Hydrological and Geochemical Investigations in Support of Watershed Restoration in Upper Schuylkill River

- ✓ Stream water quantity: Losses of surface water to underground mines can eliminate or reduce streamflow.

- ✓ Stream water quality: Elevated sulfate and metals in CMD degrade water quality and aquatic ecosystems.

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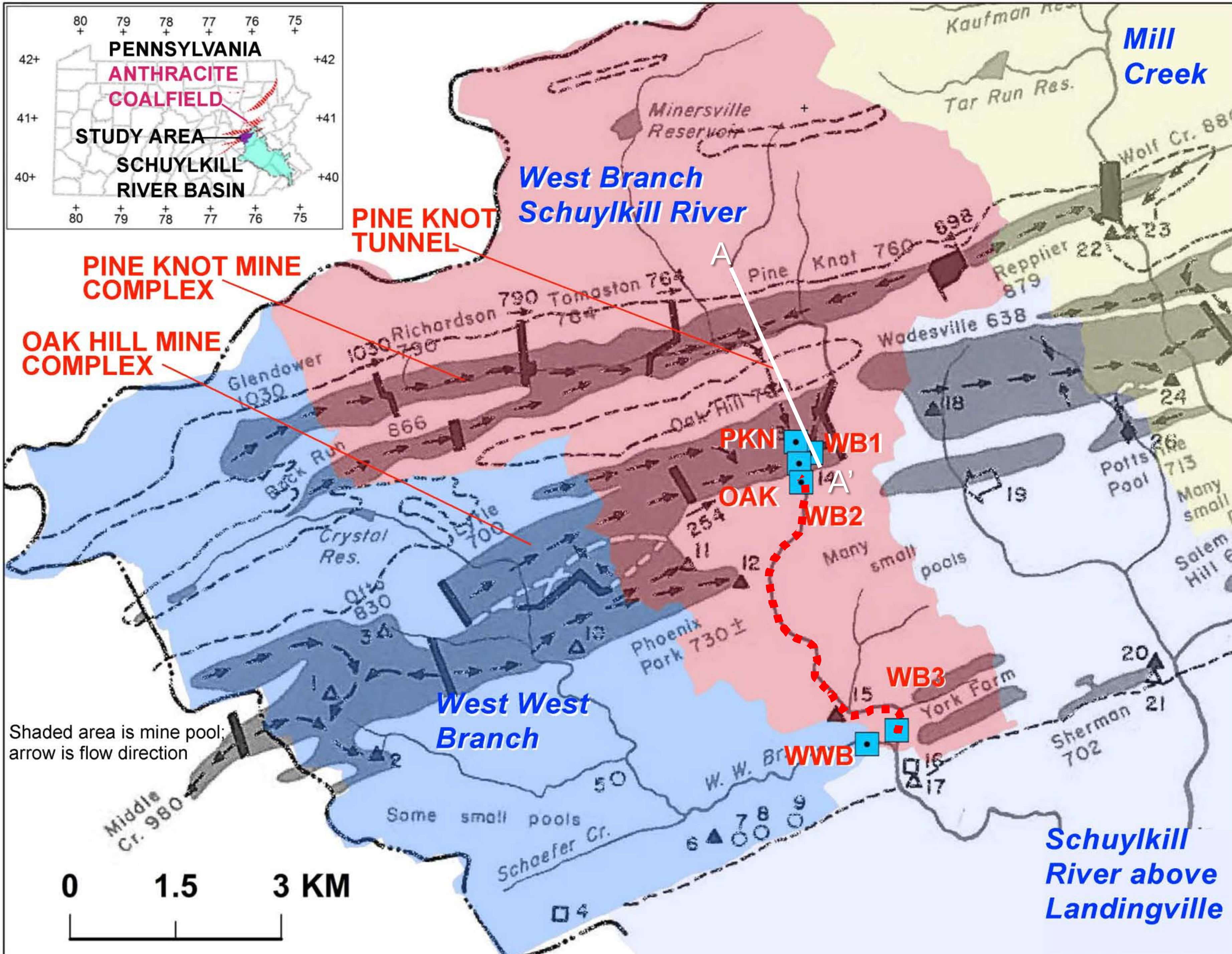
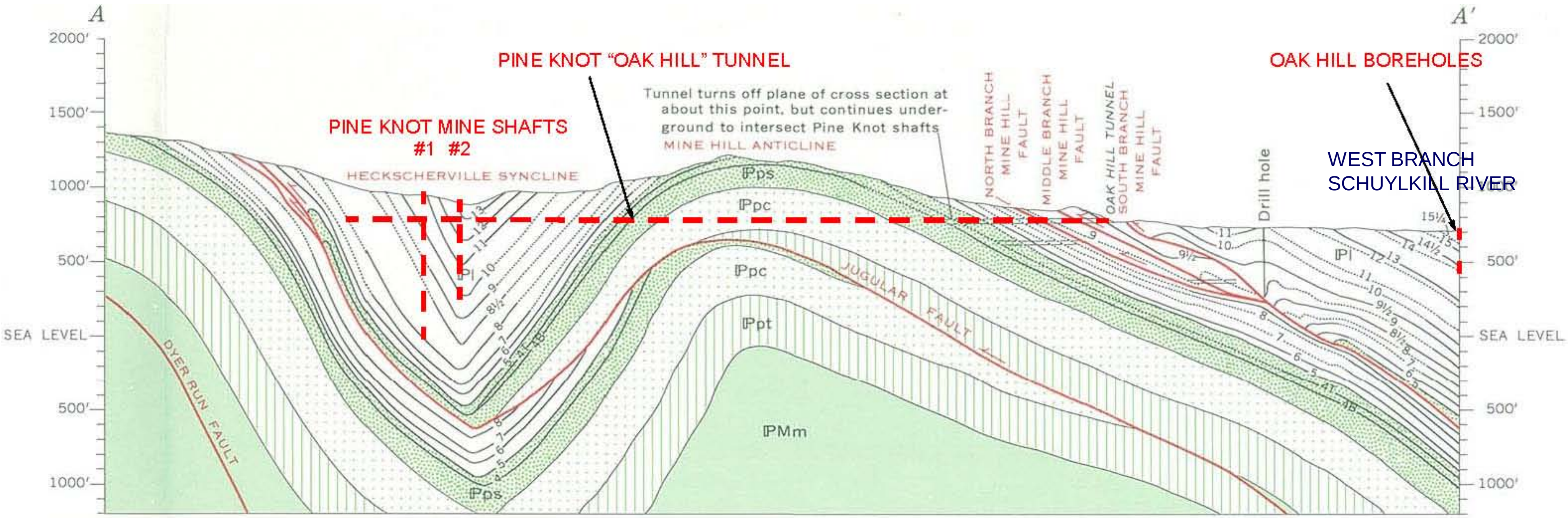


PENNSYLVANIA
ANTHRACITE
COALFIELD
STUDY AREA
SCHUYLKILL
RIVER BASIN
PINE KNOT
TUNNEL
PINE KNOT MINE
COMPLEX
OAK HILL MINE
COMPLEX
West Branch
Schuylkill River
Mill
Creek
Minersville
Reservoir
Kaufman Res.
Tar Run Res.
Wolf Cr. 880
Pine Knot 760
698
Repplier 879
Wadesville 638
Richardson 790
Tomaston 764
Glendower 1030
Oak Hill 780
866
Back Run
Crystal
Res.
Otto
830
Phoenix
Park 730±
Many small pools
Potts
Pool
Many
small
Salem
Hill
PKN
WB1
OAK
WB2
WB3
WWB
York Farm
Sherman
702
West West
Branch
W. W. Br.
Shaded area is mine pool;
arrow is flow direction
Middle
Cr. 980
Some small pools
Schaefer Cr.
Schuylkill
River above
Landingville
0
1.5
3 KM
A
A'

North

South



Synclinal basins containing coal deposits (numbered) and underground mines (now abandoned) underlie parallel valleys.

Groundwater floods the Pine Knot Mine (mine pool) to the Pine Knot Tunnel level and then flows 1,400 m by gravity to the tunnel outlet on south side of Mine Hill.

The Oak Hill Mine pool level is maintained by artesian discharge from the Oak Hill Boreholes within the flood plain of the West Branch Schuylkill River.


West Branch above Pine Knot (WB1)

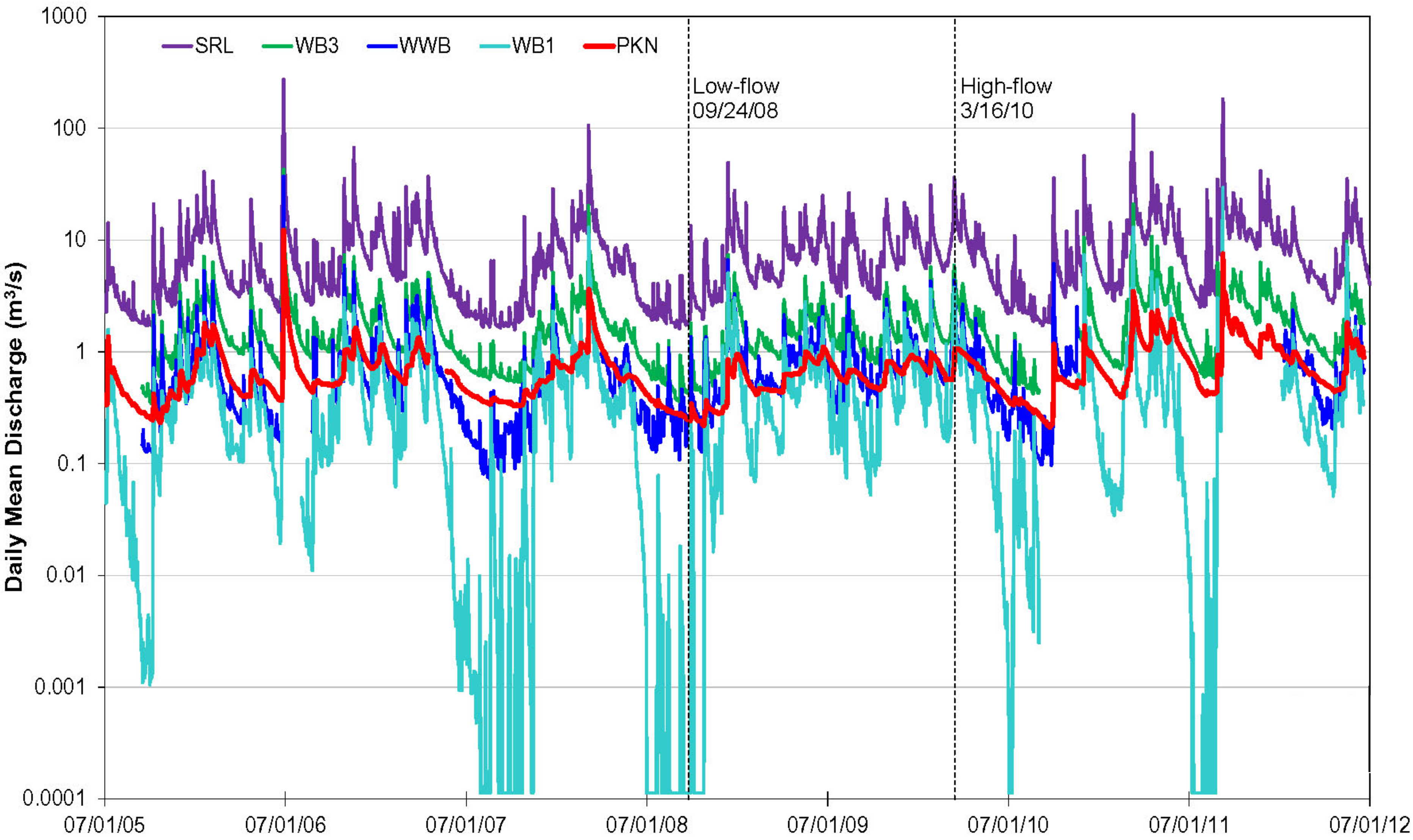

Pine Knot Tunnel (PKN)
PKN ~1400-m long
70+ m underground
PKN ~400-m
from tunnel opening


Oak Hill Boreholes (OAK)

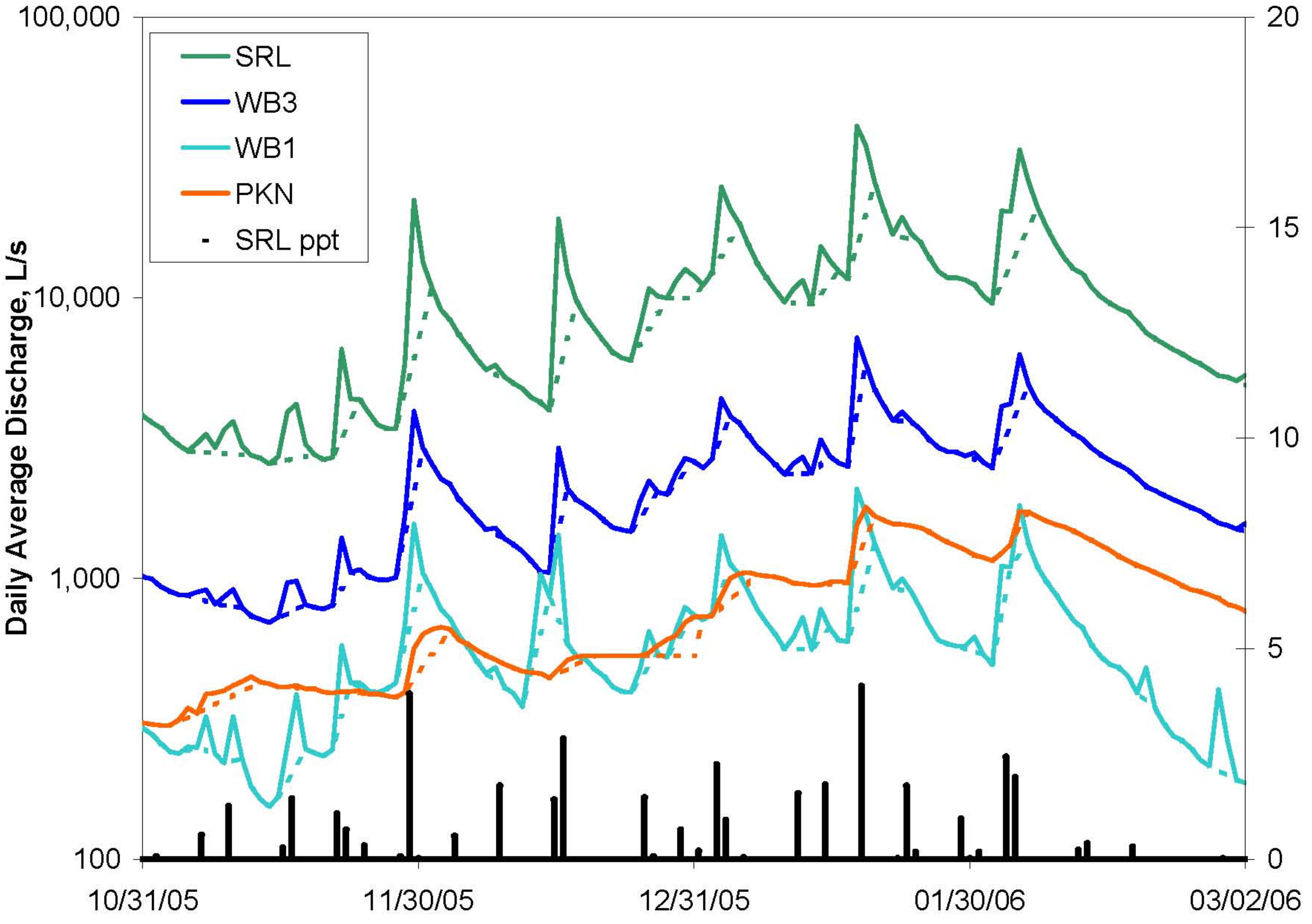

OAK 300-m
from borehole
West Branch bl
PKN+OAK (WB2)


West Branch 5-km below
WB2 (WB3)

Variations in Discharge (Jul 2005 – Jul 2012)



Hydrograph Separation Analysis
WB1, PKN, WB3, SR5L--Winter WY06



Hydrograph Separation Analysis WY06

October 1, 2005 - September 30, 2006

[mi^2, square miles; ft^3/s, cubic feet per second; in/yr, inches per year]

Map ID	Drainage Area, mi^2	Mean Streamflow[b]		Mean Baseflow[c]			Streamflow/ Rainfall[d]
		ft^3/s	in/yr	ft^3/s	in/yr	Index (%)	53.6 in/yr
WB1	19.46	15.9	11.1	10.1	7.1	63.7	0.21
PKN	19.19	26.1	18.5	24.2	17.1	92.6	0.34
(PKN+WB1)	19.46	42.0	29.3	35.2	24.6	83.9	0.55
WB3	24.1	67.9	38.3	56.3	31.7	82.9	0.71
WWB	18.6	31.9	23.3	20.6	15.1	64.6	0.43
MCR	25.5	61.7	32.9	43.1	23.0	69.9	0.61
SR4	27.2	64.8	32.4	44.0	22.0	67.9	0.60
LSR1	42.9	109.0	34.5	81.4	25.8	74.7	0.64
LSR2	65.7	173.1	35.8	129.0	26.5	73.9	0.67
SRL	133	300.3	30.7	203.5	20.8	67.7	0.57
SRB	355	858.0	32.8	515.8	19.7	60.1	0.61

a. Hydrograph separation conducted using "PART" computer program (Rutledge, 1998) with daily average flow during Water Year 2006.

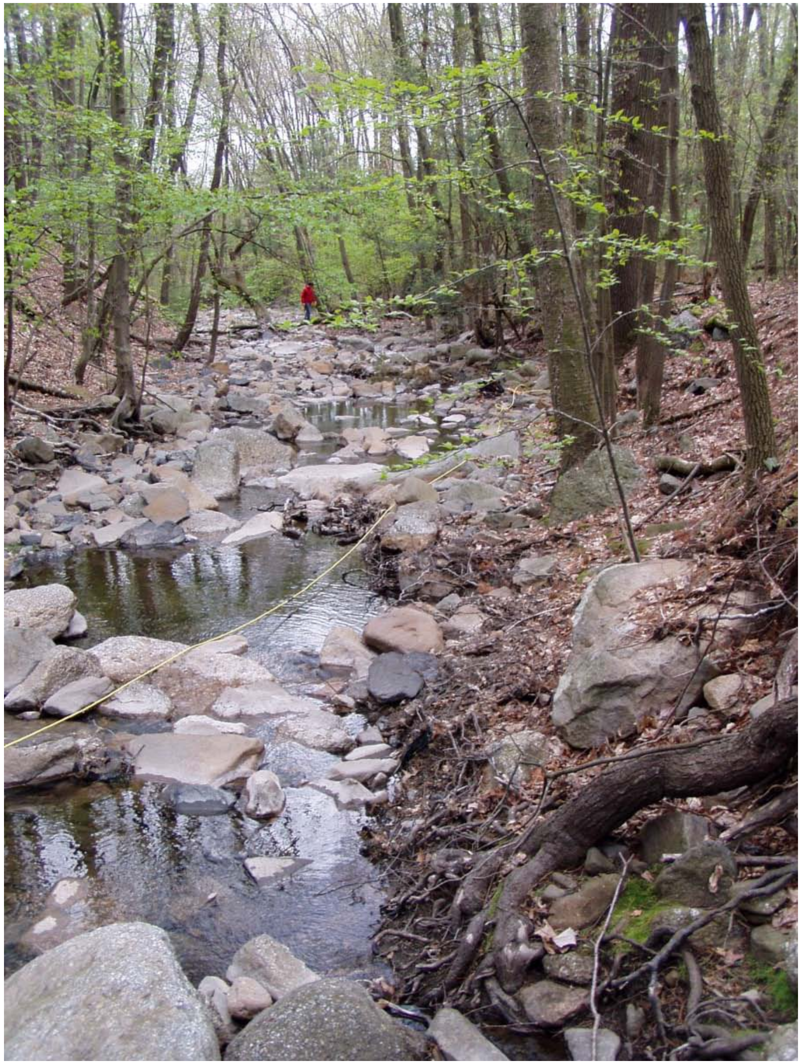
b. Streamflow expressed as inches per year by dividing streamflow in cubic feet per second by drainage area in square miles and then multiplying by the factor 13.584.

c. Baseflow expressed as cubic feet per second, inches per year, and "index" as percentage of total annual streamflow.

d. Ratio of total annual streamflow to total annual rainfall given for measured rainfall of 53.6 in/yr at SRB during Water Year 2006.

Streamflow Losses to Underground Mines West Creek (Headwaters of West West Branch)

West Creek above Forestville, perennial



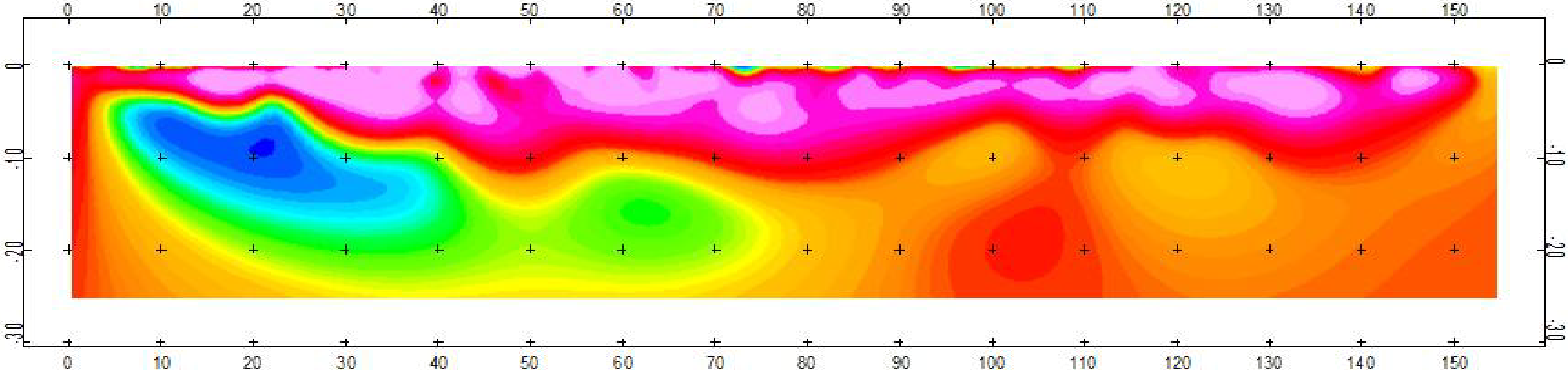
West Creek below Forestville, intermittent

West Creek Flow Loss Survey – March 2012

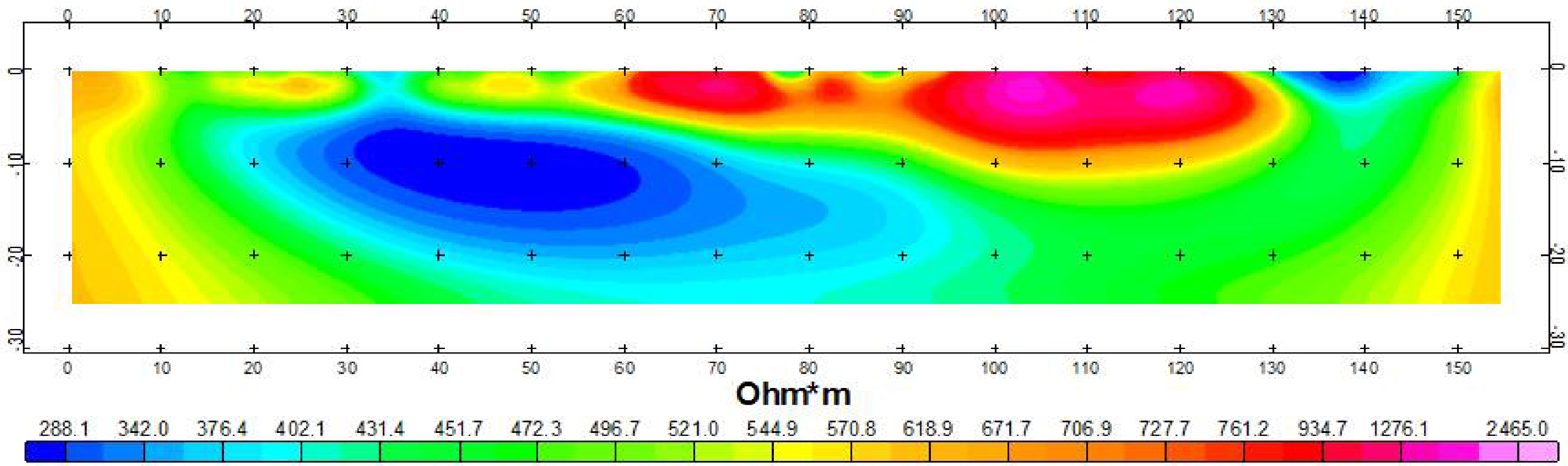
MAP NUM	SNAME	LAT	LON	DATE	FLOW	FIELD WATER QUALITY METER READINGS							
					Qcfs	TempC	SC25	DO.mg	pH	Eh.mv	Q Loss	Q Gain	
4	WestCr_1	40.69366	-76.30820	20120313	0.633	6.9	44	10.61	3.88	605		0.633	
4X	WestCr_loss	40.69144	-76.30453	20120418	-								
5	WestCr_2	40.69131	-76.30200	20120313	0.131	8.89	57	10.73	3.98	538	-0.502		
6	WestCr_3	40.68986	-76.29631	20120313	0.355	8.82	154	10.59	4.42	573		0.224	
7A	WCr_4 ab UNN	40.68243	-76.29431	20120313	0.267	10.7	125	11.2	4.9		-0.088		
7	UNN_1	40.68234	-76.29431	20120313	0.045	12.3	136	9.7	6.6				
8	WestCr_4	40.68197	-76.29408	20120313	0.312	10	159	11.4	5.6			0.045	
9A	WCr_5 ab seepag	40.68000	-76.28815	20120313	0.170	10.4	405	9.1	6.56		-0.142		
9B	WCr_5 seepage	40.67993	-76.28822	20120313	0.011	13.8	1068	7.7	7				
9	WestCr_5	40.67986	-76.28815	20120313	0.182	10.6	451	90	6.55			0.011	
10	PhoenixPark	40.68061	-76.28703	20120313	0.000						**-0.731**	**0.913**	**-80.1%**
14	WWBranch_2	40.66877	-76.23796	20120313	12.425	8.54	261	11.57	7.31	377	**loss from starting point**		
15	WBranch_APine	40.70413	-76.24969	20120313	8.44	7.52	143	11.65	4.91	282			
16	PineKnot	40.70409	-76.24989	20120313	19.25	10.62	538	10.7	6.36	151			
17	OakHill	40.70203	-76.25158	20120313	6.6	14.67	1010	1.68	6.34		**Q loss percentage**		**11.1%**
18	WBranch_BOak	40.70169	-76.25199	20120313	34.29					253	**flow of Oak Hill Boreholes**		
19	WBranch3	40.66869	-76.23642	20120313	42.38	10.09	522	10.42	6.86	294			

West Creek Hydrogeology & Geophysics

4X West Creek Resistivity Survey Segment 3 4W



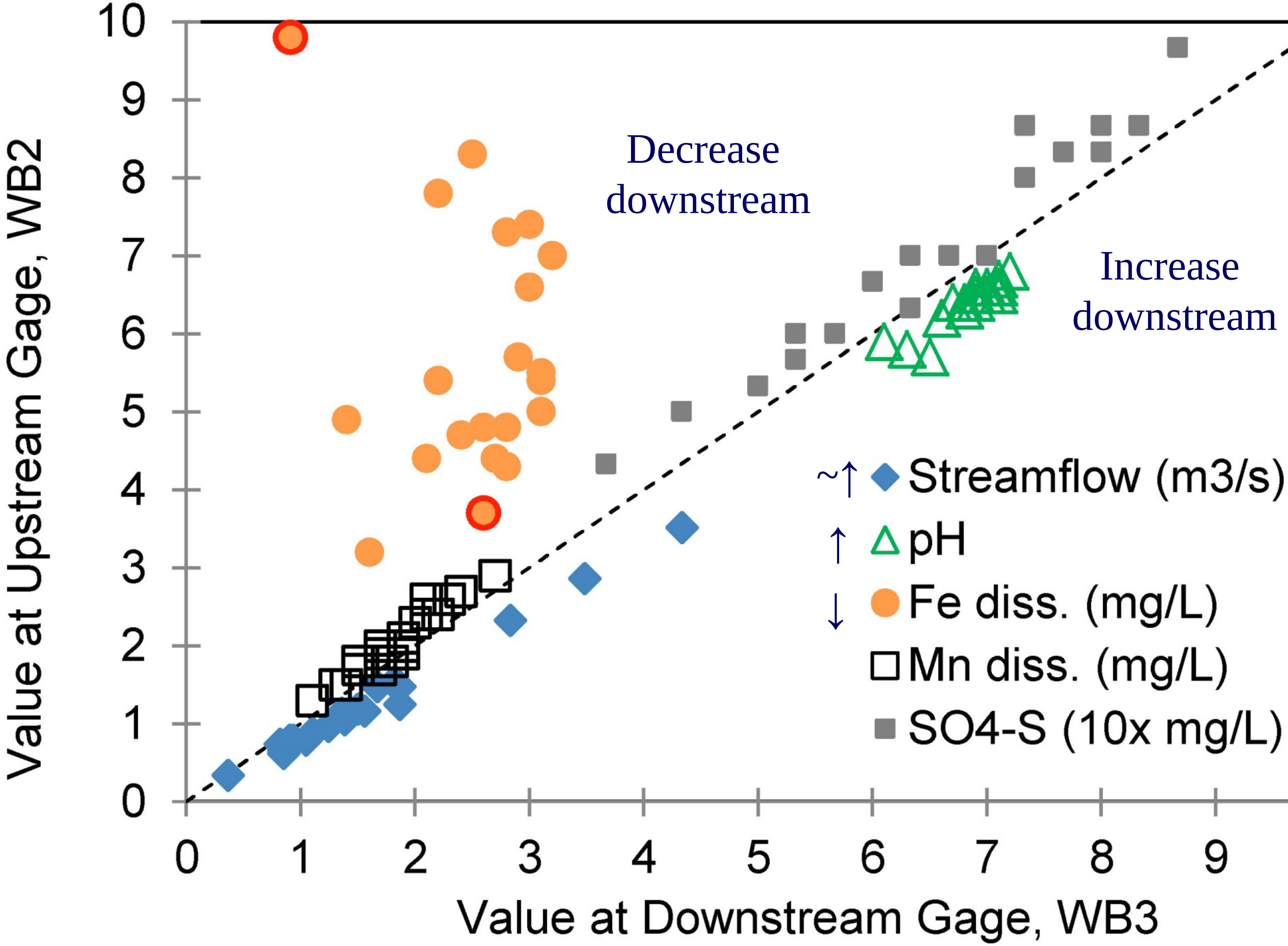
4Y West Creek Resistivity Survey Segment 2 4X



Variations in Water Quality (Jul 2005 - Jul 2012)

	Upstream		CMD				Downstream				
	WB1		PKN		OAK		WB2		WB3		WWB
Flow (m^3/s)	0.20	+	0.57	+	0.18	=	0.96	≤	1.20		0.51
Temp. (°C)	13.0		10.9		14.7		12.0		12.0		11.4
DO	9.4		9.9		2.0		9.0		9.5		9.8
Eh (mV)	405		320		220		300		270		330
SC (μS/cm)	155		570		1000		560		570		350
pH (units)	5.2		6.4		6.3		6.4	<	6.9	↑	7.4
Alkalinity	2		34		150		45		47		52
Acidity	3		-22		-113		-30		-40	↓	-48
SO_4, diss.	52		240		390		210		190		110
Cl, diss.	14.0		17.5		8.8		16.0		20.0		7.4
Ca, diss.	9.6		40.5		99.0		41.5		43.0		30.0
Mg, diss.	6.8		42.0		55.0		34.5		33.0		18.0
K, diss.	0.7		1.4		2.3		1.4		1.9		1.4
Na, diss.	8.0		10.0		32.0		14.0		18.0		11.0
Al, diss.	0.50		0.07		0.06		0.04	>	0.01	↓	0.01
Fe, diss.	0.07		5.15		18.00		5.45	>	2.60	↓	0.04
Mn, diss.	0.33		2.45		3.70		2.05		1.90		0.31
Ni, diss.	0.02		0.05		0.04		0.04		0.03		0.01
Zn, diss.	0.04		0.12		0.05		0.08		0.07		0.02

∆ Water-Quality WB2 to WB3 (Jul 2005 – Jul 2012)



Iron Oxidation & Hydrolysis (pH decrease, overall)

Fe(II) $Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O$

Oxidation (rate limiting): 7 mg/L Fe^{2+} = 1 mg/L of D.O.

Fe(III) $Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$

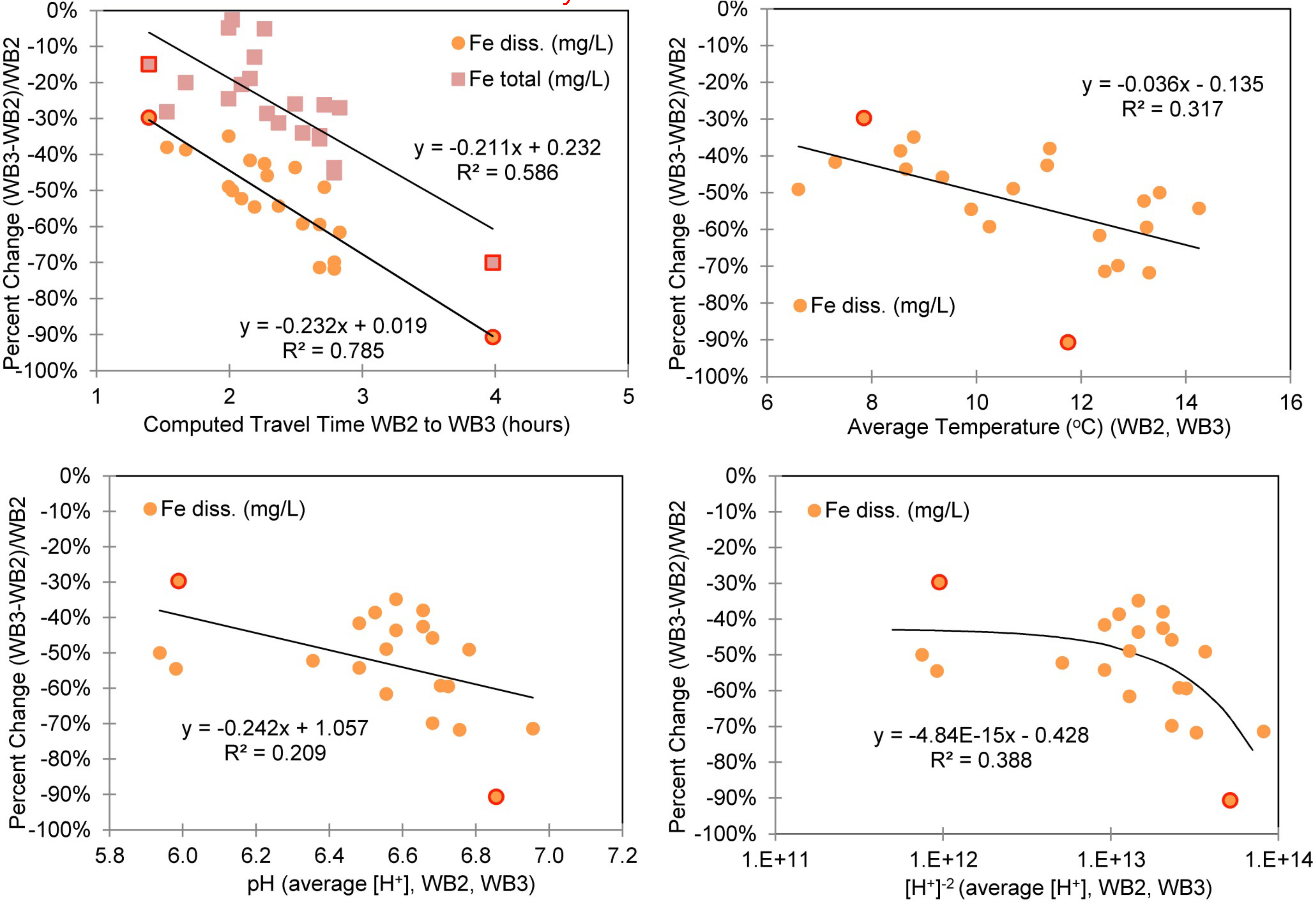
Hydrolysis: 1 mg/L Fe^{2+} = 1.8 mg/L as $CaCO_3$

Overall, 1 mol Fe(II) oxidized/hydrolyzed to $Fe(OH)_3$ yields 2 mol [H^+]:

$$Fe^{2+} + 0.25\ O_2 + 2.5\ H_2O \rightarrow Fe(OH)_3 + 2\ H^+$$

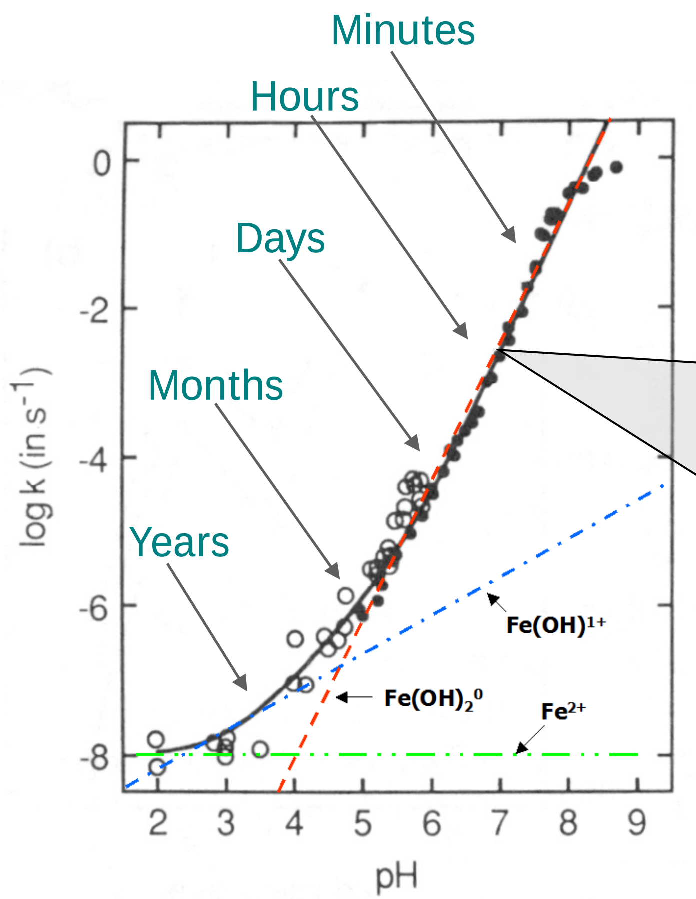
Δ Iron: Travel Time, Temp, pH (WB2 to WB3)

Travel Time = Distance / Velocity



Linear regression; log-transformation

Abiotic Homogeneous Fe(II) Oxidation Rate (importance of pH)



*Extrapolation of homogeneous rate law:

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

$k_H = 3 \times 10^{-12}$ mol/L/min

Between pH 5 and 8 the Fe(II) oxidation rate increases by 100x for each pH unit increase.*

At a given pH, the rate increases by 10x for a 15 °C increase. Using the activation energy of 23 kcal/mol with the Arrhenius equation, the rate can be adjusted for temperature.

$\log k_{T1} = \log k_{T2} + Ea / (2.303 * R) \cdot (1/T_2 - 1/T_1)$

At $[O_2]$ = 0.26 mM (pO_2 = 0.21 atm) and 25°C. Open circles (o) from Singer & Stumm (1970), and solid circles (•) from Millero et al. (1987).

Dashed lines are estimated rates for the various dissolved Fe(II) species.

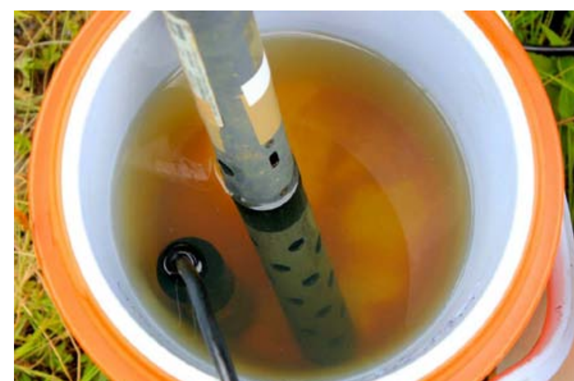
Development & Testing of Geochemical Kinetic Model for Iron Removal

Batch Aeration Tests at Oak Hill Boreholes: Effects of CO_2 Outgassing on pH & Fe(II) Oxidation Rates

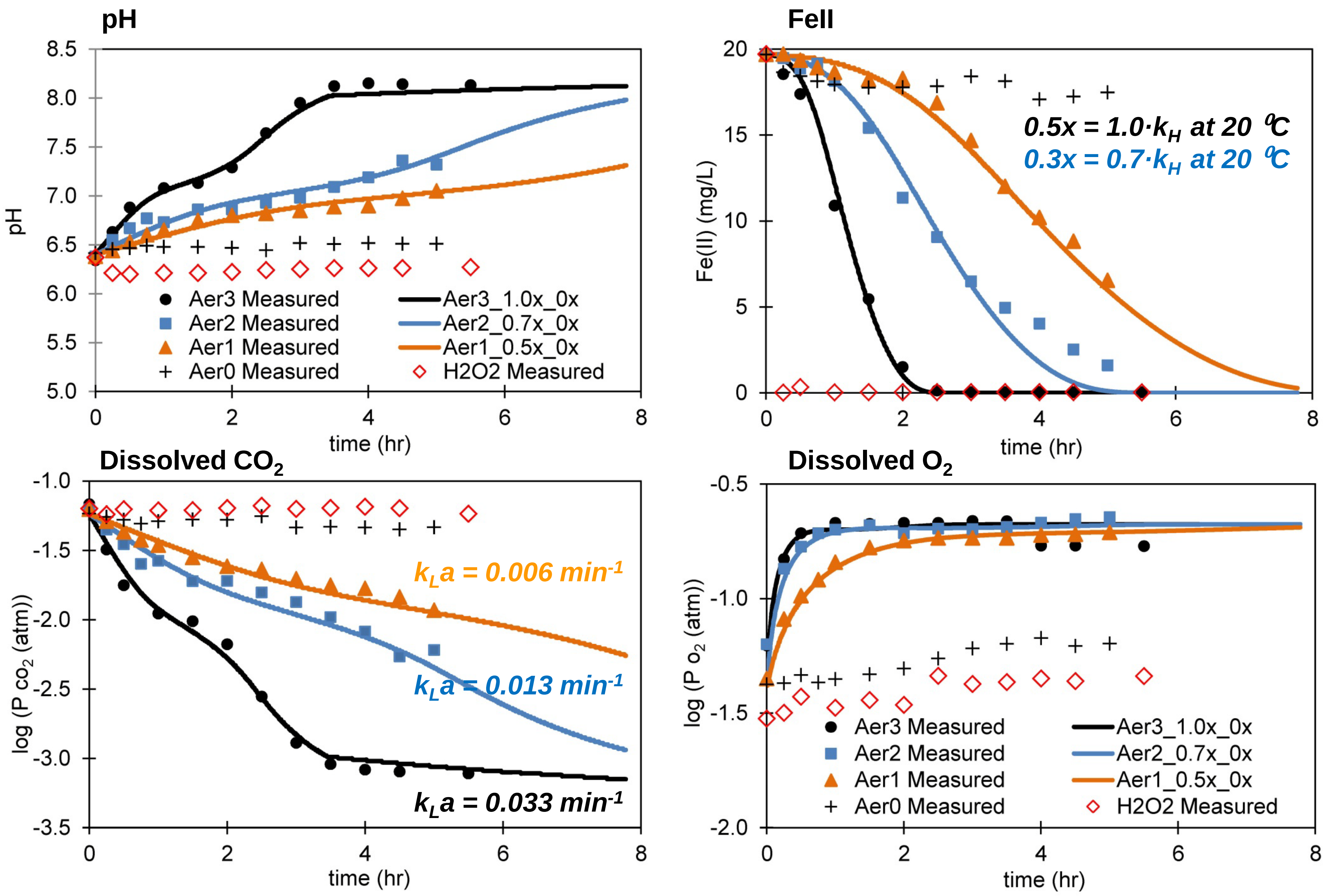
Control Not Aerated

Aerated

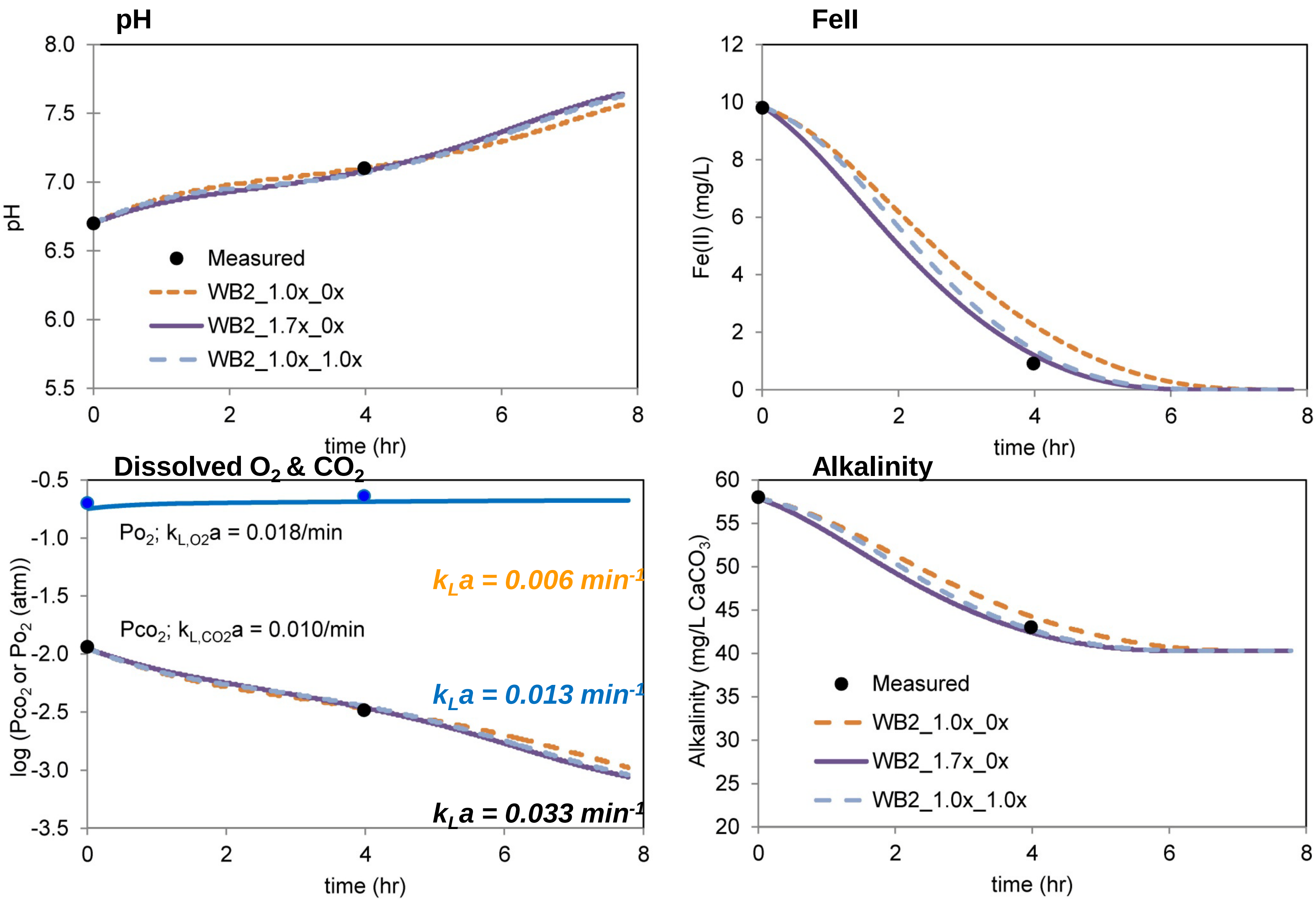
H_2O_2 Addition



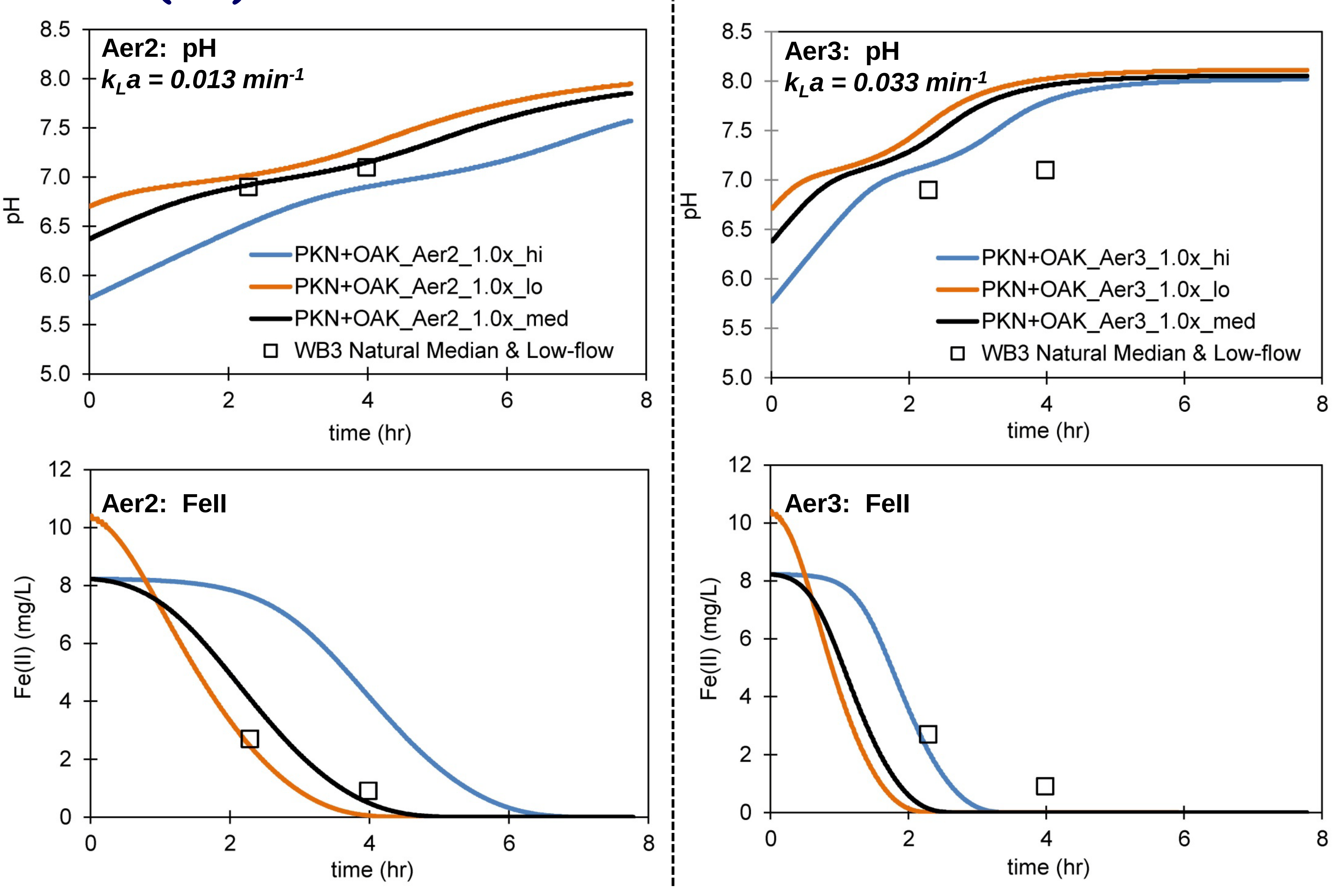
PHREEQC Coupled Kinetic Models of CO_2 Outgassing & Fe(II) Oxidation—Oak Hill Boreholes Aeration



PHREEQC Coupled Kinetic Models of CO_2 Outgassing & Fe(II) Oxidation (WB2 to WB3, Low Flow)



PHREEQC Coupled Kinetic Models of CO_2 Degassing & Fe(II) Oxidation—3:1 Pine Knot + Oak Hill CMD



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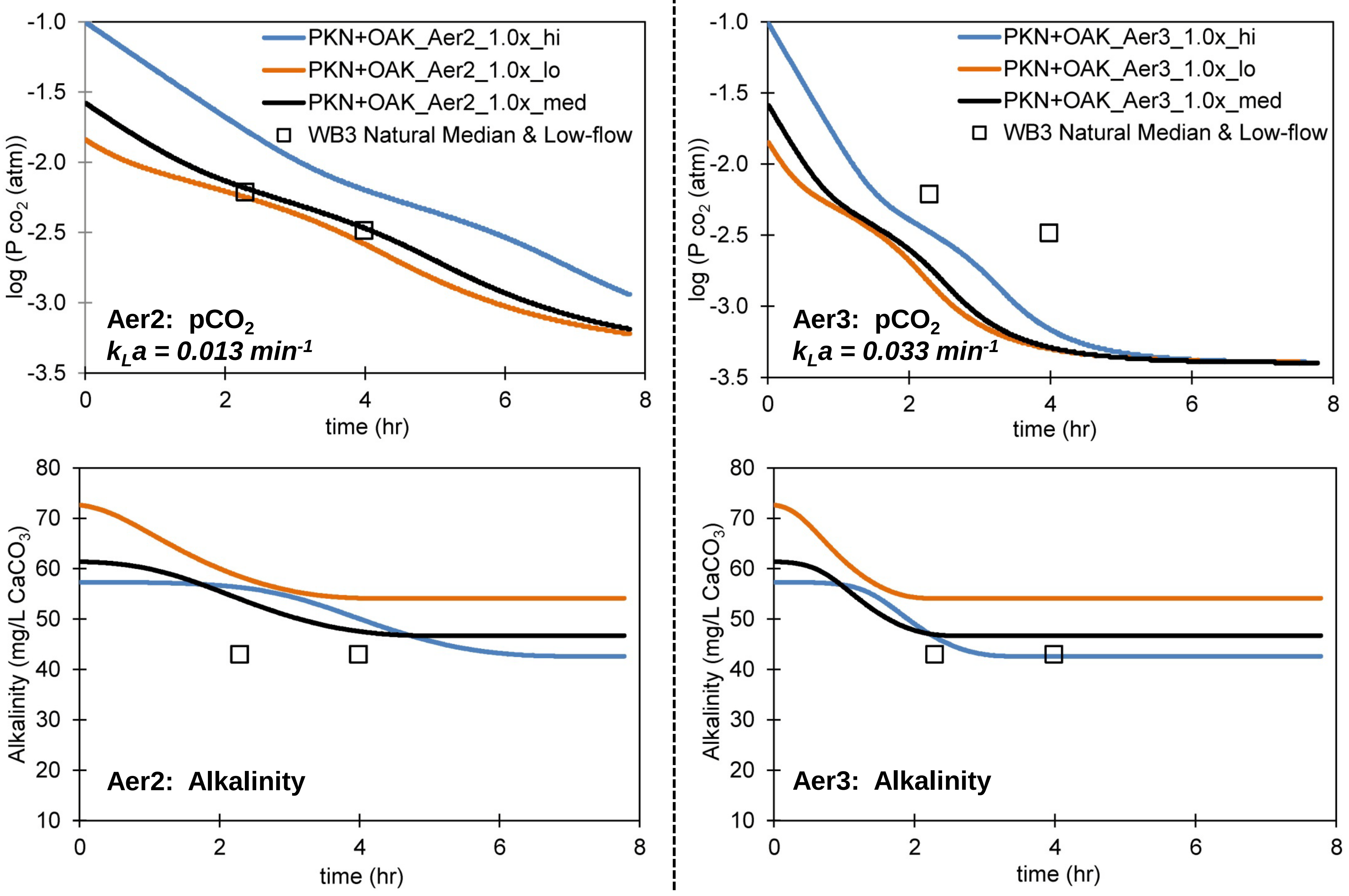

Conclusions

- Streamflow losses to underground mines cause aquatic habitat loss and contribute to contaminated CMD at downgradient outfalls.

- Attenuation of iron below CMD in West Branch and during aeration tests on CMD increased with time, temperature, and pH, consistent with 1st-order kinetic control of Fe(II) oxidation.

- Aerobic treatment of net alkaline CMD could decrease Fe loading.

  - ✓ Mechanical aeration may be incorporated to outgas CO_2, thereby increasing pH and the rate of iron oxidation in a treatment system.

  - ✓ Combined aeration augmented with H_2O_2 treatment may be appropriate given small area available to treat CMD from Oak Hill Boreholes and Pine Knot Tunnel.