00
6:	0.0028	12.15	0.005	0	1.00	0	1.00	70.0	30.00	0.00
7:	6.1	12.04	0.00005	0	1.00	0	5.00	60.0	40.00	0.00
8:	0.0028	12.04	0.005	0	1.00	0	1.00	60.0	40.00	0.00
9:	1.1	11.88	0.00001	0	1.00	0	1.00	60.0	40.00	0.00
10:	0.0042	11.88	0.005	0	1.00	0	0.0	60.0	40.00	0.00
11:	0.0	11.88	0.0	0	1.00	0	0.0	100	0.00	0.00

☑ Plot Dis. Metals ☐ Plot Ca, Acidity ☐ Plot Sat Index ☐ Plot PPT Solids

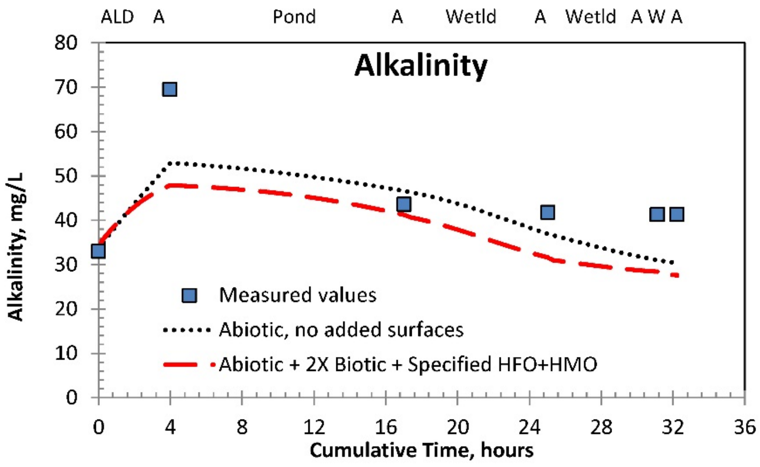
Treatment

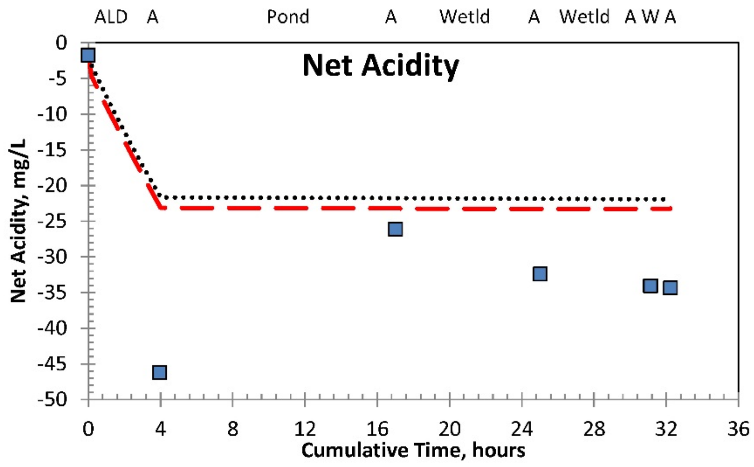
ALD
Aeration, LS riprap
Pond
Riprap
Aerobic Wetland
Cascades
Aerobic Wetland
Cascades
Aerobic Wetland
Ditch, LS riprap
NULL

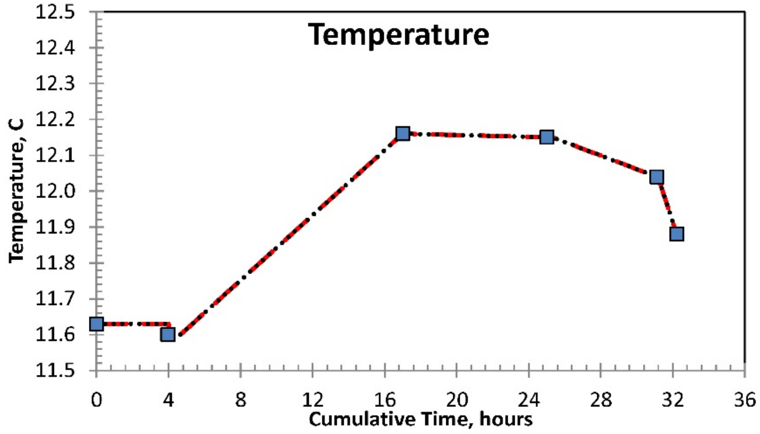
Pine Forest ALD + Aerobic Wetlands

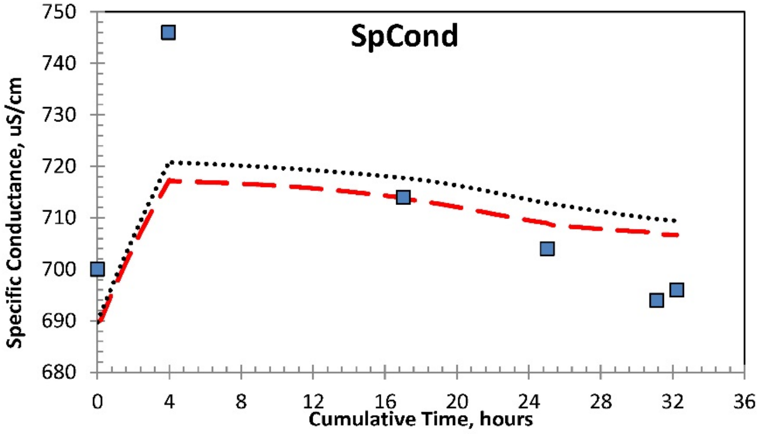


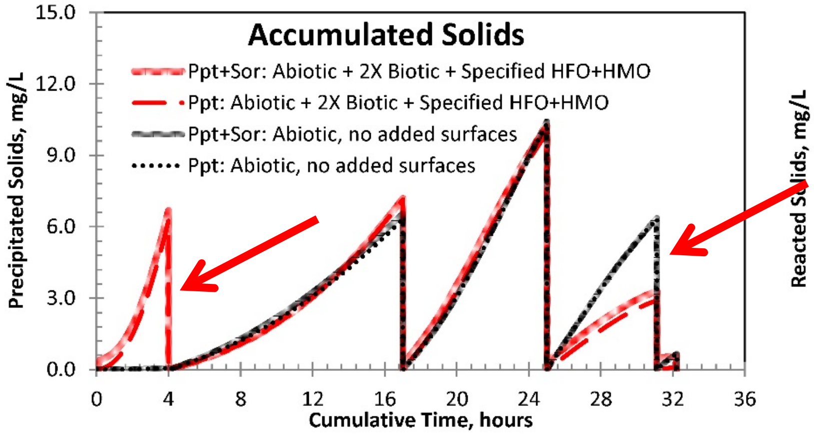
Pine Forest ALD + Aerobic Wetlands

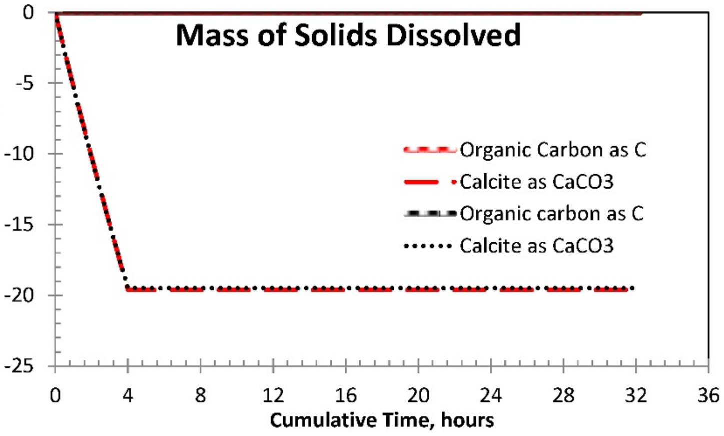












Demonstrations

- Oak Hill Aeration experiments (parallel):
  - ✓ Aer3, Aer2, Aer1, Aer0, H_2O_2
- Morea (sequential treatment steps):
  - ✓ VFP + A + Pond + A + Wetlands + A + Mn bed + A
- Pine Forest (sequential treatment steps):
  - ✓ ALD + A + Pond + A + 3x(Wetlands + A)

Conclusions

- ✓ Geochemical kinetics tools using PHREEQC have been developed to evaluate mine effluent treatment options.
- ✓ Graphical and tabular output indicates the pH and solute concentrations in effluent.
- ✓ By adjusting kinetic variables or chemical dosing, various passive and/or active treatment strategies can be simulated.
- ✓ AMDTreat cost-analysis software can be used to evaluate the feasibility for installation and operation of treatments that produce the desired effluent quality.

Disclaimer / Release Plans

“Although this software program has been used by the U.S. Geological Survey (USGS), no warranty, expressed or implied, is made by the USGS or the U.S. Government as to the accuracy and functioning of the program and related program material nor shall the fact of distribution constitute any such warranty, and no responsibility is assumed by the USGS in connection therewith.”

- ✓ FY2017-2018 Development, beta testing and review.
- ✓ FY2018 Provisional USGS “software release” planned:
- ✓ https://water.usgs.gov/software/lists/geochemical
- ✓ FY2019 Incorporation of PHREEQC treatment simulations with AMDTreat to be released by OSMRE:
- ✓ http://amd.osmre.gov/

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