Advances in the use of limestone aggregate for passive treatment of acid mine water

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Factors that influence the utility of limestone aggregate in AMD treatment

- **Mineralogy**: calcite >> dolomite
- **Hardness**: pass harness test
- **Particle size**: smaller = more SA
- **Solids**

Solids influence the long-term effectiveness of limestone aggregate

- Accumulation on surfaces can lessen reactivity
- Accumulation in the pore space can lessen permeability
- Management of solids is often key to extracting the most treatment value from limestone aggregate

82% $CaCO_3$ limestone after 25 years

Solids that form from mine water reactions

Types of Limestone Beds

Anoxic closed

Oxic open

Fe^{2+}, Mn^{2+}
(DO, Fe^{3+} and Al < 1mg/L)

↓

Anoxic Closed Limestone Bed

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

↓

Pond/Wetland

$Fe^{2+}, Mn^{2+} + O_2 \rightarrow FeOOH, MnO_2$

↓

Effluent

Goals of system

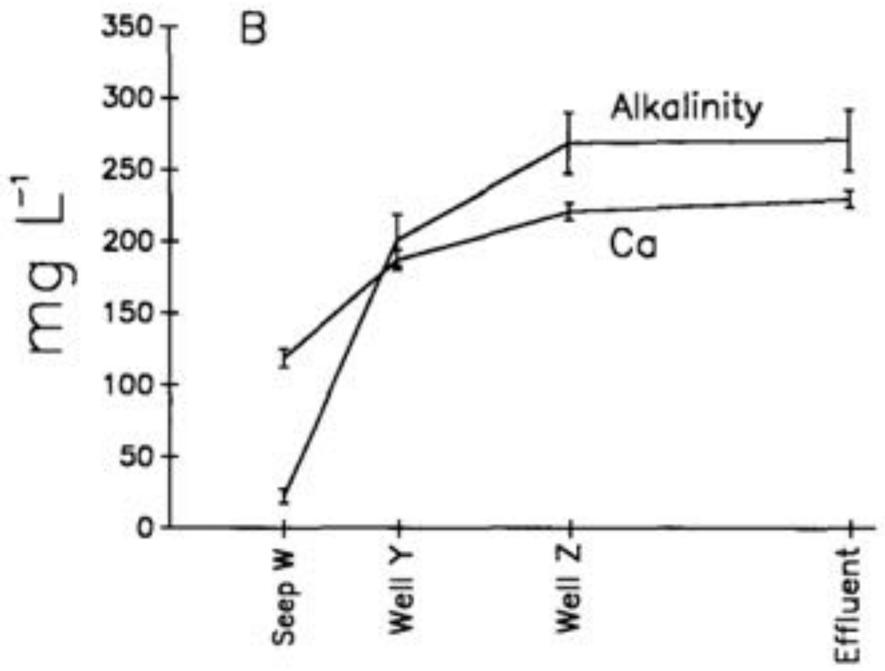
- Maximize alkalinity generation
- Minimize solids formation within bed
- Promote Fe and Mn removal *outside* of bed

Anoxic (closed) limestone bed

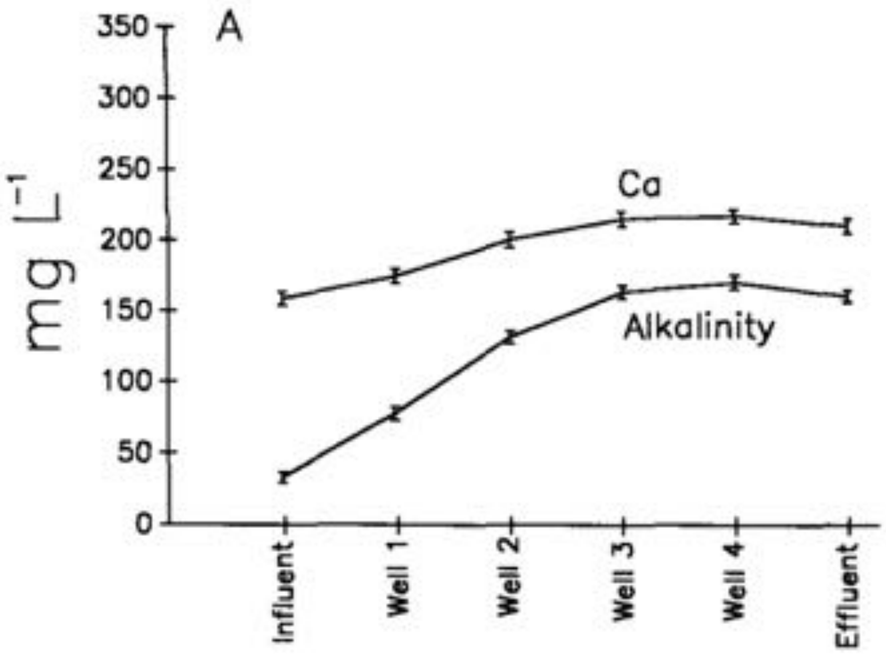
During construction

Completed (buried)

Morrison ALD



Howe Bridge ALD



Outcome of Pre-treating Mine Water with Anoxic Limestone Beds

- Alkalinity generated **>** acid-producing potential of Fe^{2+} and Mn
  - aeration and retention can yield effluent with neutral pH and low metals

- Alkalinity generated **<** acid-producing potential of Fe^{2+} and Mn
  - Aeration and retention will lower Fe, but final pH will be < 6 and little removal of Mn will occur
  - Accept incompletely treated effluent or add another alkalinity-generating step

Anoxic Limestone Bed systems that produce more than alkalinity than is produced from Fe and Mn removal

Site		Year installed	Tons	Status
SCV Area 1	Mining company	1995	6,000	Operational
SR114D	DMO	1995	1,300	Operational (rehabilitated 2020)
Little Hefren	PADEP	2001	500	Operational (rehabilitated 2020)
C&K Pit 601	Mining company	2006	2,800	Operational (bankrupt)
Filson 7	Watershed Assoc	2006	2,300	Operational
LC20D	Township	2006	1,800	Operational
Bilger	Watershed Assoc	2008	1,380	Operational

Mine waters that do not generate sufficient alkalinity from limestone under anoxic, closed conditions

Site	pH	Alk	CO_2	Fe	Mn	Al	Zn	Ca	Metal Acid	LS-Alk	Deficit
		$CaCO_3$	$\log(P_{CO2})$	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L $CaCO_3$		
Howe (PA)	5.6	47	-0.98	128	21	<1	na	86	267	177	90
Clarion (PA)	5.1	16	-0.94	187	37	2	na	115	401	280	121
Lambert (PA)	5.9	58	-1.19	161	12	<1	0.1	227	310	169	141
Elizabeth (VT)	6.5	163	-1.34	150	3	<1	<1	430	274	220	54
Tyler #1 (PA)	5.6	31	-1.16	133	9	<1	na	na	254	189	65
Inclined Plane (PA)	5.9	111	-0.89	142	2	<1	<1	131	257	236	21
Truetown (OH)	5.2	21	-0.93	264	5	2	na	170	482	266	216
Red&Bon (CO)	5.9	40	-1.35	95	31	4	14	432	247	160	87

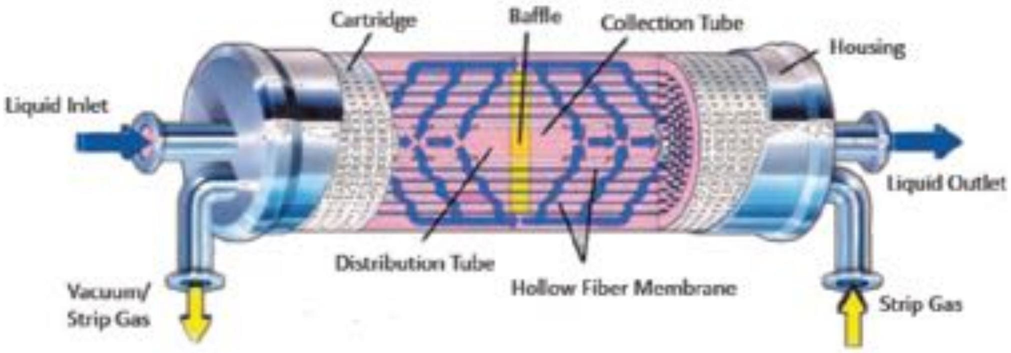
How can alkalinity generation be increased?

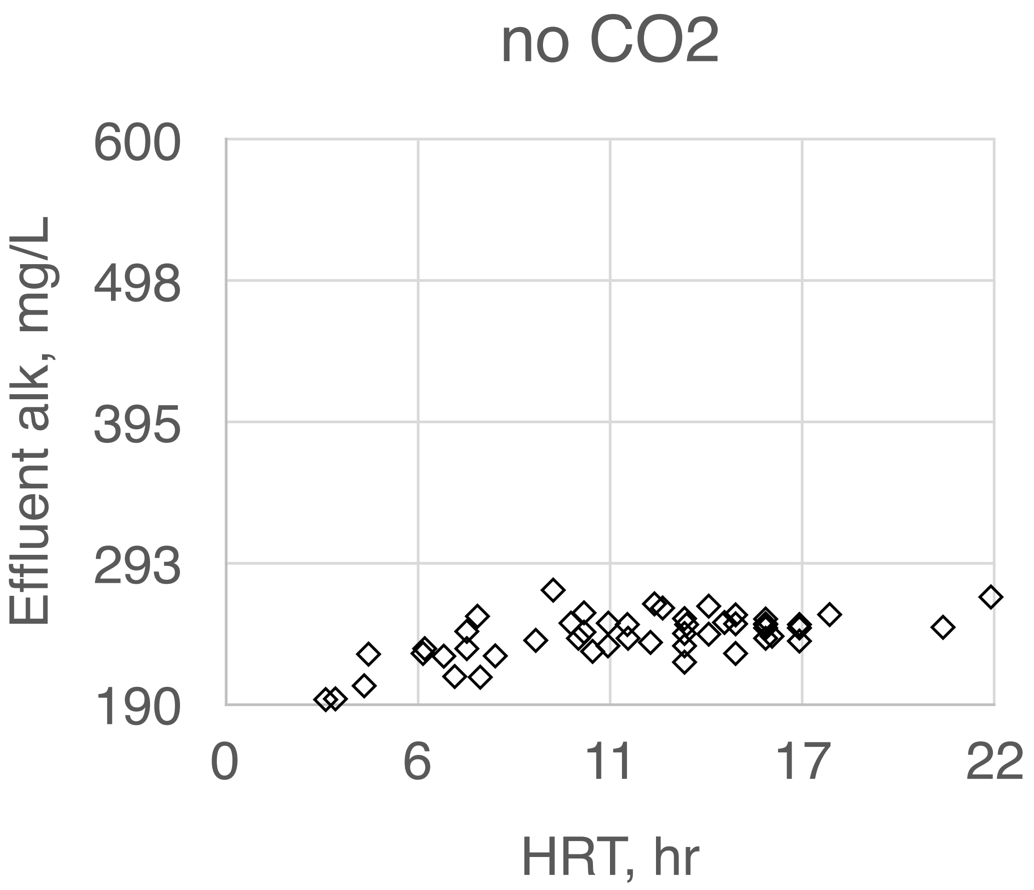
$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$

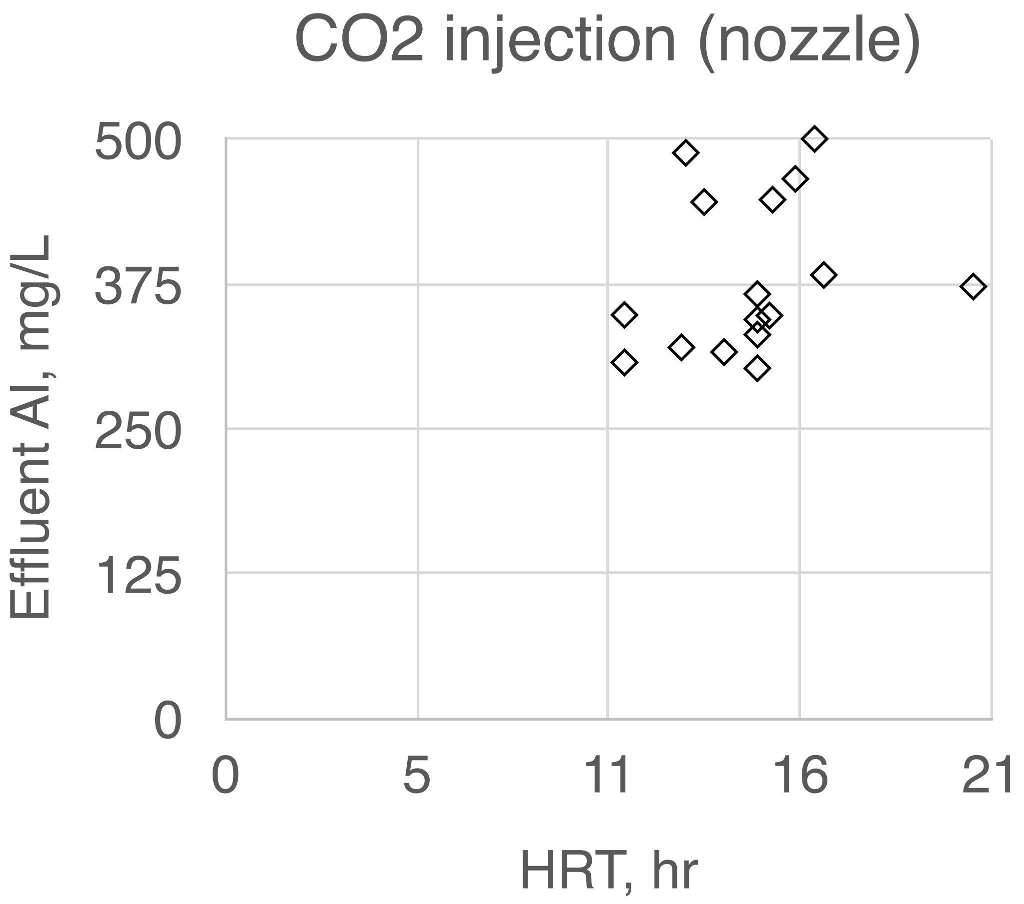
$$[Ca^{2+}]\,[HCO_3^-]^2 / [P_{CO2}] = K$$

$$[HCO_3^-] = [P_{CO2}] / [Ca^{2+}]$$

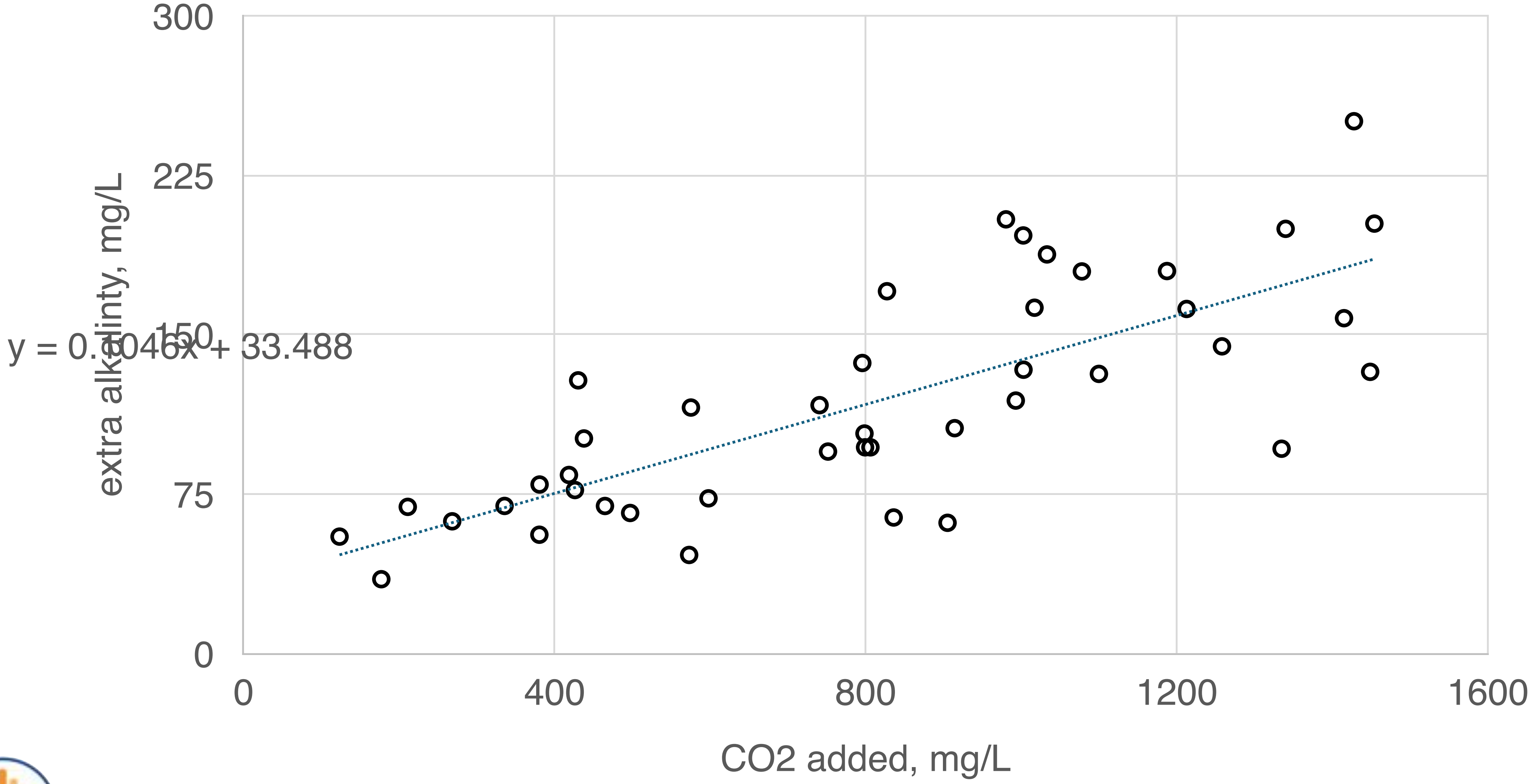
Increase

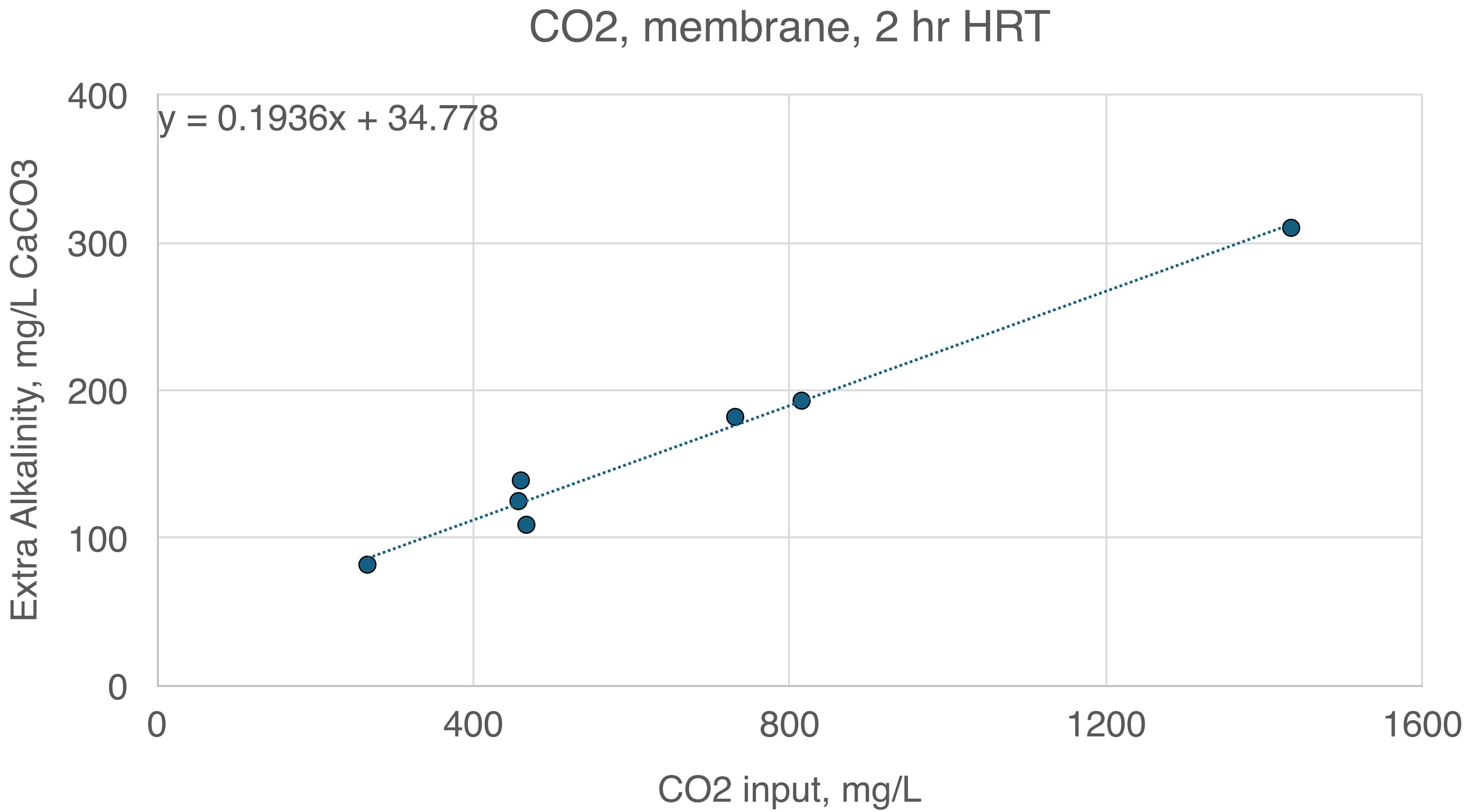

Cartridge
Baffle
Collection Tube
Housing
Liquid Inlet
Liquid Outlet
Distribution Tube
Hollow Fiber Membrane
Vacuum/
Strip Gas
Strip Gas


no CO2
600
498
395
293
190
Effluent alk, mg/L
0
6
11
17
22
HRT, hr


CO2 injection (nozzle)
500
375
250
125
0
Effluent Al, mg/L
0
5
11
16
21
HRT, hr

CO_2, nozzle,10-18 hr TRT

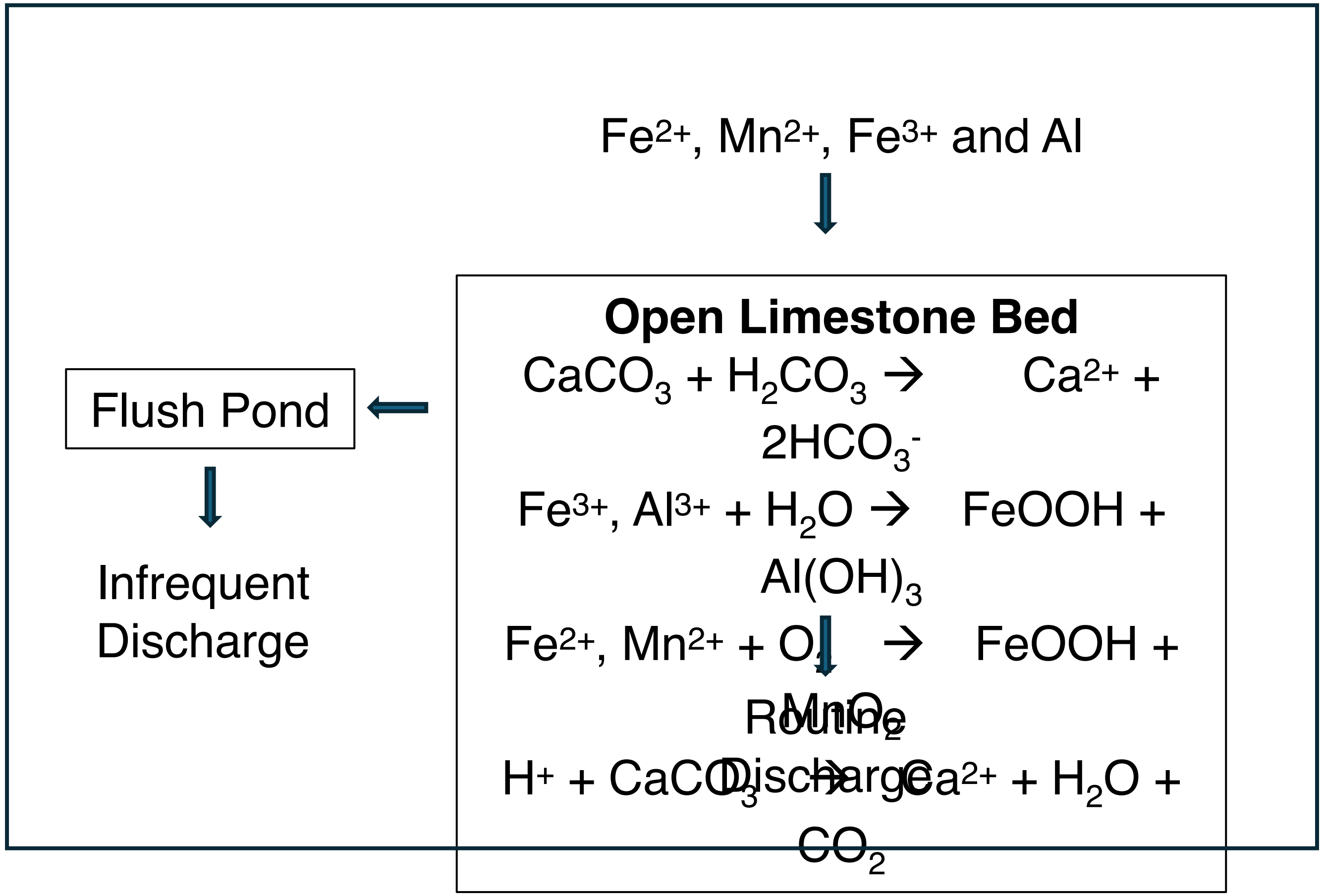



CO2, membrane, 2 hr HRT
y = 0.1936x + 34.778
Extra Alkalinity, mg/L CaCO3
CO2 input, mg/L
400
300
200
100
0
0
400
800
1200
1600

Site	MW chem	System	LS size	CO_2 injection	HRT, hr	CO_2 / (extra alk)
Orcutt	pH 5, Fe 95, Mn 30	Anoxic LS Bed Roll-off	19 mm	Nozzle	12	6.8
Orcutt	pH 5, Fe 95, Mn 30	Anoxic LS Bed Roll-off	11 mm	Membrane	2	3.9

Carbonation provides an opportunity to increase the effectiveness of anoxic limestone beds

Oxic, open limestone treatment system



Goals of system

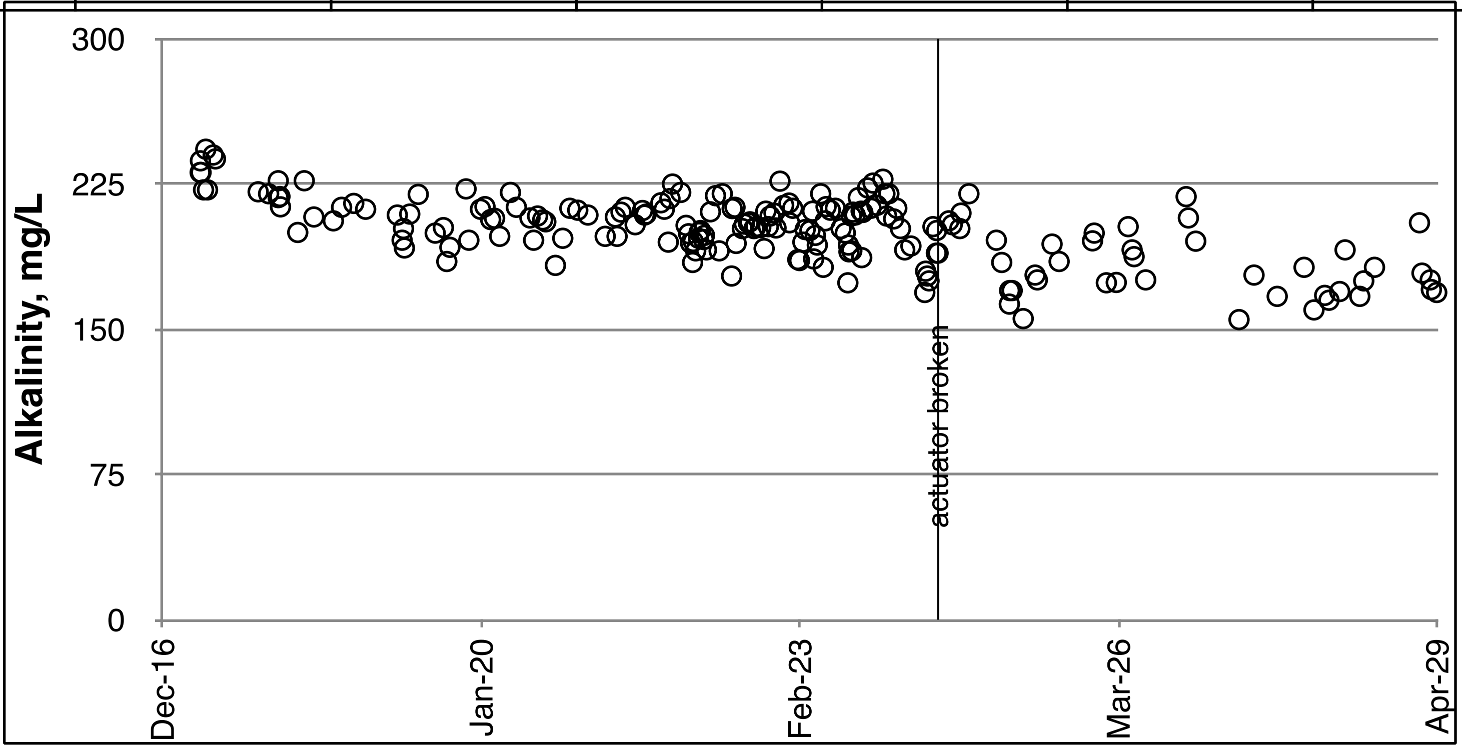
- Maximize neutralization of acidity
- Convert dissolved metals to solids within the bed
- Optimize solids removal through draining (flushing) actions

routine effluents from oxic limestone beds can be good quality

Site/year	LS Bed	Point	Flow	pH	Acid	Fe	Al	Mn
	Tons		gpm	s.u.	$CaCO_3$	mg/L	mg/L	mg/L
Scootac	1,000	In		4.0	84	0.1	10.0	22.5
2010		LS out	42	7.3	-157	0.1	0.2	1.5
PBG Lotus	450	In		3.3	142	0.5	17.7	0.8
2013		LS out	8	6.7	-193	0.1	0.7	0.2
Sterrett	3,500	In		3.4	103	8.0	8.4	16.1
2015		LS out	98	7.3	-92	0.3	0.7	2.6
K1	4,200	In		4.7	22	0.7	4.7	0.3
2019		LS out	280	7.2	-58	0.1	0.2	0.1
Greene	6,000	In		3.6	86	6.7	3.1	30.8
2015		Final mix	95	7.8	-61	0.4	0.1	0.8

Pittsburgh Botanic Garden Lotus Pond oxic limestone bed routine discharge, 2013 - 2025

Location	Flow	pH	Alk	Acid	Al	Fe	Mn	SO4
	gpm	s.u.	mg/L $CaCO_3$		mg/L	mg/L	mg/L	mg/L
Influent	na	3.3	0	142	17.7	0.6	0.8	506
Effluent	8	6.7	201	-193	0.7	<0.1	0.2	506



Managing the solids in Oxic Limestone Bed

1. Remove solids through regular maintenance of the aggregate
2. Periodically mix the aggregate to restore permeability
3. Periodically clean the aggregate to remove solids

Suspended solids can be removable through draining

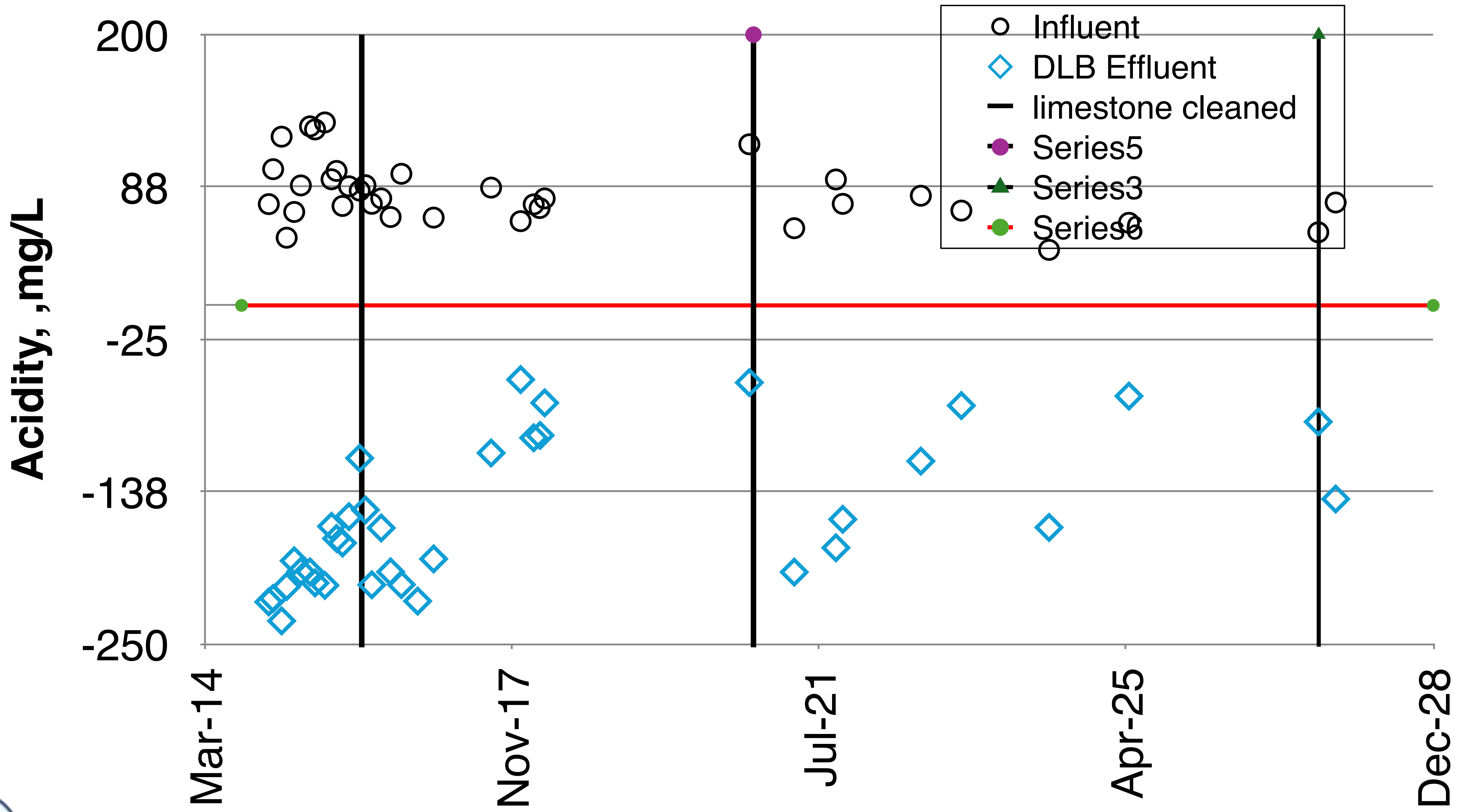
Pittsburgh Botanic Garden Oxic Limestone Bed solids basin at end of draining event

Agri Drain Smart Drainage System
(solar powered computer-controlled gate valve)

Aggregate mixing and cleaning

- Initiated when routine effluent quality deteriorates
  - Depends on design; generally, every 3-10 years
- Mixing restores treatment effectiveness, but does not remove solids
- Cleaning removes solids

Aggregate cleaning methods


Acidity, ,mg/L
200
88
-25
-138
-250
Mar-14
Nov-17
Jul-21
Apr-25
Dec-28
Influent
DLB Effluent
limestone cleaned
Series5
Series3
Series6

Limestone replacement: $40-50/ton

Limestone aggregate can be mixed for $3-5/ton

Limestone aggregate can be cleaned for $8-15/ton

Mn removal with Limestone Aggregate

Site/year	LS Bed	Point	Flow	pH	Acid	Fe	Al	Mn
	Tons		gpm	s.u.	$CaCO_3$	mg/L	mg/L	mg/L
Scootac	1,000	In		4.0	84	0.1	10.0	22.5
2010		LS out	42	7.3	-157	0.1	0.2	1.5
PBG Lotus	450	In		3.3	142	0.5	17.7	0.8
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K1	4,200	In		4.7	22	0.7	4.7	0.3
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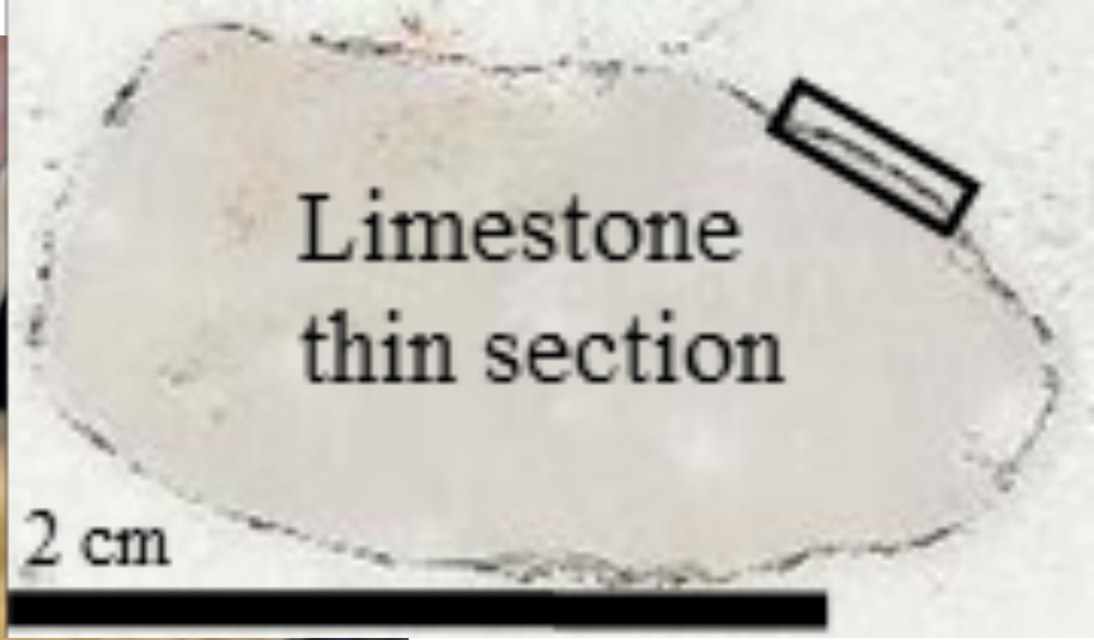
Greene	6,000	In		3.6	86	6.7	3.1	30.8
2015		Final mix	95	7.8	-61	0.4	0.1	0.8


Limestone
thin section
2 cm

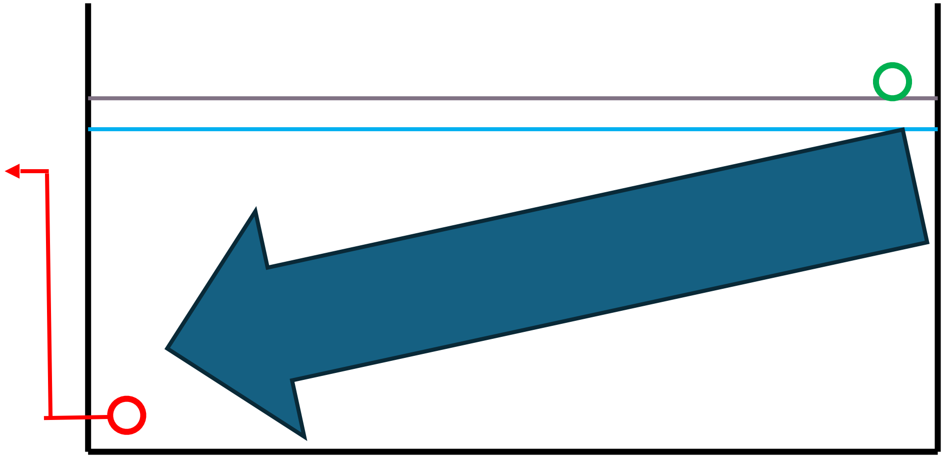
PADEP & WPC Mn Project

- PA DEP proposed 0.3 mg/L Mn effluent standard
- Public comment pushback
- Experiments to determine if the limit could be met with passive system

Horizontal flow

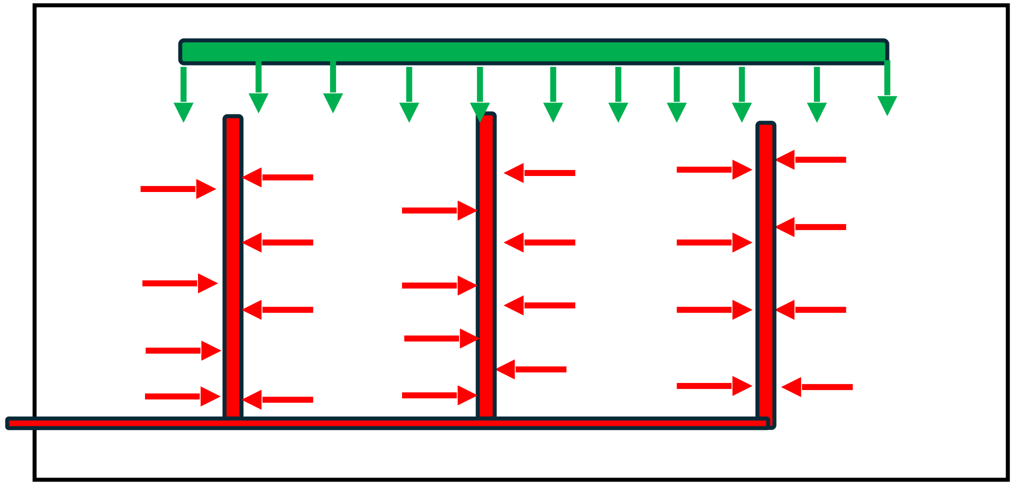
Plan view

Cross Section

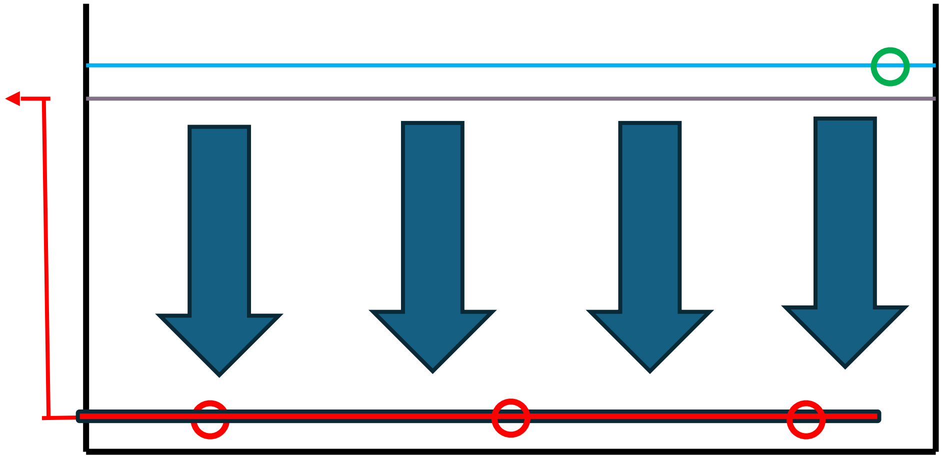


Vertical flow

Plan view



Cross Section



Periods of sustained treatment (does not include startup periods)

Mode	Period	Flow	Mn^{in}	Mn^{eff}	> 0.3 mg/L
		gpm	mg/L	mg/L	# of total
Horizontal	8/20 – 11/7	6.0	5.65	0.109	3 of 68
Vertical	3/29 – 7/9	6.2	5.64	0.081	0 of 66

Passive treatment with aggregate to very low concentrations is feasible

Periods of sustained treatment
(does not include startup periods)

Mode	Period	Flow	Mn^{in}	Mn^{eff}	> 0.3 mg/L	HRT
		gpm	mg/L	mg/L	# of total	hour
Horizontal	8/20 – 11/7	6.0	5.65	0.109	3 of 68	2.1
Vertical	3/29 – 7/9	6.2	5.64	0.081	0 of 66	2.7

Passive treatment with aggregate to very low concentrations is feasible;
at crazy short retention times

Brandy Camp Mn removal calculations		
k, average	$\ln(Mn^{out}/Mn^{in})/TRT$	$-1.785\ hr^{-1}$
½ reaction, average	0.693 / k	-0.41 hr
½ reaction, average	0.693 / k	-25 min

Passive Mn removal as secondary treatment at a conventional treatment plant

Treatment plant

- 900 gpm
- Primary treatment effluent
  - pH > 6.5;
  - DO > 8 mg/L;
  - Fe & Al <1 mg/L
  - Mn 6 mg/L
- Final effluent target: 1.0 mg/L Mn

Site	k	HRT	Aggregate
	hr^{-1}	hr	tons
Traditional (retention time)		24 - 48	21,600 - 43,200
Brandy Camp (kinetics)	-0.756		2,153

Summary: Opportunities for increased use of limestone in passive mine water treatment systems

Anoxic limestone beds:

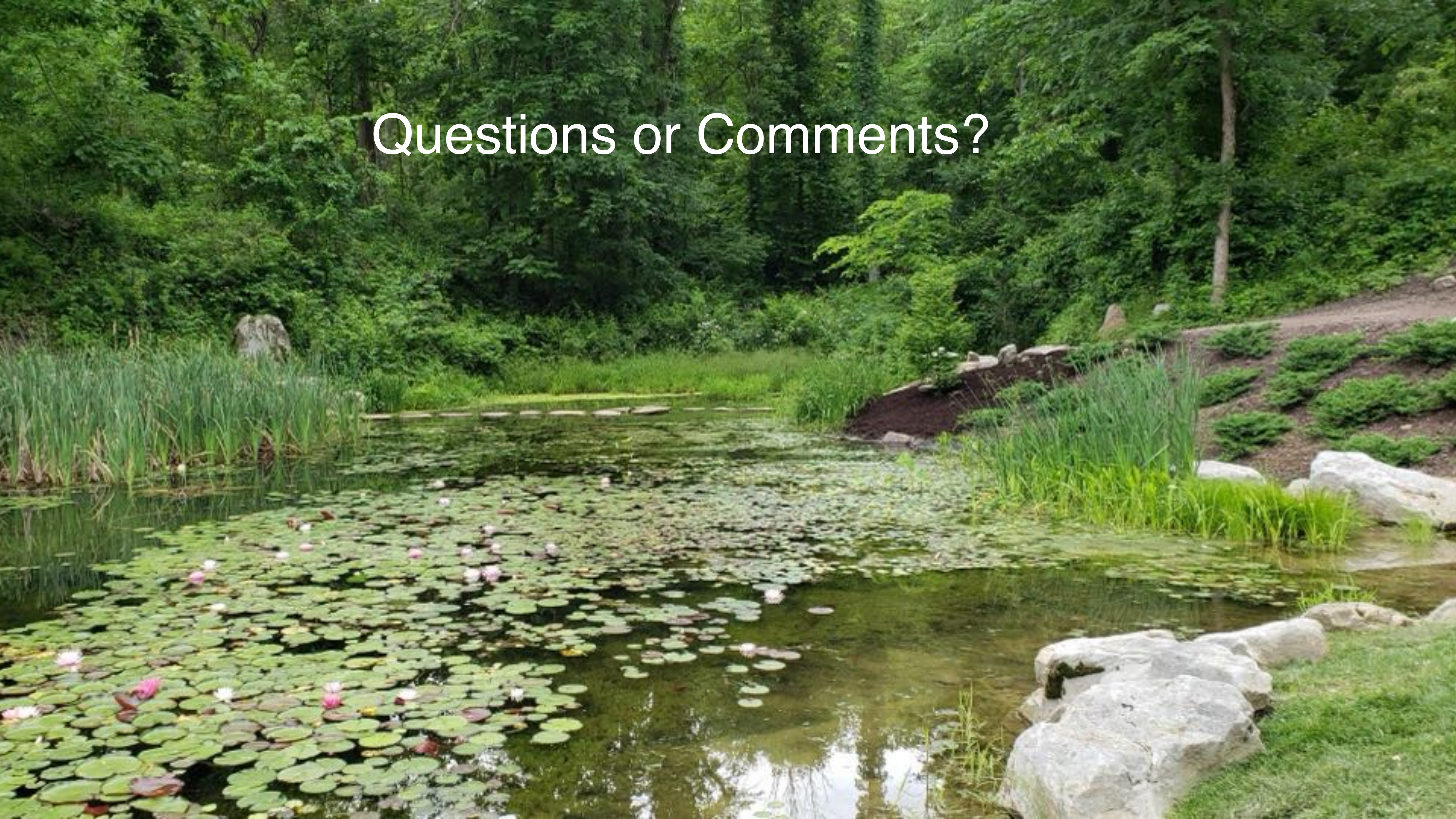
- Already highly reliable
- CO_2 additions can increase rate and amount of alkalinity generation

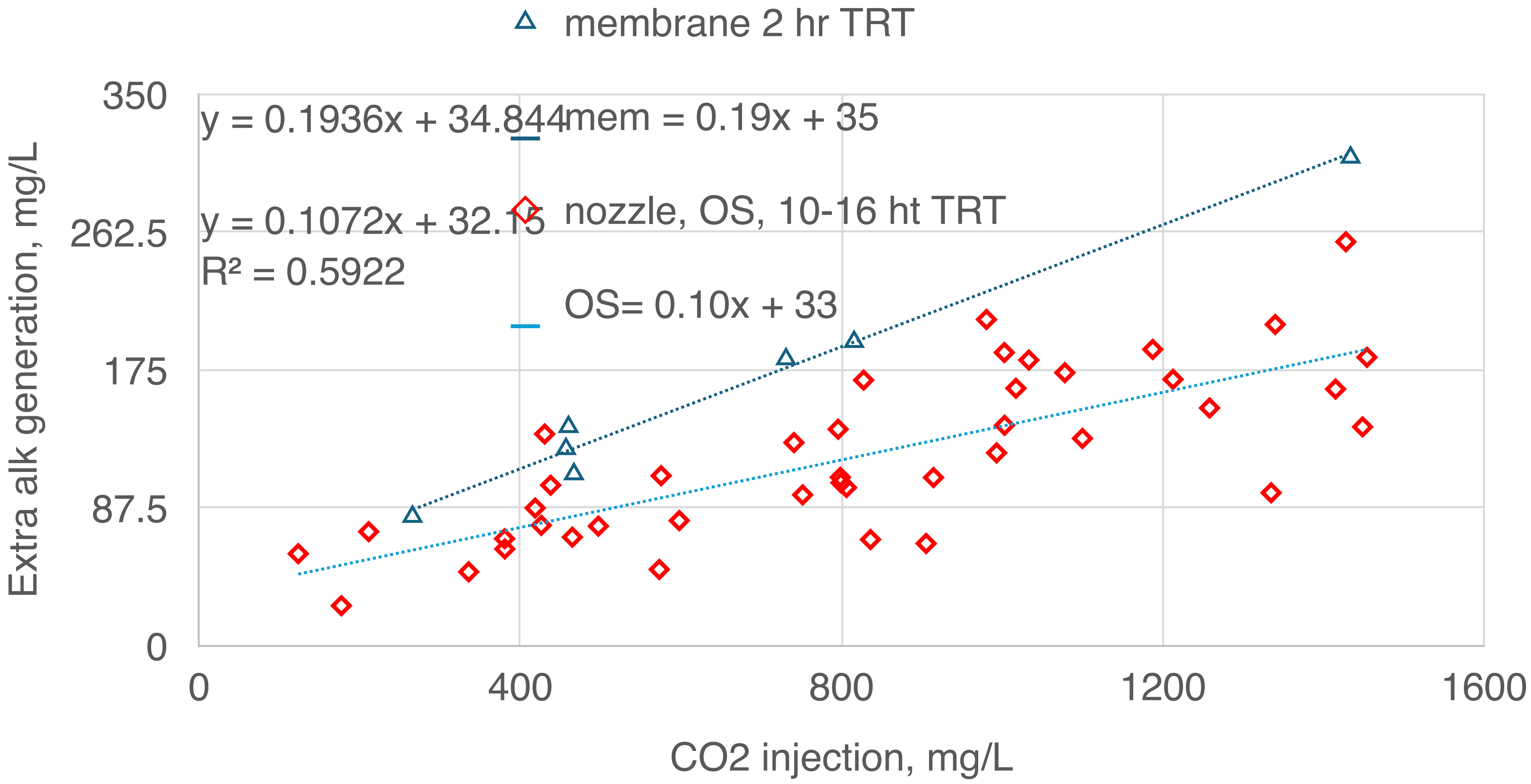
Oxic limestone beds

- Can produce high quality effluent directly from limestone beds
- Maintenance of aggregate necessary, but costs are low

Limestone beds for Mn treatment

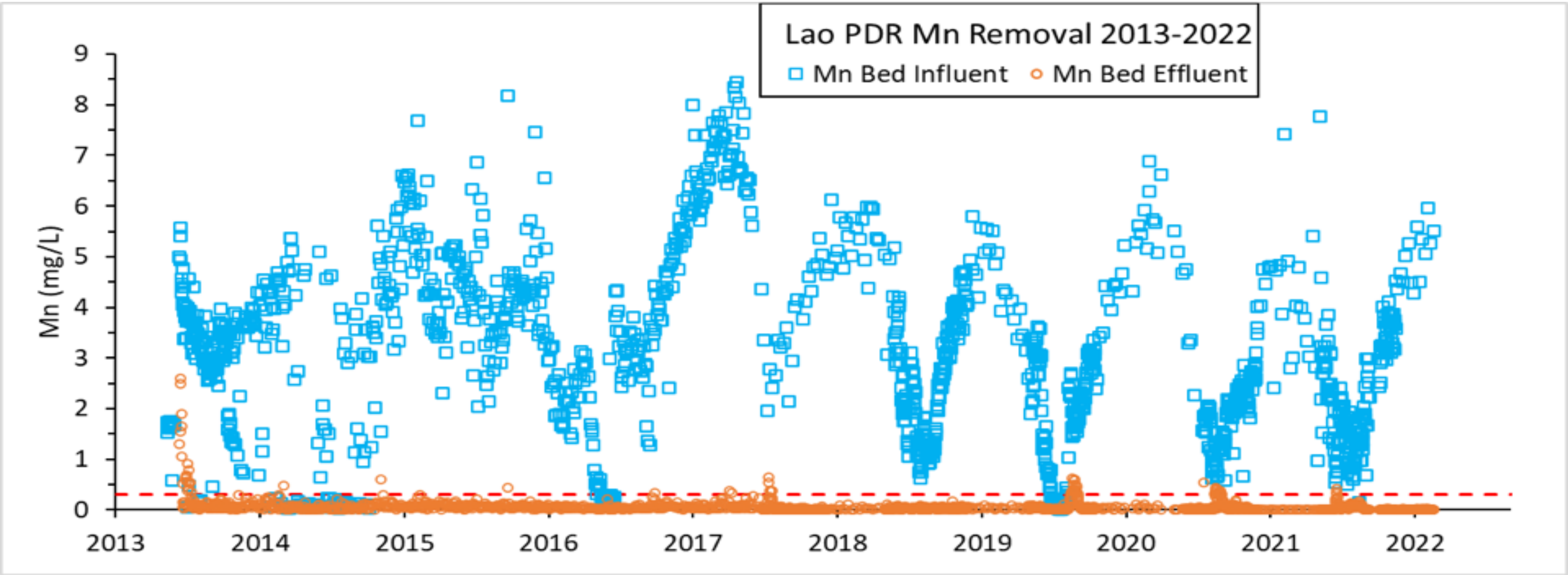
- Mn removal is possible at rates >> faster than current assumptions

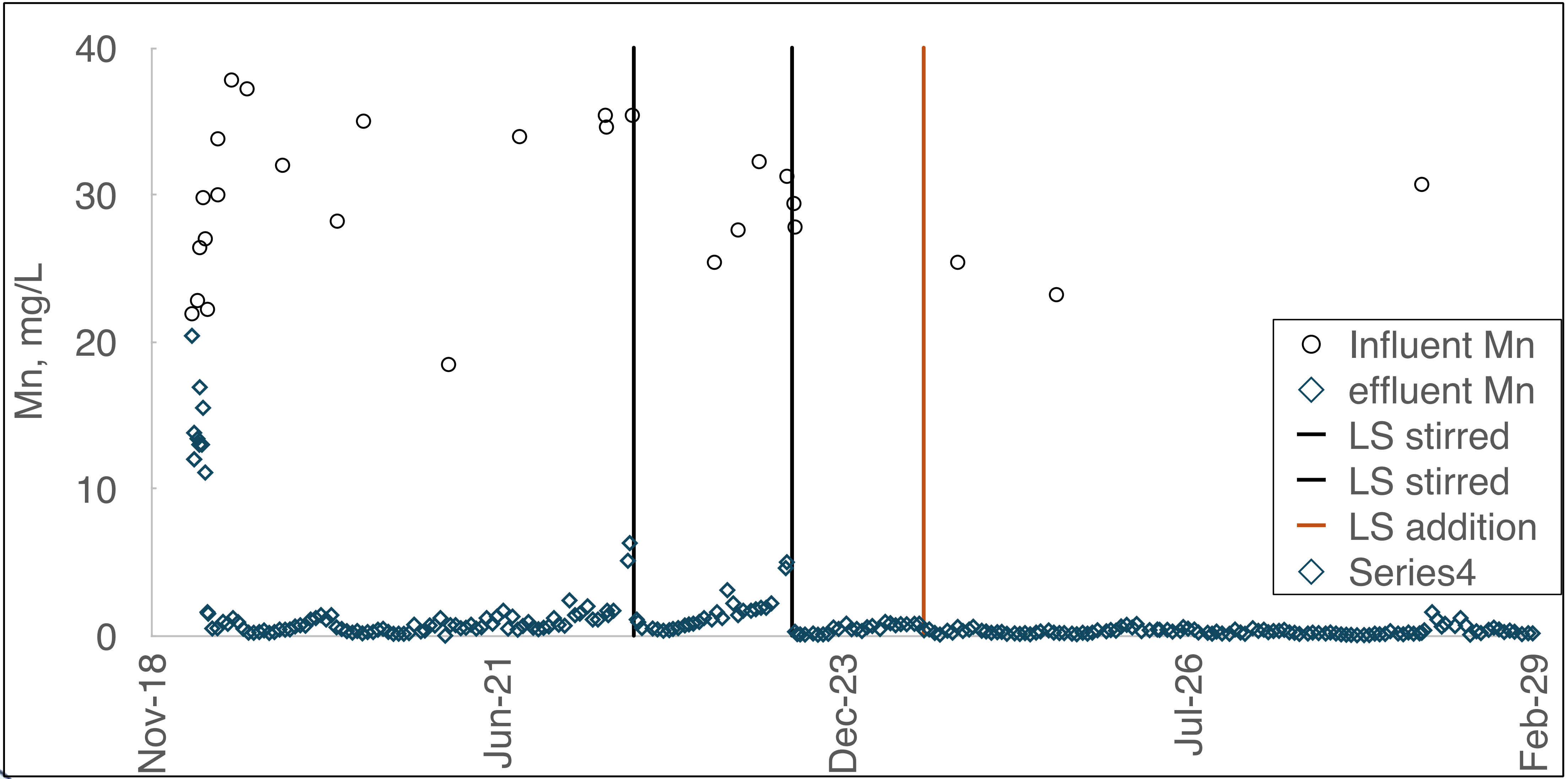

Questions or Comments?

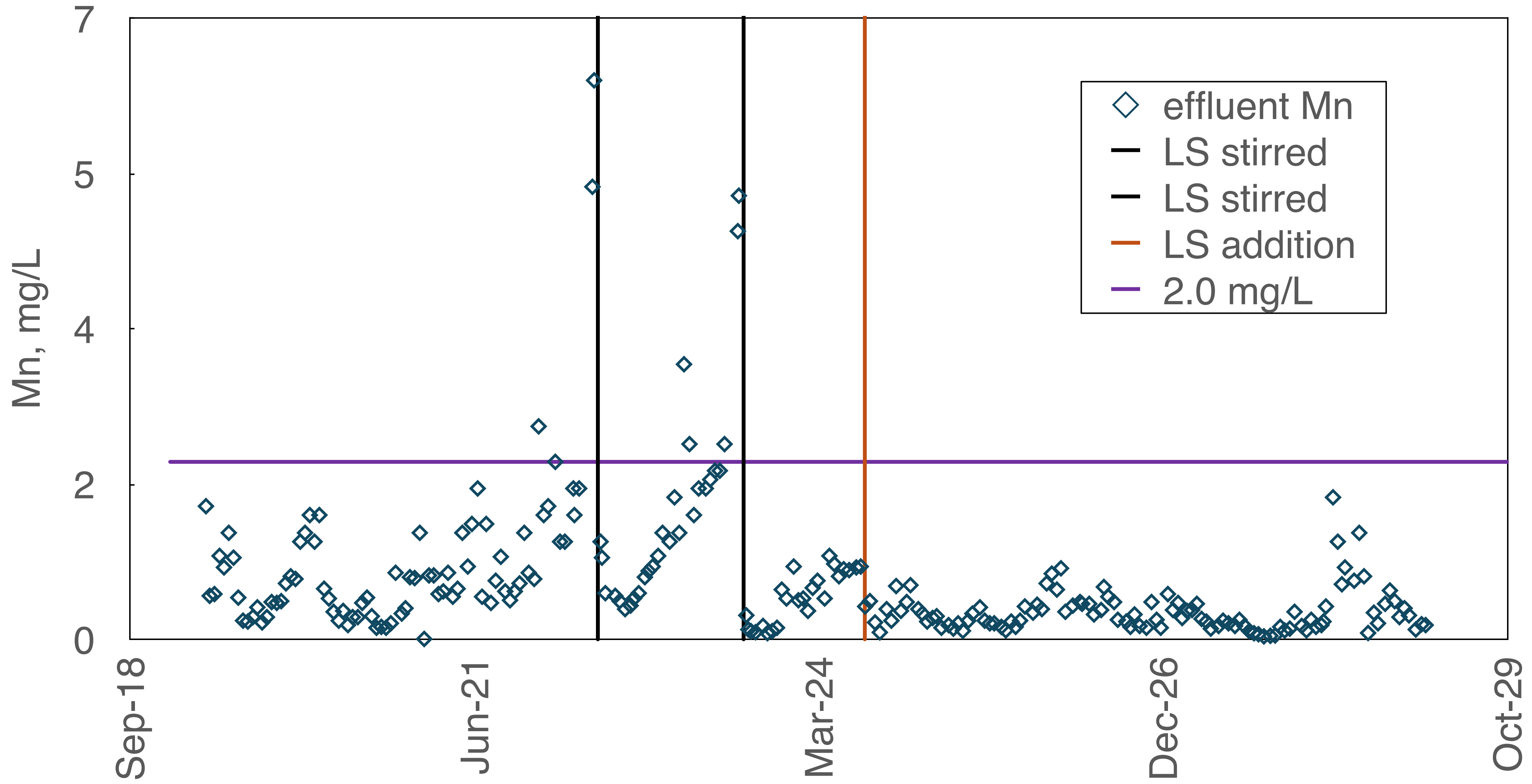

membrane 2 hr TRT
y = 0.1936x + 34.844
mem = 0.19x + 35
nozzle, OS, 10-16 ht TRT
y = 0.1072x + 32.15
R² = 0.5922
OS= 0.10x + 33
Extra alk generation, mg/L
350
262.5
175
87.5
0
0
400
800
1200
1600
CO2 injection, mg/L

Phu Kham copper mine, Laos

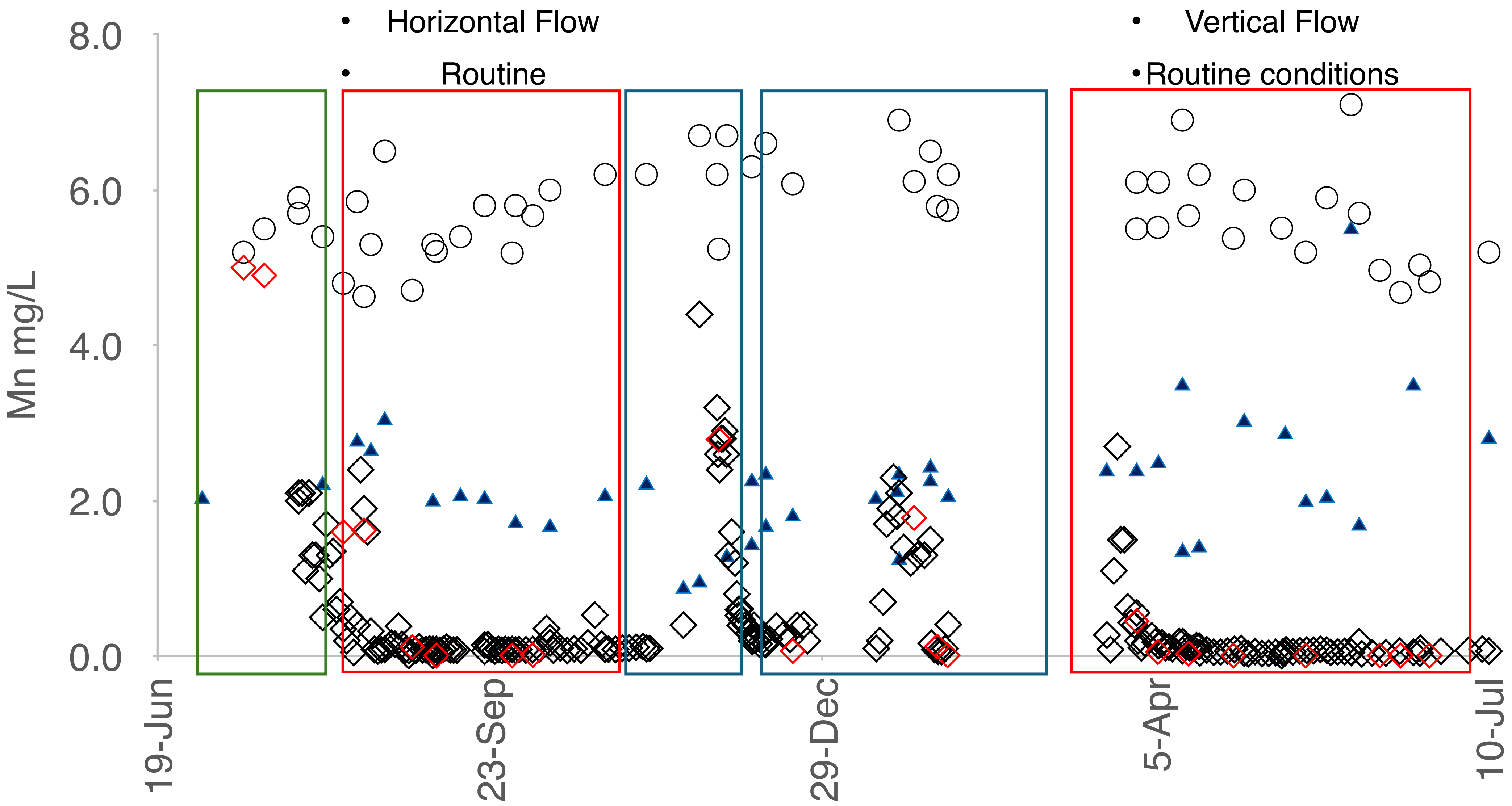
- In: 840 gpm (3,175 lpm), 2 – 10 mg/L Mn in
- Out: <0.3 mg/L Mn in 97% of measurements over 9 years

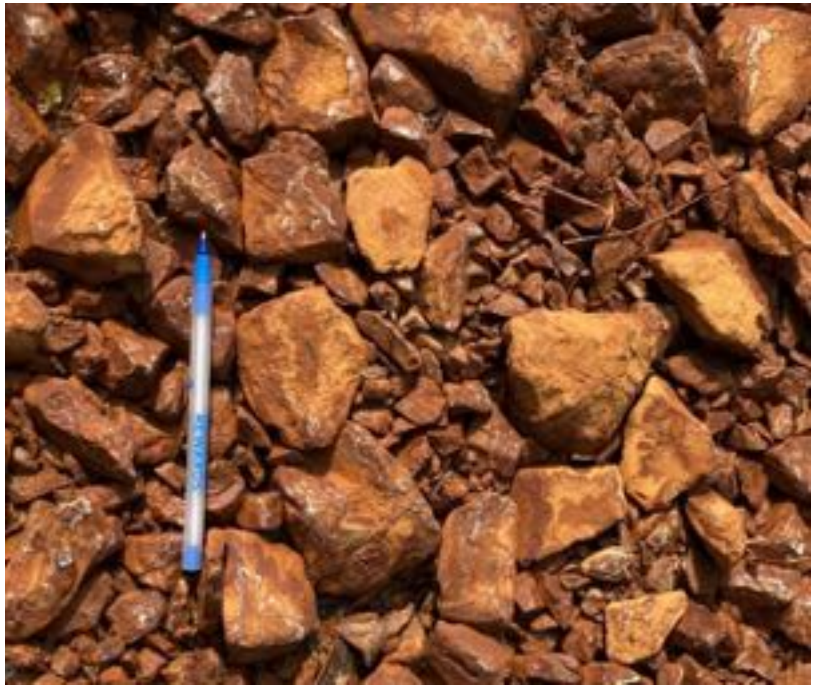



40
30
20
10
0
Mn, mg/L
Nov-18
Jun-21
Dec-23
Jul-26
Feb-29
Influent Mn
effluent Mn
LS stirred
LS stirred
LS addition
Series4



7
5
4
2
0
Mn, mg/L
Sep-18
Jun-21
Mar-24
Dec-26
Oct-29
effluent Mn
LS stirred
LS stirred
LS addition
2.0 mg/L


• Horizontal Flow
• Routine
• Vertical Flow
•Routine conditions
Mn mg/L
8.0
6.0
4.0
2.0
0.0
19-Jun
23-Sep
29-Dec
5-Apr
10-Jul



Iron

Aluminum

Manganese